State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Air-Phase Petroleum Hydrocarbons

by the

Massachusetts DEP APH Method

Version 1.0

December 2014

Written by the Connecticut DEEP QA/QC Workgroup

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<td>1.0</td>
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<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>APH</td>
<td>Air-Phase Petroleum Hydrocarbons</td>
</tr>
<tr>
<td>BFB</td>
<td>4-Bromofluorobenzene</td>
</tr>
<tr>
<td>CAM</td>
<td>Compendium of Analytical Methods</td>
</tr>
<tr>
<td>%D</td>
<td>Percent Difference</td>
</tr>
<tr>
<td>DEEP</td>
<td>Connecticut Department of Energy &amp; Environmental Protection</td>
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<tr>
<td>DF</td>
<td>Dilution Factor</td>
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<tr>
<td>GC/MS</td>
<td>Gas Chromatography / Mass Spectrometry</td>
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<tr>
<td>HPLC</td>
<td>High Pressure Liquid Chromatography</td>
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<tr>
<td>IDLC</td>
<td>Initial Demonstration of Laboratory Capability</td>
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<tr>
<td>IS</td>
<td>Internal Standard</td>
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<tr>
<td>LCS</td>
<td>Laboratory Control Sample</td>
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<tr>
<td>LMB</td>
<td>Laboratory Method Blank</td>
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<td>MassDEP</td>
<td>Massachusetts Department of Environmental Protection</td>
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<td>MCP</td>
<td>Massachusetts Contingency Plan</td>
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<tr>
<td>MDL</td>
<td>Method Detection Limit</td>
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<tr>
<td>MTBE</td>
<td>Methyl tertiary butyl ether</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<tr>
<td>QA/QC</td>
<td>Quality Assurance / Quality Control</td>
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<tr>
<td>%R</td>
<td>Percent Recovery</td>
</tr>
<tr>
<td>r</td>
<td>Correlation Coefficient</td>
</tr>
<tr>
<td>r²</td>
<td>Coefficient of Determination</td>
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<tr>
<td>RL</td>
<td>Reporting Limit</td>
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<tr>
<td>RPD</td>
<td>Relative Percent Difference</td>
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<td>RRF</td>
<td>Relative Response Factor</td>
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<td>RRT</td>
<td>Relative Retention Time</td>
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<tr>
<td>%RSD</td>
<td>Percent Relative Standard Deviation</td>
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<tr>
<td>Rt</td>
<td>Retention Time</td>
</tr>
<tr>
<td>SOP</td>
<td>Standard Operating Procedure</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra High Purity</td>
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<tr>
<td>VPH</td>
<td>Volatile Petroleum Hydrocarbons</td>
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</table>

NOTE: Abbreviations of units (e.g., amu, in. or mm Hg, m/e, μg/m³, mL, min, ng, ppbV, psia, psig, etc.) are not included.

DEFINITION OF TERMS

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tr>
<td>Absolute Pressure</td>
<td>Is defined as the pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as, mm Hg, or psia.</td>
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<td>Air-Phase Petroleum Hydrocarbons</td>
<td>Are defined as collective ranges of hydrocarbon compounds eluting from isopentane to n-dodecane, excluding Target APH Analytes. APH is comprised of C₅-C₈ aliphatic hydrocarbons, C₉-C₁₂ aliphatic hydrocarbons, and C₉-C₁₀ aromatic hydrocarbons.</td>
</tr>
<tr>
<td>Aliphatic Hydrocarbon</td>
<td>Is defined as acyclic or cyclic, saturated or unsaturated compounds, excluding aromatic compounds that contain only carbon and hydrogen atoms.</td>
</tr>
<tr>
<td>APH Calibration Check Standard</td>
<td>Is defined as a gaseous-phase mixture of APH components that is used to periodically check the calibration state of the GC/MS system. The APH Calibration Check Standard is prepared from the APH working standards and is generally one of the mid-level concentrations.</td>
</tr>
<tr>
<td><strong>APH Calibration Standard</strong></td>
<td>Is defined as a gaseous-phase mixture of APH components that is used to calibrate the GC/MS system. The APH calibration standards are prepared from the APH working standards and are prepared at a minimum of five or six different concentrations, depending on the method used to evaluate the calibration.</td>
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<tr>
<td>Target APH Analytes</td>
<td>Are defined as 1,3-butadiene, MTBE, benzene, toluene, ethylbenzene, m- &amp; p-xylene, o-xylene, and naphthalene.</td>
</tr>
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</table>
1. **SCOPE AND APPLICATION**

This 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: C5 through C8 and C9 through C12. Volatile aromatic hydrocarbons are collectively quantified within the C9 to C10 range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 28°C (isopentane) and 218°C (naphthalene).

This method is based on the collection of whole air samples in passivated stainless steel canisters, with subsequent analysis by gas chromatography/mass spectrometry (GC/MS). This method should be used by, or under the direct supervision of, analysts experienced in the use of GC/MS instrumentation for the identification and quantification of contaminant concentrations in air.

This method may also be used to directly quantify the individual concentrations of the Target APH Analytes 1,3-butadiene, methyl-tert-butylether (MTBE), benzene, toluene, ethylbenzene, m- & p-xylene, o-xylene and naphthalene in air and soil gas samples.

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.

The Reporting Limit (RL) of this method for each of the Target APH Analytes is determined by the lowest applicable Calibration standard. The nominal RL for the individual target analytes is approximately 2 to 5 µg/m3. The RLs for the collective hydrocarbon ranges are empirically determined based on the number and lowest concentration of the component standards used in the calibration of the individual ranges. The nominal RLs for the aliphatic and aromatic ranges are 12 µg/m3 and 10 µg/m3, respectively.

This method includes a series of data adjustment steps to determine the concentrations of the collective aliphatic and aromatic hydrocarbon ranges of interest. These steps must be taken by the laboratory.

Data reports produced using this method must contain all of the information presented in Appendix 3. The format of these reports is left to the discretion of individual laboratories (but must include the same certification statement presented in the aforementioned Appendix and must be provided in a clear, concise, and succinct manner).
There may be better, more accurate, and/or less conservative ways to produce APH target and range data. The Connecticut Department of Environmental Protection (DEEP) encourages methodological innovations that: (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes.

All significant modifications to this method, however, must be disclosed and described on the data report, as detailed in Section 11.1.2. Laboratories that make such modifications, and/or develop and utilize alternative approaches and methods, are further required to demonstrate that:

- Such modifications or methodologies adequately quantify the petroleum hydrocarbon target ranges, as defined in Sections 3.1.9 through 3.1.11 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

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

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

This method is one way to quantify collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons within specified carbon number ranges. It has been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been structured into the method to help ensure protective, though not overly conservative, data.

As an example, DEEP recognizes that branched alkanes have lower boiling points than their n-alkane counterparts while many of the cycloalkane constituents of gasoline-range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

- Depending upon the specific chromatographic column used, most branched C9 alkanes are expected to elute before n-nonane, the beginning marker compound for the C9 through C12 aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C5 through C8 aliphatic hydrocarbon range;
• Depending upon the specific chromatographic column used, most branched C5 alkanes will elute before n-pentane and before isopentane, the beginning marker compound for the C5 through C8 aliphatic hydrocarbon range, and will not be counted at all in the C5 through C8 aliphatic hydrocarbon range; and

• Depending upon the specific chromatographic column used, most cycloalkanes within the C5 through C8 and C9 through C12 aliphatic hydrocarbon ranges will be counted within their proper range, with the exception of some C12 cycloalkanes which will elute after dodecane, the end marker compound for the C9 through C12 aliphatic hydrocarbon range.

This method should be used in conjunction with the current version of 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). WSC-CAM-IX A was developed by MassDEP to complement the APH (MassDEP-APH-09) and to provide more detailed guidance regarding compliance with the quality control requirements and performance standards of the MassDEP APH Method.
2. SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

Samples are collected in pre-cleaned, evacuated, passivated stainless steel canisters.

A concentrator system capable of the automated collection, trapping, focusing, and injection of measured aliquots of the sample that employs a suitable mechanism for sample moisture control is recommended. Depending on the water retention properties of the packing material, some or most of the water vapor contained in the sample should completely pass through the concentrator during sample processing. Additional drying of the “trapped” sample aliquot, if required, can be accomplished by forward purging the trap with clean, dry helium (or other inert gas). Other water management approaches are also acceptable providing their use does not compromise method performance (see Section 10.2).

Following preconcentration, the sample is then transferred and cryogenically refocused onto the inlet of the system’s capillary column, further concentrating the sample.

The sample is then released by thermal desorption and carried onto the gas chromatographic capillary column, which separates the individual compounds and hydrocarbon ranges of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantified using characteristic ions. Collective concentrations of C₉-C₁₀ aromatic hydrocarbons are quantified using extracted ions. Collective concentrations of aliphatic hydrocarbon ranges are quantified using the total ion chromatogram.

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)*.

Data Quality Objectives should be developed and applied for sampling and analytical efforts involving the use of this method. Key parameters of interest include: (a) the need for and extent of time-integrated air samples, (b) the acceptability of RLs achievable by the laboratory for the contaminants of interest, and (c) the identification and reporting of target and non-target analytes.
3. **UNITS OF MEASURE**

The units of measure referenced in this method for volume, concentration, and pressure are reflective of the conventions and standards that are commonly used by practitioners within this field, and/or the conventions and standards associated with commonly available instrumentation and equipment.

Concentrations of APH target analytes must be reported in $\mu g/m^3$. Collective aliphatic and aromatic hydrocarbon range data can only be reported in $\mu g/m^3$ (See Section 9.6.2).

Other physical measurements (pressure, volume, etc.) should only be reported in units specifically referenced in the APH Method.
4. INTERFERENCES AND METHOD LIMITATIONS

Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

System carryover can be a potential problem, particularly for heavier molecular weight hydrocarbons such as naphthalene. Carryover can occur after the analysis of high concentration standards or samples. Measures that must be taken to remove this system contamination can include the analysis of multiple blanks, the use of humidified air through the system, and occasional bake out or replacement of the concentrator system components.

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 RLs 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 for a list of potential non-petroleum compounds, which may contribute to hydrocarbon range concentrations.
5. HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.
6. **APPARATUS AND MATERIALS**

6.1 **Sample Canisters**

Certified clean, leak-free, stainless steel polished or silica–lined, passivated air sampling canisters of 1.0, 2.7, 3.0, and 6.0 liter capacity are most commonly used for the collection of APH Method samples, depending on project requirements.

6.2 **Canister Sample Concentrator**

Two current systems include: Tekmar-Dohrmann AutoCan Autosampler & Cryogenic Concentrating Trap and Entech 7100A Preconcentrator/7016 Canister Autosampler. The mention of these canister sample concentrator systems by name does not preclude the use of other equivalent technologies for the APH Method.

Minimum Sample Concentrator Capabilities:

- Concentrator system must have the ability to remove moisture.

- Internal standards must be added to all standards, field samples, and QC samples using the same technique.

- Concentrator system must have the ability to minimize elevated levels of carbon dioxide (can affect integration of C₅-C₈ aliphatic range).

6.3 **Gas Chromatograph System**

An analytical system complete with a temperature programmable gas chromatograph for use with a capillary column is required.

The required chromatographic column phase is 100% dimethyl polysiloxane (e.g., RTX-1, DB-1, etc.); required column dimensions are 60 meters, 0.25 mm ID, 1-micron film thickness, or a column with demonstrated and documented equivalent chromatographic properties (i.e., same compound elution order).

**NOTE:** Based upon data obtained from the MassDEP Volatile Petroleum Hydrocarbon (VPH) Method Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantification of aliphatic and aromatic compounds within the collective hydrocarbon ranges specified in the method. Substitution of the required column is not allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and elution order for the aliphatic and aromatic compounds and ranges of interest.
To demonstrate equivalency of column chromatography, a mid-range APH calibration standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C$_5$-C$_8$ and C$_9$-C$_{12}$ aliphatic hydrocarbons, C$_9$-C$_{10}$ aromatic hydrocarbon ranges and target analytes must be determined for each column. The relative percent difference (RPD) between the concentrations of each hydrocarbon range and target analyte, excluding naphthalene, obtained from each column must be ≤25. The RPD for naphthalene must be ≤40. The elution order of APH Components on the proposed substitute column must be equivalent to the elution order on the required column.

6.4 Mass Spectrometer System

The mass spectrometer must be capable of scanning from 35 to 250 amu every three seconds or less, utilizing 70 eV in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when at least 50 ng of 4-bromofluorobenzene (BFB) is injected.

A data station is required that is capable of storing and reintegrating chromatographic data and capable of determining peak areas using a forced baseline projection.
7. **REAGENTS AND STANDARDS**

7.1 **Reagents**

- HPLC-grade water for canister humidification.
- UHP helium for the GC/MS system.
- Liquid nitrogen for the concentrator system and GC.
- Ultra zero air or UHP nitrogen for the concentrator system and standard preparation

7.2 **Stock Standard**

Gaseous cylinder containing all aliphatic and aromatic range calibration compounds and target analytes (see Table 1). Recommended concentration is 1 mg/m$^3$ for all components.

At the time this document was published, National Institute of Standards and Technology (NIST)-certified APH Stock Standards were commercially available from Air Liquide America Specialty Gases (formerly Scott Specialty Gases, Plumsteadville, PA) and Spectra Gases, Inc. (Branchburg, NJ). The mention of any trade name, product or vendor in this document does not constitute an endorsement or recommendation by the MassDEP.

7.3 **APH Working Standards**

The preparation of gaseous working standards and calibration standards described in the following sections is based on the use of mass flow controllers to accurately measure and dispense volumes of the gaseous standards used in the preparation of intermediate (working) and final (calibration) standards. Other gas metering or measuring devices may be used to prepare working standards and calibration standards for the APH Method so long as the accuracy and precision of standards prepared using these devices is documented and consistent with the overall quality objectives of the method.

**NOTE:** It is unacceptable to use methanol-based stock standards for preparation of working standards due to fluctuations observed in the analytical system response when high levels of methanol are present in the canister. This option was acceptable in the Draft version of the APH Method but is no longer acceptable.

Prepare gaseous-phase APH working standards in pre-evacuated passivated canisters. The usual laboratory practice is to prepare working standards at two concentration levels (20 µg/m$^3$ and 500 µg/m$^3$, as shown in Tables 3a and 3b).
Using a mass flow controller, flow-inject a measured volume (flow rate * time) of the Stock Standard(s) into a pre-evacuated passivated canister using ultra zero air or UHP nitrogen for dilution/pressurization. For example, the working standard concentration to be used to establish the lower end of the calibration range (20 µg/m³ nominal concentration) should allow for a flow-injection volume of at least 25 mL over a minimum of 10 seconds (150 mL/min x 10 seconds) for the lowest calibration point (the target RL). The working standard concentration to be used to establish the higher end of the calibration range (500 µg/m³ nominal concentration) should allow for a flow-injection volume of at least 25 mL over 10 seconds (150 mL/min x 10 seconds) for the mid-range calibration point. In practice a known flow rate of ultra zero air or UHP nitrogen is added concurrently with the Stock Standard in most automated devices.

**NOTE 1:** Other mass flow controllers may allow for lower volumes to be injected. At a minimum, the laboratory should not exceed the mass flow controller manufacturer’s minimum flow rate or volume.

**NOTE 2:** Gas-tight syringes can also be used in lieu of mass flow controllers in certain instances. Syringes may be more appropriate when preparing standards in low volume canisters (e.g., 1-liter canisters). In general, the use of the mass flow controllers is preferred for preparation of all working standards.

All working standards must be humidified to a minimum of 30% relative humidity. A ratio of 7.2 µL water/liter of gaseous standard is acceptable for humidification of working standards if the laboratory’s calibration preparation system is not equipped with a humidification chamber (e.g., 6-liter canister = 18 liters when pressurized and therefore requires 7.2 µL x 18 L = 130 µL of water). After the addition of the stock standard, dilution gas, and humidification liquid (if required), the working standard canister must be pressurized (maximum 30 psig) with ultra zero air or UHP nitrogen. The internal pressure of the working standard canister should be accurately measured and documented.

It is recommended that all working standard canisters be allowed to equilibrate for at least 24 hours before use.

### 7.4 APH Calibration Standards

APH calibration standards consist of a series of measured flow-injected volumes of the APH working standards directly injected into the concentrator/GC/MS system.

For the individual APH calibration standards, a pre-designated concentration is directly flow-injected into the concentrator/GC/MS by varying the volumes of the working standards. At a minimum, five different concentrations are required for a valid calibration curve. If non-linear (i.e., quadratic) regression is used, a minimum of six (6) concentrations are required for a valid calibration curve (see Section 9.4.11.1). In either case, the calibration concentrations must be evenly dispersed over the full working range of the
detector with the lowest calibration point corresponding to the target RL. Tables 3a and 3b provide recommended concentrations and preparation methods for each calibration standard used for a 5-point initial calibration of hydrocarbon ranges and Target analytes, respectively.

The range of volumes used for the APH calibration standards must be inclusive of the minimum and maximum sample volumes that will be used during routine sample analysis (e.g., as shown in Tables 3a and 3b, the minimum volume is 25 mL and the maximum volume is 250 mL). If sample volumes outside the range of calibration volumes are utilized, the laboratory must statistically demonstrate acceptable recovery of all target analytes over the full dynamic range of the calibration curve using the out-of-range injection volume. This statistical demonstration will be performed using the procedure described in Section 10.4, using the injection volume of interest with the higher concentration working standard. In any case, the minimum sample volume used should not be less than the manufacturer’s recommendation for the concentrator (typically 20-25 mL).

7.5 **Internal Standard and MS Tuning Standard**

The recommended internal standards (IS) are Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5. The required MS tuning standard is BFB. Stock standards of these compounds should be prepared or purchased in a humidified canister at a concentration to accurately flow-inject a concentration of 10 ppbV or 10 µg/m³ into the trap during the collection time for all calibration, blank, and sample analyses, whether through a mass flow controller or a sample loop injector. The volume of internal standard mixture added for each analysis must be the same from run to run. The concentrations of internal standards can be assigned a nominal value of 10 ppbV or 10 µg/m³ for comparison and consistency with the laboratory’s selected reporting units. This will vary among laboratories depending on which units are used during the calibration of the instrument.
8. SAMPLE COLLECTION AND HANDLING

8.1 Canister and Flow Controller Cleaning

All canisters must be leak tested and certified clean prior to being used for sampling. Associated canister sampling equipment (e.g., flow controllers, critical orifice assemblies) must also be deemed clean and appropriate for use prior to sampling. Cleaning techniques and acceptance criteria may vary between laboratories but, in general, procedures should include backflushing with humidified ultra zero air or UHP nitrogen. Flow controllers are calibrated with NIST-traceable flow meters. A detailed procedure for canister cleaning and maintenance is presented in Appendix 4.

8.2 Sample Collection

All samples must be accompanied by a chain-of-custody form, or equivalent, that documents the canister and flow controller serial numbers, date and time of sample collection, and all other pertinent sampling information.

Grab samples are collected by opening the sampling valve of a pre-evacuated canister (initial vacuum ≥ 28 in. Hg) and allowing the canister to fill to ambient pressure. Equalization to atmospheric pressure under these conditions may be completed in a minute or less.

Time-integrated samples require the use of a properly calibrated flow controller. The flow controller’s calibration must be performed and verified (by the laboratory) prior to sample collection. Upon receipt at the laboratory, a post-sampling flow controller calibration verification must be performed. The RPD between the initial and post sampling calibration readings must be calculated. As long as the RPD is ≤ 20, the calibration and associated time interval are considered valid. If the RPD is >20, a notation must be provided in the data report form and laboratory narrative disclosing the deficient RPD value. The flow controller RPD is one line of evidence in the proper collection of samples for APH analysis. If the canister vacuum is acceptable after sampling and the flow controller RPD is outside of the acceptance criteria, data quality is not adversely affected.

Sampling Note: Flow controllers will be calibrated such that a small amount of vacuum will remain in the canister at the end of sampling (approximately 5 in. Hg). The post-sampling canister vacuum will be measured by the laboratory using an annually calibrated, NIST-traceable vacuum/pressure gauge. The vacuum should be approximately 5 in. Hg to ensure a consistent flow rate throughout the measured time interval. However, due to temperature/pressure differences in the field, as well as site-specific conditions for various sampling applications (e.g., moisture levels, soil type, site access issues), the actual post-sampling canister pressure may be slightly different than 5 in. Hg.

Upon receipt at the laboratory, all samples must be assigned unique laboratory identification numbers.
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 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 the client indicates that the analysis should proceed, the noted anomalies should be documented on the data report form or the laboratory narrative.

Samples may be pressurized to a maximum of 5 psig with humidified ultra zero air or UHP nitrogen after receipt in the laboratory. Refer to Section 9.5.1.3 for the calculation of dilution factors for pressurized samples.

8.2.1 Documentation Requirements

Pre-Sampling Information: Provided by the Laboratory:

- Canister serial number
- Individual or batch certification results
- Canister volume
- Pre-sampling canister vacuum
- Flow controller serial number
- Date canister released by laboratory

Sampling Information Provided by the Sampler:

- Site location
- Sampling date
- Sampling location
- Sample identification (ID)
- Canister serial number for each sample ID
- Canister volume (liters) for each sample ID
- Sampling duration
• Flow controller identification number (if utilized) for each sample ID

• Sampling start and end times

• Initial and final ambient temperatures and atmospheric pressures

• Initial and final interior temperatures

• Initial and final canister vacuums (in. Hg)

• Date shipped to laboratory

Post Sampling Information: Provided by the Laboratory

• Date received

• Laboratory ID

• Vacuum of canister upon receipt at laboratory

• Flow controller calibration RPD

8.3 **Holding Time**

Canisters should be used in the field in a timely manner (i.e., they should not be stockpiled at the site prior to use). The maximum holding time for the analysis of passivated canister samples for APH analyses is 30 days from the date of sample collection.
9. ANALYTICAL PROCEDURE

9.1 Sample Preparation and Concentration

Ensure the integrity of the canister sample as described in Section 8.0.

Connect the canister(s) valve to the concentrator autosampler or sample inlet line. The canister must remain closed.

Leak check all canister inlet connections. Analysis may not begin until the leak check has passed for each canister being tested. Refer to the concentrator manufacturer’s specifications for leak check criteria. For example, the pressure change should not exceed 2.0 psia over a 30 second period for an Entech 7100A concentrator.

Open the canister valves.

For the analysis of low concentration samples, set up the concentrator system to withdraw the nominal sample volume (i.e., “1x” volume) of air from each canister. If high concentrations are expected, lower volumes may be used, but they should be within the range of volumes used for the initial calibration standards (See Section 7.4.3). The nominal (1x) volume for typical analytical applications is 0.25 liters.

General description of the whole-air sample concentration procedure: commercially available systems typically consist of a 2- to 3-stage trapping procedure that “freezes out” analytes of interest while simultaneously removing as much of the matrix (i.e., nitrogen, oxygen, carbon dioxide, methane, and moisture) as possible. Sample volume and flow rates are controlled via a mass flow controller, which negates the effect of variations in the pressure and temperature of the samples and calibration standards. The sample is withdrawn from the canister by creating a pressure differential with a vacuum pump across the mass flow controller which is in line with the canister. An aliquot of sample is withdrawn at a constant flow rate onto a trap containing a sorbent material capable of adsorbing the analytes of interest. After equilibration, the target analytes are transferred to a cryofocusing unit, and when the GC is ready, the sample is injected by ballistic heating of the cryofocuser. The heating of the cryofocuser transfers the target analytes to the GC/MS system.

9.2 GC/MS Conditions

**NOTE**: Conditions described below are for an Agilent 6890/5973 GC/MS system.

9.2.1 Gas Chromatograph

Recommended oven program: initial temperature 25°C, hold for 5.0 min. Increase temperature to 100°C at 8.0°C/min, and then increase temperature to 220°C at 25°C/minute. Hold for 4.0 min.
GC conditions may vary, but a minimum separation requirement of 50% (maximum peak height to valley height) must be met, particularly for hexane and bromochloromethane (IS1) in a 20 µg/m³ Calibration standard.

Gas Flows: Helium carrier gas flow of 2 mL/min is the recommended flow rate.

Recommended Sample Injection

- Injection mode: splitless.
- Injection port temperature: 220°C.
- Inlet pressure: 25.77 psi.
- Purge flow: 36.3 mL/min at 0 minutes.
- Gas saver flow: 20 mL/min.

Recommended MS Conditions

- Temperature of MS transfer line: 240°C.
- Temperature of MS Quad: 150°C.
- Temperature of MS Source: 230°C. Solvent Delay: 4.0 minutes.
- Scanning Parameters: minimum range 35-250 amu.
- MS must be tuned to pass BFB criteria listed in Table 2.

9.3 Retention Time Windows

The APH retention time (Rt) window for the C₅ - C₈ aliphatic hydrocarbons is defined as beginning 0.1 minutes before the elution of isopentane and ending 0.01 minutes before the elution of nonane. The C₉ - C₁₂ aliphatic hydrocarbon range begins 0.01 minutes before the elution of nonane; therefore there is no overlap of the two ranges and the nonane peak is only included in the C₉ - C₁₂ aliphatic hydrocarbon range. The C₉ - C₁₂ aliphatic hydrocarbon range ends 0.1 minutes after the elution of dodecane.

The APH Rt window for the C₉ - C₁₀ aromatic hydrocarbons is defined as beginning 0.1 minutes after the Rt of the beginning marker compound (o-xylene) and ending 0.1 minutes before the Rt of the ending marker compound (naphthalene).
APH marker compounds and windows are summarized in Table 4.

9.4 Calibration

**NOTE:** Calibration and sample analysis calculations presented in this section are based on the GC/MS system response to multiple calibration standards expressed in units of “nominal” concentration (μg/m³). Other quantitative approaches such as GC/MS system response to multiple calibration standards expressed in units of on-column mass (μg) are also acceptable.

The APH working standards are used to calibrate the GC/MS system. Two distinct calibration operations are necessary:

- **Target APH Analytes:** Relative Response Factors (RRFs) are calculated for the Target APH Analytes, based upon a correlation between the concentration of analyte and area counts for the relevant quantitation ions. This allows for the individual identification and quantitation of these specific compounds. It is not necessary to develop response factors for any other individual APH Components.

- **Collective Aliphatic/Aromatic Hydrocarbon Ranges:** RRFs are calculated for C₅-C₈ aliphatic hydrocarbons and C₉-C₁₂ aliphatic hydrocarbons based upon a correlation between the TOTAL concentration of aliphatic APH Components eluting within the range of interest and the total ion area count. An RRF is calculated for C₉-C₁₀ aromatic hydrocarbons based upon a correlation between the TOTAL concentration of aromatic APH Components eluting within this range and the total area count of extracted ions 120 and 134. Specified APH Components are designated marker compounds to define the beginning and end of the hydrocarbon ranges (see Table 4).

Primary (quantitation) and secondary extracted ions for all APH Components and the recommended internal standards are provided in Table 5. The recommended internal standards used for quantitation of each Target APH Analyte and hydrocarbon range are provided in Table 6. A listing of the hydrocarbon range compounds used to establish response factors for each hydrocarbon range of interest and their individual component concentration (μg/m³) is provided in Table 3a.

**Initial Calibration:** The use of RRFs is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations for the APH Method. It is also permissible to utilize linear or non-linear regression (see Section 9.4.11.1). The linear regression approach for APH target analytes and collective ranges is described in Appendix 6. Detailed guidance regarding the use of a non-linear regression calibration model, may be found in SW-846 Method 8000B, Section 7.5.3.
NOTE: A sample calculation demonstrating the proper application of the equations shown in the following sections is presented in Appendix 5, APH METHOD CALCULATIONS.

In all but the most extreme cases, an initial calibration is performed using a minimum of five different concentrations prepared using various volumes of the APH working standards. Recommended range and target analyte calibration standard concentrations are provided in Tables 3a and 3b, respectively. If non-linear (quadratic) regression is used under the circumstances described in Section 9.4.11.1, a minimum of six (6) calibration concentrations must be used. In either case, the calibration concentrations must be evenly dispersed over the full working range of the detector with the lowest calibration point corresponding to the target RL.

Analyze each Calibration standard according to the procedures specified in Sections 9.1 and 9.2.

**Target APH Analytes** - Tabulate the area response of the primary (or quantitation) ions against the concentration for each Target APH Analyte and internal standard, and calculate an RRF for each compound using Equation 1. Perform this calculation for each Target APH Analyte.

**Equation 1: Relative Response Factor for Target APH Analytes**

\[
RRF = \frac{(A_{EC})*(C_i)}{(A_{EI})*(C_c)}
\]

where:
- \( RRF \) = relative response factor
- \( A_{EC} \) = area count of the primary (quantitation) ion for the analyte of interest
- \( C_i \) = concentration of the associated internal standard (µg/m³); See Sec. 7.5
- \( A_{EI} \) = area count of the primary (quantitation) ion for the associated internal standard
- \( C_c \) = concentration of analyte of interest (µg/m³): refer to last column of Table 3b

**Hydrocarbon Ranges** - Establish retention time windows for the hydrocarbon ranges using the APH Component marker compounds shown in Table 4.

Calculate an RRF for the C₅-C₈ aliphatic hydrocarbon range using the following steps.

- Using total ion integration, sum the individual peak areas of the six APH Components that are used to establish an average range RRF for C₅-C₈ aliphatic hydrocarbons, as designated in Table 3a. Do not include the peak areas of internal standards (all of the recommended internal standards elute in this range).

- Using the total area generated in Section 9.4.7.1, calculate the C₅-C₈ aliphatic hydrocarbon range RRF using Equation 2.
Equation 2: Relative Response Factor for C₉-C₈ Aliphatic Hydrocarbons

\[
\text{Range } RRF = \frac{\left[ (A_T) \cdot (C_{IT}) \right]}{\left[ (A_{EI}) \cdot (C_{IT}) \right]}
\]

where:

\( A_T \) = total ion area count of the six aliphatic APH Components which elute within this range (see Table 3a)

\( C_T \) = summation of the concentrations of the six aliphatic APH Components (µg/m³) which elute within this range: refer to the last column of Table 3a

Calculate an RRF for the C₉-C₁₂ aliphatic hydrocarbon range using the following steps.

- Using total ion integration, sum the individual peak areas of the six APH Components that are used to establish an average range RRF for C₉-C₁₂ aliphatic hydrocarbons, as designated in Table 3a. Do not include the peak area of BFB.

- Using the total area generated in Section 9.4.8.1, calculate the C₉-C₁₂ hydrocarbon range RRF using Equation 3.

Equation 3: Relative Response Factor for C₉-C₁₂ Aliphatic Hydrocarbons

\[
\text{Range } RRF = \frac{\left[ (A_T) \cdot (C_{IT}) \right]}{\left[ (A_{EI}) \cdot (C_{IT}) \right]}
\]

Calculate an RRF for the C₉-C₁₀ aromatic hydrocarbon range using the following steps.

- Using extracted ion m/e 120, sum the individual peak areas of the five APH Components that are used to establish an average range RRF for C₉-C₁₀ aromatic hydrocarbons, as designated in Table 3a.

- Using extracted ion m/e 134, sum the individual peak areas of the five APH Components that are used to establish an average range RRF for C₉-C₁₀ aromatic hydrocarbons, as designated in Table 3a.

- Sum the area counts from Sections 9.4.9.1 and 9.4.9.2.

- Using the area count generated in 9.4.9.3, calculate the C₉-C₁₀ aromatic range RRF using Equation 4.
Equation 4: Relative Response Factor for C₇-C₁₀ Aromatic Hydrocarbons

\[
\text{Range } RRF = \frac{\sum (A_{T}^{*} \cdot C_{T})}{\sum (A_{E}^{*} \cdot C_{T})}
\]

where:
\( A_{T} \) = summation of area counts for extracted ions 120 and 134 for the five aromatic APH Components which elute within this range (see Table 3a)
\( C_{T} \) = summation of the concentrations of the five aromatic APH Components (µg/m³), which elute within this range: refer to the last column of Table 3a

Calculate the average RRF for each of the Target APH Analytes and each hydrocarbon range.

Calculate the percent relative standard deviation (%RSD) of the RRFs over the working range of the curve for each of the Target APH Analytes and each hydrocarbon range using Equation 5.

**Equation 5: Percent Relative Standard Deviation**

\[
\%RSD = \frac{SD_{n-1}}{AVG_{x}} \times 100
\]

where:
\( \%RSD \) = percent relative standard deviation
\( SD_{n-1} \) = standard deviation (n-1 degrees of freedom)
\( AVG_{x} \) = average RRF from the initial calibration curve

If the %RSD is ≤30, linearity can be assumed for the associated Target APH Analyte or hydrocarbon range. For naphthalene, the %RSD can be ≤40.

If, under extenuating analytical circumstances (e.g., extending the RL beyond the expected linear range of the detector, difficult analytes with non-linear mass/response ratios), the %RSD criteria specified in Section 9.4.11.1 cannot be achieved, then a linear (least squares) or non-linear (quadratic) regression may be used to generate a calibration curve consistent with the guidance provided in SW-846 Method 8000B, Sections 7.5.2 and 7.5.3. **Use of the non-linear calibration alternative must be documented in the laboratory narrative.**

**NOTE:** It is not the intent of this alternative calibration approach to allow for a non-linear calibration model to be used to compensate for detector saturation or to avoid proper instrument maintenance. As such, non-linear regression must not be employed for analytes that consistently met %RSD criteria specified in Section 9.4.11.1 in previous calibrations.

In order for the linear or non-linear regression model to be used for quantitative purposes, \( r \) (Correlation Coefficient) or \( r^{2} \) (Coefficient of Determination) must be greater than or equal to 0.99. In addition, the resulting calibration curve from the linear or non-linear regression must be verified by recalculating concentrations of the target analytes and hydrocarbon ranges in the lowest calibration standard using the final calibration equation. Recoveries must be 70-130% (except naphthalene 60-140%).
If recalculated concentrations from the lowest calibration standard are outside 70-130% (or 60-140% for naphthalene) recovery range, either:

Report the RL as an estimated value, or Raise the RL to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration equation.

The statistical considerations in developing non-linear calibration curves require more data than the linear calibration approach. As described in Section 9.4.3, the linear regression model requires five equally distributed calibration concentrations for initial calibration while the non-linear regression model requires a minimum of six equally distributed calibration concentrations.

For the linear or non-linear regression calculation, the origin (0,0) cannot be included as a calibration point.

For any calibration model, the concentration of the lowest initial calibration standard, adjusted for sample size, dilution, etc., establishes the method RL.

The initial calibration must be verified through the analysis of an LCS. This analysis must be performed every time an initial calibration is performed and prior to sample analyses on a daily basis.

The LCS must be prepared in a certified-clean canister from a different stock standard than that used to prepare the calibration standard. The LCS should be prepared at a mid-range calibration curve concentration.

At a minimum, the LCS must contain 1,3-butadiene, benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, and naphthalene, and at least one compound from each hydrocarbon range (recommended representative range compounds: heptane for C₅-C₈ aliphatics, decane for C₉-C₁₂ aliphatics, and 1,3,5-trimethylbenzene for C₉-C₁₀ aromatics). The concentration of the representative range compounds must be greater than the lowest summed range concentration in Table 3a (suggest using 20-50 µg/m³).

Calculate the percent recovery of each Target APH Analyte and hydrocarbon range using Equation 6. Percent recoveries must be between 70-130% for target analytes except for naphthalene, which must exhibit percent recoveries between 50-150%.
Equation 6: Percent Recovery

\[ \% R = \left( \frac{C_{\text{found}}}{C_{\text{true}}} \right) \times 100 \]

where:

\( \% R \) = Percent Recovery

\( C_{\text{found}} \) = Concentration of the analyte or hydrocarbon range detected in the LCS (µg/m³)

\( C_{\text{true}} \) = True concentration of the analyte or hydrocarbon range in the LCS (µg/m³)

Continuing Calibration - A continuing calibration check must be performed daily prior to sample analysis. It should be noted that the Percent Differences (%Ds) are calculated (Equation 7) when RRFs are used for the initial calibration and Percent Drifts (Equation 6-5, Appendix 6) are calculated when calibration curves using linear or non-linear regression are used for the initial calibration.

The concentration of the APH Calibration Check Standard must be near the midpoint of the calibration curve.

Calculate the RRF for each APH Target analyte and hydrocarbon range from the Calibration Check Standard using Equations 1 through 4.

Calculate the %D of the Calibration Check Standard RRF from the initial calibration average RRF using Equation 7.

Equation 7: Percent Difference

\[ \% D = \left[ \frac{RRF_C - RRF_I}{RRF_I} \right] \times 100 \]

where:

\( \% D \) = Percent Difference

\( RRF_C \) = RRF from the APH Calibration Check Standard

\( RRF_I \) = average RRF from the initial calibration curve

The %D or Percent Drift for each APH Target analyte and hydrocarbon range must be ≤30. If more than one compound fails to meet the applicable criterion, or if the %D or Percent Drift for any one compound is greater than 50, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

Retention Time Windows - The range retention time windows must be established daily based upon the retention time of the marker compounds in the APH Calibration Check Standard. The marker compounds used for each range are defined in Table 4.

Daily GC/MS Performance Check - A check of the GC/MS tuning must be performed daily prior to sample analyses. The GC/MS system is checked to confirm that acceptable performance criteria for mass
spectral ion abundance ratios are met for BFB. These criteria must be met prior to analyzing any additional standards, blanks and samples.

Performance criteria for the required tuning standard, BFB, are provided in Table 2. If the tuning criteria are not met, the GC/MS must be retuned and the analysis repeated.

9.5 GC/MS Analysis of Samples

Pre-concentrate the pre-established nominal volume of sample (typically 0.25 liters) on the concentrator and inject it onto the GC column. When the nominal volume of the sample is analyzed, the dilution factor is 1.0.

Dilution Factors and Sub-Atmospheric Samples - For dilutions, sample volumes smaller than the nominal volume can be analyzed. The smallest volume used should not be less than that used for the initial calibration. See Section 7.4.3 for further instructions on sample volumes. When volumes less than the nominal sample volume are analyzed, the dilution factor is calculated as follows:

\[ DF = \frac{\text{nominal sample volume}}{\text{actual volume analyzed}} \]

For more concentrated samples where analysis of smaller volumes will not be adequate to ensure concentrations are within the calibration range, the canister must be pressurized and an aliquot of sample removed and injected into another canister. The dilution factor is calculated using the following steps:

- Calculate the dilution factor (DF1) due to the pressurization of the sample using Equation 8 below.
- Calculate the dilution factor (DF2) of the prepared sample:
  \[ DF(2) = DF(1) \times \frac{\text{volume of sample removed from original canister}}{\text{volume of new canister}} \]
- Calculate the final dilution factor:
  \[ DF = DF(2)^* \times \frac{\text{nominal sample volume}}{\text{actual volume analyzed}} \]

Samples which arrive at the laboratory with a high vacuum (i.e., > 15 in. Hg) must be pressurized with ultra zero air or UHP nitrogen. The laboratory may also choose to pressurize all canisters upon receipt. This pressurization results in sample dilution. The resultant dilution factor is calculated using Equation 8.
Equation 8: Dilution Factor for Pressurization of Subatmospheric Samples

\[
DF = \frac{(P_f + 14.7)}{(P_i + 14.7)}
\]

where:

\( P_i \) = pressure reading of canister prior to pressurization (units = psig)

\( P_f \) = pressure reading of canister after pressurization (units = psig)

\( DF \) = dilution factor

Note: To convert from in. Hg to psig: \( \text{psig} = \text{in. Hg} \times 0.491159 \)

9.5.1 Identification of APH Target Analytes

The Target APH analytes in field samples must be identified by a qualified mass spectrometrist competent in the interpretation of chromatograms and mass spectra.

The laboratory must report all APH target analytes that meet the following criteria:

- The relative retention time (RRT) of the target analyte in the sample agrees with the RRT of the target analyte in the associated Calibration Check Standard within + 0.33 minutes; and

- The relative intensities of the primary (quantitation) and secondary ions (Table 5) for the target analyte in the sample agree within ± 20% of the relative intensities of the same ions in the Calibration Check Standard.

If co-elution of interfering components prohibits accurate identification of the sample component RRT from the total ion chromatogram, the RRT should be assigned using extracted ion current profiles for the ion unique to the component of interest.

If the above-referenced criteria are met but in the analyst’s opinion a false positive result is suspected, this must be reported and explained in the laboratory narrative.

For comparison of the target analyte’s mass spectra between samples and standards, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required (e.g., from the calibrations). Once obtained, these standard spectra must be used for identification and reference purposes.

9.6 Calculations

The concentration of Target APH Analytes and hydrocarbon ranges in a sample may be determined from the peak area response, using the RRF determined in Section 9.4. If linear regression was used for calibration, refer to Appendix 6 for sample concentration calculations. If non-linear regression was used,
refer to SW-846 Method 8000B, Section 7.5.3 for guidance. Use of non-linear regression for concentration calculations must be reported in the laboratory narrative.

9.6.1 Individual Target APH Analytes

The average response factor from the initial calibration is used to calculate the concentration of an analyte detected in the sample. Equation 9 is used to calculate the concentration of Target APH Analytes in µg/m³. Equation 10 is used to convert µg/m³ to ppbV.

Equation 9: Calculation of Sample Concentration (µg/m³)

\[
C_x = \frac{(A_x) \times (C_{IS})}{(A_{IS}) \times (RRF_{avg})} \times DF
\]

where:
- \(C_x\) = concentration of target analyte, µg/m³
- \(A_x\) = area of primary (quantitation) ion for the Target APH Analyte (see Table 5)
- \(C_{IS}\) = concentration of the associated internal standard, µg/m³: See Section 7.5
- \(A_{IS}\) = area of primary (quantitation) ion for the associated internal standard (see Table 5)
- \(RRF_{avg}\) = average RRF for the Target APH analyte to be measured
- \(DF\) = dilution factor (See Section 9.5.1)

Equation 10: Conversion of µg/m³ to ppbV

\[
ppbV = \frac{C_x \times 24.45}{MW}
\]

where:
- \(MW\) = molecular weight of the compound of interest, g/mol (see Table 1 for a list of the molecular weights of the Target APH Analytes)
- 24.45 = molar gas constant; assumes \(R = 0.08206\ L\cdot atm\/mole\cdot K\), \(T = 298\ K\) and \(P = 1\ atm\)

9.6.2 Hydrocarbon Ranges

When calculating the APH Method aliphatic and aromatic hydrocarbon range concentrations, the laboratory must include the area of all peaks eluting within the retention time windows specified for these ranges, excluding internal standards and target analytes, as described in Sections 9.6.2.1, 9.6.2.2, and 9.6.2.3 below.

The average hydrocarbon range RRF from the initial calibration is used to calculate the concentration (µg/m³) of hydrocarbon ranges in samples. Collective peak area integration for the hydrocarbon ranges must be from baseline (i.e., must include the unresolved complex mixture).

NOTE: Hydrocarbon range concentrations can only be reported in µg/m³.

At the discretion of the data user, the contribution of non-APH compounds (compounds not meeting the definitions in Sections 3.1.9, 3.1.10 and 3.1.11) that elute within the method-defined retention time
windows for the aliphatic and aromatic ranges may be excluded from collective range concentration calculations. Specifically, the total ion area counts (aliphatic ranges) and the 120/134 m/e area counts (aromatic range) for these non-APH compounds may be excluded providing the compound is positively identified by GC/MS. However, if the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count cannot be subtracted from the range. In addition, in complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible. All data adjustments and the presence of these non-APH compounds must be disclosed on the laboratory report form and laboratory narrative. A list of common non-APH compounds that elute within the aliphatic and aromatic ranges is presented in Table 7.

Detailed guidance regarding the identification criteria for these non-APH compounds is presented in Section 11.2.

9.6.2.1 \( C_5-C_8 \) Aliphatic Hydrocarbons

Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.

From this sum, subtract the total ion area counts of all internal standards which elute in this range (all of the recommended internal standards elute in this range).

Calculate a preliminary concentration in µg/m³ using Equation 11.

\[
\text{Equation 11: Calculation of Preliminary Sample Concentration (µg/m³)}
\]

\[
C_x = \left( \frac{(A_x) \times (C_{IS})}{(A_{IS}) \times \text{RRF}_{avg}} \right)
\]

where:
- \( C_x \) = concentration of hydrocarbon range, µg/m³
- \( A_x \) = \( C_5-C_8 \) aliphatics: total ion area count of all peaks eluting within aliphatic hydrocarbon range window (excluding the internal standards)
- \( C_{IS} \) = concentration of the associated internal standard (µg/m³): See Section 7.5
- \( A_{IS} \) = area count of the primary (quantitation) ion for the associated internal standard
- \( \text{RRF}_{avg} \) = average RRF for the hydrocarbon range of interest

From the preliminary concentration (µg/m³), calculate an adjusted concentration of \( C_5-C_8 \) aliphatic hydrocarbons by subtracting the concentrations of target APH analytes, which elute in this range (typically MTBE, benzene, toluene, ethylbenzene, and m-, p- & o- xylenes for the \( C_5-C_8 \) aliphatic hydrocarbons).
9.6.2.2  95-C_{10} Aromatic Hydrocarbons

Using extracted ion 120, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.

Using extracted ion 134, sum all peaks in the appropriate retention time window, as determined in Section 9.3 and Table 4.

Sum the area counts of extracted ions 120 and 134 from the above two steps.

9.6.2.3  99-C_{12} Aliphatic Hydrocarbons

Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.

From this sum, subtract the total ion area count of the BFB peak.

Calculate a preliminary concentration in µg/m³ using Equation 11, using the area count generated from the previous step for Ax.

From the preliminary concentration, calculate an adjusted concentration of C_{9}-C_{12} aliphatic hydrocarbons by subtracting the concentrations of target APH analytes, which elute in this range (possibly naphthalene depending on GC conditions), and by subtracting out the concentration of C_{9}-C_{10} aromatic hydrocarbons.
10. QUALITY CONTROL

10.1 General Requirements and Recommendations

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an Initial Demonstration of Laboratory Capability (IDLC) and an ongoing analysis of prepared QC samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data produced. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method.

At a minimum, for each analytical batch (every 24 hours), an Initial Calibration or Calibration Check Standard, LMB, LCS, and a Matrix Duplicate must be analyzed. The Initial Calibration or Calibration Check Standard, LMB, and LCS must be analyzed prior to samples.

The recommended sequence of analysis is as follows:

- Analytical batch calibration standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration), either of which are used to evaluate BFB for GC/MS tuning. [REQUIRED]
- Analytical batch LCS. [REQUIRED]
- Analytical batch LMB. [REQUIRED]
- Batch samples (up to 20).
- Matrix Duplicate. [REQUIRED]

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

10.2 Minimal Instrument QC

10.2.1 Internal Standards

Internal standards must be adequately resolved from individual compounds in the APH Calibration standard. A minimum separation requirement of 50% (maximum peak height to valley height) must be met, particularly for hexane and bromochloromethane (IS1) in a 20 µg/m³ calibration standard.

Internal standard recoveries must be evaluated with each field sample, blank, LCS and Sample Duplicate. The internal standard area counts in each field sample, blank, and LCS must be evaluated. The internal standard area counts must be within 50-200% of the internal standard area counts in the corresponding
Calibration Check Standard. If the internal standard area counts fall outside of this range, check calculations to locate possible errors, check the sample introduction system for leaks or other malfunctions, and check for changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

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

If a sample with an internal standard recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the data report form and discussed in the laboratory narrative.

Analysis of the sample on dilution may diminish matrix-related internal standard recovery problems. This approach can be used as long as RLs less than or equal to the applicable MCP standards will still be achieved with the dilution. If not, reanalysis without dilution must be performed, unless the concentrations of target analytes do not allow an undiluted run. Recoveries of internal standards outside of the acceptable range after re-analysis must also be noted on the data report form and discussed in the laboratory narrative.

**Mass spectrometer tuning** must be performed daily (once every 24 hours) before any analyses are conducted. Acceptance criteria for the recommended tuning standard, BFB, are provided in Table 2.

**Laboratory Method Blanks** must be analyzed daily (once every 24 hours) prior to sample analyses and after samples, which are highly contaminated (i.e., at concentrations above the highest calibration standard) to determine if sample carryover has occurred. If samples have been analyzed using an autosampler, data should be evaluated for potential carryover and reanalysis conducted, as appropriate. The laboratory method blank must be free of target APH analyte and hydrocarbon range contamination at or above the RL. However, C_{12} hydrocarbons and naphthalene may be present at up to two times the RL.

**Relative Retention Times** must be established for each analyte and hydrocarbon range of interest each time a new GC column is installed and must be verified and/or adjusted on a daily basis. (See Section 9.3).

10.2.2  Calibration

**Initial Calibration:** RRFs must be calculated for each APH target analyte and hydrocarbon range based upon the analysis of a minimum of 5 calibration standards (or 6 calibration standards for non-linear regression). With the exception of naphthalene, the linearity of RRFs may be assumed if the %RSD over
the working range of the calibration curve is ≤ 30. (See Section 9.4). For naphthalene, the %RSD must be ≤ 40. For linear or non-linear regression, r or \( r^2 \), respectively, must be ≥0.99.

**Calibration Check Standard:** The Calibration Check Standard must be analyzed prior to sample analysis to verify the accuracy of the calibration of the instrument. For analytes of interest, the %D must be ≤ 30. If more than one compound fails to meet this criterion, or if the %D for any one compound is greater than 50, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

**10.2.3 Laboratory Control Samples**

**Laboratory Control Samples** must be analyzed daily (once every 24 hours) prior to sample analyses. Recoveries of APH target analytes and representative aliphatic and aromatic range compounds must be between 70 and 130% (or 50-150% for naphthalene).

- If the recoveries are low and outside of the acceptance limits, reanalyze the LCS and associated samples. If still outside of the acceptance limits, recalibrate.

- If the recoveries are high and outside of the acceptance limits and the affected compound was detected in the associated samples, reanalyze the LCS and the associated samples. If recoveries are still outside of the acceptance limits, recalibrate.

- If the recoveries are high and sample results were nondetect, data can be reported without qualification; however, the high recoveries should be noted in the laboratory narrative.

**10.2.4 Matrix Duplicate**

One matrix duplicate must be analyzed once every 24 hours per matrix. Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. Equation 12 is used to calculate the RPD of the target APH analyte and hydrocarbon range concentrations. The RPD of detected results in the matrix duplicate samples must not exceed 30 when the results are >5x the RL.

- If the RPD exceeds 30 and both results are >5x the RL, the sample analysis must be repeated.

- If an analyte is detected in one analysis at >5x the RL and not detected in the duplicate analysis, the analysis must be repeated.

- If an analyte is detected in one analysis at ≤5x the RL and not detected in the duplicate analysis, the RPD is not calculable and the analysis does not have to be repeated.
• If an analyte is not detected in both the original and duplicate analyses, the RPD is not calculable.
  No further action is required.

Equation 12. Relative Percent Difference Calculation:

\[
RPD = \left[ \frac{(C_s - C_d)}{(C_s + C_d)/2} \right] \times 100
\]

where:
\( C_s \) = concentration in original sample analysis
\( C_d \) = concentration in duplicate sample analysis

If any of the performance standards specified in Section 10.2 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be rerun. These QC samples include the Calibration Check Standard, LMB and LCS. If this is not possible, that data must be reported as suspect.

10.3 Initial and Periodic Method QC Demonstrations

The procedure specified below must be conducted, successfully completed and documented as an IDLC prior to the analysis of any samples by the APH Method. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, training new analysts, and/or in response to confirmed or suspected systems, method, or operational problems.

The IDLC includes an initial demonstration of accuracy and precision. The following procedure must be used:

Analyze a minimum of four (4) replicate samples of a Calibration Check Standard.

Calculate the measured concentrations of each analyte and hydrocarbon range in all replicates, the mean accuracy (as a percentage of the true value) for each analyte and hydrocarbon range, and the precision (as %RSD) of the measurements for each analyte and hydrocarbon range.

For each analyte and hydrocarbon range, the mean accuracy, expressed as a percentage of the true value (i.e., recovery), must be between 70% and 130%, and the replicate precision, expressed as %RSD, must be \( \leq 25 \). The IDLC must meet these conditions for analysis to proceed.

**NOTE:** Method detection limit (MDL) studies are not required to be performed for the APH method.
11. DATA PRODUCTION AND REPORTING

11.1 General Reporting Requirements

The required data report content for the APH Method is presented in Appendix 3. While it is permissible to alter the form and presentation of the data, all of the information must be provided in a clear, concise, and succinct manner. This information provides data users with a succinct and complete summary of pertinent information and data, as well as a clear affirmation that the QC procedures and standards specified in this method were evaluated and achieved.

If a significant modification to the APH Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.9 on a matrix-specific and petroleum product-specific basis.

“Significant Modifications” to the APH Method shall include, but are not limited to, any of the following:

- The use of sample collection devices other than evacuated, passivated stainless steel canisters (i.e., Tedlar bags).
- The use of alternative detectors other than GC/MS to quantify target APH analytes and/or hydrocarbon range concentrations.
- The use of extracted ions other than 120 and 134 to quantify C9-C10 aromatic hydrocarbons.
- The failure to provide all of the data and information required in the report form presented in Appendix 3.

Data produced using an analytical method incorporating any of the “Significant Modifications” described above may not be reported as APH data. APH range concentrations are method-defined parameters and as such may only be reported as APH data when produced using the method without “Significant Modifications.”

Positive affirmation that all required QA/QC procedures and performance standards were followed and achieved means that all of the required steps and procedures detailed in Sections 9.0 and 10.0 have been followed, and that all data obtained from these steps and procedures were within the acceptance limits specified for these steps and procedures.

In addition to sample results, the APH data report must contain the following items:

- LMB results.
- LCS results.
• Matrix duplicate results.

• Internal standard results (for all field samples and QC samples).
  
  o Results of re-analyse If re-analysis due to internal standard issues yields similar non-conformances, the laboratory must report both results.

  o If re-analysis due to internal standard issues is performed outside of holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses.

  o If sample is not re-analyzed for internal standard issues due to obvious interference, the laboratory must provide the chromatogram in the data report.

  o If diluted and undiluted analyses are performed, the laboratory must report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, LCS, etc.) for each analysis must be reported. This may result in more than one analysis per sample being reported.

• If a significant modification to the analytical method is utilized, demonstration of compliance with analytical performance standards specified in Section 1.9 on a matrix-specific and petroleum product-specific basis must be included as an attachment to the analytical report. If the modification was not an analytical modification (e.g., use of tedlar bags), the demonstration of compliance is not required; however, the modification must be noted in the laboratory narrative.

General laboratory reporting requirements are outlined in WSC-CAM-VII A, Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data.

11.2 Reporting Requirements for Non-APH Compounds

As described in Section 9.6.2, the contribution (i.e., area count) of compounds not meeting the regulatory definition of the aromatic and/or aliphatic hydrocarbons, defined in Sections 3.1.9, 3.1.10 and 3.1.11, that elute within the method-defined retention time windows for these hydrocarbon ranges, may be excluded from collective range concentrations at the discretion of the data user, providing the compound meets the requirements for positive GC/MS identification as described in Section 11.2.1.

• If the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count may not be subtracted from the aliphatic range.

• In complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible.
All data adjustments and the presence of these positively identified non-APH compounds must be disclosed on the laboratory report form and laboratory narrative. If this data adjustment is requested by the data user, the laboratory will be required to evaluate those peaks with a peak height \( \geq \frac{1}{2} \) of the peak height of the closest internal standard. Refer to Table 7 for a list of common non-APH compounds that elute within the aliphatic and aromatic hydrocarbon ranges.

11.2.1 Requirements for Positive GC/MS Identification of Non-APH Compounds

- Spectral identification must be evaluated by a qualified mass spectrometrist.
- The spectral library match must be \( \geq 85\% \) for an identification to be made.
- The major ions in the reference spectrum (i.e., ions greater than 10\% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within \( \pm 20\% \).
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.
- Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25\% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs (as a mixture of two isomers).
  
  \[ \text{NOTE: The analyst may use professional judgment for the identification of non-APH compounds. If non-APH compounds are identified using criteria different than the criteria listed above, this should be disclosed in the laboratory narrative.} \]

- If the data user determines that the presence of the non-APH compound reported by the laboratory may appreciably increase the overall risk posed by the site or the utility/cost of the potential remedial measures under consideration, additional analytical work is recommended to verify the identification and/or concentration of the reported non-APH compound, either by
reanalysis or resampling. This contingency will require additional coordination and communication between the laboratory and the data user.
12. REPORTING LIMITS

The RLs for Target APH Analytes and hydrocarbon ranges will be determined as follows.

12.1 Target APH Analyte RLs

The RLs for the Target APH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

Example: Benzene:

- Lowest calibration standard concentration = 2 µg/m³
- RL for benzene = 2 µg/m³

12.2 C9-C10 Aromatic Hydrocarbons

The RL for the C₉-C₁₀ aromatic hydrocarbons range is determined empirically and is based upon the concentration of the lowest range calibration standard for the components which make up this range. The RL is calculated by multiplying the concentration of the lowest calibration standard by the number of APH range component compounds used in the calibration of the range.

Example: C₉-C₁₀ aromatic hydrocarbons:

- Lowest calibration standard concentration = 2 µg/m³
- Number of APH components in this range = 5
- Total concentration of lowest calibration standard = 2 µg/m³ * 5 = 10 µg/m³
- RL for C9-C10 aromatic hydrocarbons = 10 µg/m³

12.3 C₅-C₈ and C₉-C₁₂ Aliphatic Hydrocarbons

The RLs for the C₅-C₈ aliphatic and C₉-C₁₂ aliphatic hydrocarbons range are determined empirically and are based upon the concentration of the lowest range calibration standard for the components which make up these ranges. The RLs are calculated by multiplying the concentration of the lowest calibration standard by the number of APH range component compounds used in the calibration of these ranges.

Example: C₅-C₈ aliphatic hydrocarbons:

- Lowest calibration standard concentration = 2 µg/m³
• Number of APH components in this range = 6

• Total concentration of lowest calibration standard = 2 µg/m³ * 6 = 12 µg/m³

• RL for C5-C8 aliphatic hydrocarbons = 12 µg/m³

NOTE: The empirical determination of RLs for the aliphatic and aromatic hydrocarbon ranges is supported by past MDL studies performed by laboratories. Appendix 1 summarizes the results of MDL studies performed by five different laboratories for the hydrocarbon ranges. In all cases, the calculated RLs (3x the MDL) were below or close to the empirically determined RLs above.
13. METHOD PERFORMANCE

MDL study results from five laboratories for APH Method aliphatic and aromatic hydrocarbon ranges are provided in Appendix 1. An example APH Method chromatogram is provided in Appendix 2.
14. REFERENCES


MassDEP, 2002b: Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach, Massachusetts Department of Environmental Protection, WSC Policy # 02-411, October 31, 2002


15. TABLES

15.1 Table 1. APH Components

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS Number</th>
<th>Boiling Point (°C)</th>
<th>Mol. Wt. (g/mol)</th>
<th>APH Analysis Function</th>
<th>Retention Time (minutes)</th>
<th>Concentration Conversion¹ (ppbV → µg/m³)</th>
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</thead>
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<tr>
<td>1,3-Butadiene</td>
<td>106990</td>
<td>- 4.4</td>
<td>54.09</td>
<td>TA</td>
<td>5.76</td>
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<td>7.27</td>
<td>2.95</td>
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<td>Methyl tertiary butyl ether (MTBE)</td>
<td>1634044</td>
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<td>TA</td>
<td>9.64</td>
<td>3.61</td>
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<td>Benzene</td>
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<td>78.11</td>
<td>TA</td>
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<td>3.19</td>
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<td>100.20</td>
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<td>4.10</td>
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<td>n-Heptane</td>
<td>142825</td>
<td>98</td>
<td>100.20</td>
<td>RC</td>
<td>13.81</td>
<td>4.10</td>
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<td>Toluene</td>
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<td>111</td>
<td>92.14</td>
<td>TA</td>
<td>15.44</td>
<td>3.77</td>
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<td>n-Octane</td>
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<td>114.23</td>
<td>RC</td>
<td>16.29</td>
<td>4.67</td>
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<td>Ethylbenzene</td>
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<td>136</td>
<td>106.17</td>
<td>TA</td>
<td>17.28</td>
<td>4.34</td>
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<td>2,3-Dimethylheptane</td>
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<td>141</td>
<td>128.26</td>
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<td>17.32</td>
<td>5.25</td>
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<td>m-Xylene</td>
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<td>106.17</td>
<td>TA</td>
<td>17.42</td>
<td>4.34</td>
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<td>p-Xylene</td>
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<td>106.17</td>
<td>TA</td>
<td>17.42</td>
<td>4.34</td>
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<td>o-Xylene</td>
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<td>Isopropylbenzene</td>
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<td>120.20</td>
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<td>18.65</td>
<td>4.92</td>
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<td>4.92</td>
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<td>n-Decane</td>
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<td>RC</td>
<td>19.08</td>
<td>5.83</td>
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<td>1,2,3-Trimethylbenzene</td>
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<td>RC</td>
<td>19.36</td>
<td>4.92</td>
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<td>p-Isopropyltoluene</td>
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<td>19.35</td>
<td>5.49</td>
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<td>Butylcyclohexane</td>
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<td>RC</td>
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<td>5.74</td>
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<td>n-Undecane</td>
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<td>156.32</td>
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<td>20.03</td>
<td>6.39</td>
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<td>Naphthalene</td>
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<td>128.17</td>
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<td>n-Dodecane</td>
<td>112403</td>
<td>216</td>
<td>170.33</td>
<td>RC/RA</td>
<td>20.92</td>
<td>6.97</td>
</tr>
</tbody>
</table>

¹ Results obtained using the RTX-1 column and chromatographic conditions described in Sections 6.3 and 9.2, respectively.

² Conversion factors assume standard temperature and pressure (R = 0.08026 L-atm/mole-K; T = 298K; P = 1 atm).

³ The elution order of naphthalene and dodecane may be reversed, depending on the exact chromatographic conditions.

<table>
<thead>
<tr>
<th>TA - Target Analyte</th>
<th>RC - Range Calibration Aliphatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM - Range Marker</td>
<td>RC - Range Calibration Aromatic</td>
</tr>
</tbody>
</table>
### 15.2 Table 2. BFB Key Ions and Abundance Criteria

<table>
<thead>
<tr>
<th>Mass</th>
<th>Ion Abundance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>8.0 to 40.0 percent of m/e 95</td>
</tr>
<tr>
<td>75</td>
<td>30.0 to 66.0 percent of m/e 95</td>
</tr>
<tr>
<td>95</td>
<td>Base peak, 100 percent relative abundance</td>
</tr>
<tr>
<td>96</td>
<td>5.0 to 9.0 percent of m/e 95</td>
</tr>
<tr>
<td>173</td>
<td>Less than 2.0 percent of m/e 174</td>
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<tr>
<td>174</td>
<td>50.0 to 120.0 percent of m/e 95</td>
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<td>175</td>
<td>4.0 to 9.0 percent of m/e 174</td>
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<tr>
<td>176</td>
<td>93.0 to 101.0 percent of m/e 174</td>
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<tr>
<td>177</td>
<td>5.0 to 9.0 percent of m/e 176</td>
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### 15.3 Table 3a. Initial Calibration of APH Hydrocarbon Range Components

<table>
<thead>
<tr>
<th>Hydrocarbon Range</th>
<th>Hydrocarbon Range Compounds Used to Establish Range Response Factor</th>
<th>Calib. Level</th>
<th>Calibration Standard Preparation</th>
<th>Component Standard Preparation</th>
<th>Standard Calibration Concentration (based on a 0.25 liter “nominal” sample volume)</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>Working Standard Concentration</td>
<td>Injection Volume (mL)*</td>
<td>Individual Component Range Concentration (µg/m³)</td>
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<td></td>
<td></td>
<td></td>
<td>(µg/m³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅-C₈ Aliphatic</td>
<td>Isopentane</td>
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<td>25</td>
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<td>2</td>
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<td>Cyclohexane</td>
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<td>6</td>
<td>500</td>
<td>250</td>
<td>500</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatic</td>
<td>Isopropylbenzene</td>
<td>1</td>
<td>20</td>
<td>25</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1-Methyl-3-ethylbenzene</td>
<td>2</td>
<td>20</td>
<td>50</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>1,3,5-Trimethylbenzene</td>
<td>3</td>
<td>20</td>
<td>250</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>4</td>
<td>500</td>
<td>25</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>p-Isopropyltoluene</td>
<td>5</td>
<td>500</td>
<td>125</td>
<td>250</td>
</tr>
</tbody>
</table>

* *nominal sample volume for purposes of this calibration is 250 mL.

** Concentration of the individual hydrocarbon range compound multiplied by the total # of hydrocarbon range compounds used to generate the range response factor.

### 15.4 Table 3b. Initial Calibration of APH Target Analytes

<table>
<thead>
<tr>
<th>Analytes</th>
<th>APH Target</th>
<th>Level</th>
<th>Working Standard</th>
<th>Calibration Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Concentration (µg/m³)</td>
<td>Volume (mL)*</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>Methyl tertiary butyl ether (MTBE)</td>
<td>1</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>2</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>3</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Ethylbenzene</td>
<td>4</td>
<td>500</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>m-Xylene</td>
<td>5</td>
<td>500</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>p-Xylene</td>
<td>6</td>
<td>500</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>o-Xylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* *nominal sample volume for purposes of this calibration is 250 mL.*
### Table 4. APH Range Marker Compounds and Range Retention Time Windows

<table>
<thead>
<tr>
<th>Hydrocarbon Range</th>
<th>Beginning Marker</th>
<th>Ending Marker</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₈ Aliphatic Hydrocarbons</td>
<td>0.1 min. before isopentane</td>
<td>0.01 min. before n-nonane</td>
</tr>
<tr>
<td>C₉-C₁₂ Aliphatic Hydrocarbons</td>
<td>0.01 min. before n-nonane</td>
<td>0.1 min. after dodecane</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatic Hydrocarbons</td>
<td>0.1 min. after o-xylene</td>
<td>0.1 min. before naphthalene</td>
</tr>
</tbody>
</table>
### Table 5. Primary (Quantitation) & Secondary Ions for APH Components/Internal Standards

<table>
<thead>
<tr>
<th>APH Components</th>
<th>CAS Number</th>
<th>Target APH Analyte</th>
<th>Primary (Quantitation) Ion</th>
<th>Secondary Ion(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromochloromethane (IS #1)</td>
<td>74975</td>
<td>✓</td>
<td>128</td>
<td>49, 130</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>106990</td>
<td>✓</td>
<td>54</td>
<td>53, 50</td>
</tr>
<tr>
<td>Isopentane</td>
<td>78784</td>
<td></td>
<td>43</td>
<td>42, 41, 57</td>
</tr>
<tr>
<td>Methyl tertiary butyl ether (MTBE)</td>
<td>1634044</td>
<td>✓</td>
<td>73</td>
<td>45</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>110543</td>
<td></td>
<td>57</td>
<td>41, 43, 56</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>110827</td>
<td></td>
<td>56</td>
<td>84, 41</td>
</tr>
<tr>
<td>1,4-Difluorobenzene (IS #2)</td>
<td>540363</td>
<td></td>
<td>114</td>
<td>63</td>
</tr>
<tr>
<td>2,3-Dimethylpentane</td>
<td>565593</td>
<td></td>
<td>56</td>
<td>43, 57, 41</td>
</tr>
<tr>
<td>Benzene</td>
<td>71432</td>
<td>✓</td>
<td>78</td>
<td>52, 51</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>142825</td>
<td></td>
<td>43</td>
<td>71, 57, 100</td>
</tr>
<tr>
<td>Toluene</td>
<td>108883</td>
<td>✓</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>Chlorobenzene-d5 (IS #3)</td>
<td>3114554</td>
<td></td>
<td>117</td>
<td>119, 82</td>
</tr>
<tr>
<td>n-Octane</td>
<td>111659</td>
<td></td>
<td>43</td>
<td>85, 57, 71</td>
</tr>
<tr>
<td>2,3-Dimethylheptane</td>
<td>3074713</td>
<td></td>
<td>43</td>
<td>84, 85</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>100414</td>
<td>✓</td>
<td>91</td>
<td>106</td>
</tr>
<tr>
<td>m- &amp; p-Xylene</td>
<td>1330207</td>
<td>✓</td>
<td>91</td>
<td>106, 105</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>111842</td>
<td></td>
<td>43</td>
<td>57, 85</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>95476</td>
<td>✓</td>
<td>91</td>
<td>106, 105</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>98828</td>
<td></td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>1-Methyl-3-ethylbenzene</td>
<td>620144</td>
<td></td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>108678</td>
<td></td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>n-Decane</td>
<td>124185</td>
<td></td>
<td>57</td>
<td>43, 71, 85</td>
</tr>
<tr>
<td>Butylcyclohexane</td>
<td>1678939</td>
<td></td>
<td>83</td>
<td>55, 82</td>
</tr>
<tr>
<td>p-Isopropyltoluene</td>
<td>99876</td>
<td></td>
<td>119</td>
<td>105, 134</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>526738</td>
<td></td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>1120214</td>
<td></td>
<td>57</td>
<td>43, 71, 85</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>112403</td>
<td></td>
<td>57</td>
<td>43, 71, 85</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91203</td>
<td>✓</td>
<td>128</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** All APH Components are listed in Table 5 for reference purposes. Only the RRFs for Target APH Analytes need to be determined on a compound-specific basis.
### Table 6. Internal Standards and Associated Target APH Analytes and Hydrocarbon Ranges

<table>
<thead>
<tr>
<th>Bromochloromethane (IS #1)</th>
<th>1,4-Difluorobenzene (IS #2)</th>
<th>Chlorobenzene-d5 (IS #3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene Methyl tertiary butyl ether (MTBE)</td>
<td>Benzene C₅-C₈ Aliphatics</td>
<td>Toluene Ethylbenzene m-&amp;p-Xylenes o-Xylene Naphthalene C₉-C₁₂ Aliphatics C₉-C₁₀ Aromatics</td>
</tr>
</tbody>
</table>

### Table 7. List of Common Non-APH Compounds That Elute Within the APH Method Ranges

<table>
<thead>
<tr>
<th>Hydrocarbon Range</th>
<th>Potential Non-APH Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₈ Aliphatic Hydrocarbons</td>
<td>Acetone may co-elute/interfere with isopentane. Isopropyl alcohol, methyl ethyl ketone, trichloroethene, tetrachloroethene, tetrahydrofuran, hexanal, 1-butanol, hexamethylsилoxane</td>
</tr>
<tr>
<td>C₉-C₁₂ Aliphatic Hydrocarbons</td>
<td>Terpenes (e.g., a-pinene, d-limonene), phenol, benzaldehyde, n-chain aldehydes, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatic Hydrocarbons</td>
<td>Siloxanes, a-pinene, and d-limonene may slightly interfere if present at high concentrations (contribute to the area of ions 120/134)</td>
</tr>
</tbody>
</table>
16. APPENDICES

16.1 APPENDIX 1: APH METHOD DETECTION LIMIT (MDL) STUDIES

Results from five laboratories

<table>
<thead>
<tr>
<th></th>
<th>MDL C5-C8 Aliphatics (μg/m³)</th>
<th>MDL C9-C12 Aliphatics (μg/m³)</th>
<th>MDL C9-C10 Aromatics (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab 1</td>
<td>1.8</td>
<td>1.0</td>
<td>0.67</td>
</tr>
<tr>
<td>Lab 2</td>
<td>3.7</td>
<td>1.0</td>
<td>0.29</td>
</tr>
<tr>
<td>Lab 3</td>
<td>5.7</td>
<td>5.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Lab 4</td>
<td>4.6</td>
<td>6.3</td>
<td>1</td>
</tr>
<tr>
<td>Lab 5</td>
<td>4.1</td>
<td>4.7</td>
<td>5.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>MDL C5-C8 Aliphatics (μg/m³)</th>
<th>Calculated RL</th>
<th>MDL C5-C10 Aromatics (μg/m³)</th>
<th>Calculated RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab 1</td>
<td>1.8</td>
<td>5.4</td>
<td>1.0</td>
<td>3</td>
</tr>
<tr>
<td>Lab 2</td>
<td>3.7</td>
<td>11.1</td>
<td>1.0</td>
<td>3</td>
</tr>
<tr>
<td>Lab 3</td>
<td>5.7</td>
<td>17.1</td>
<td>5.0</td>
<td>15</td>
</tr>
<tr>
<td>Lab 4</td>
<td>4.6</td>
<td>13.8</td>
<td>6.3</td>
<td>18.9</td>
</tr>
<tr>
<td>Lab 5</td>
<td>4.1</td>
<td>12.3</td>
<td>4.7</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Calculated RL = 3xMDL

MDL studies performed in Fall 2008.
16.2 APPENDIX 2: APH METHOD CHROMATOGRAM
## APPENDIX 3: REQUIRED APH DATA REPORTING INFORMATION

### SAMPLE INFORMATION (check all that apply)

<table>
<thead>
<tr>
<th>Sample Type(s)</th>
<th>Grab</th>
<th>Time-integrated:</th>
<th>2 hour</th>
<th>4 hour</th>
<th>8 hour</th>
<th>24 hour</th>
<th>Other:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Container(s)</td>
<td>Canister(s) size:</td>
<td>Other:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Flow Controller(s)</td>
<td>Mechanical</td>
<td>Fixed-Orifice</td>
<td>Electronic</td>
<td>Other:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Flow Meter(s)</td>
<td>RPD of pre- &amp; post-sampling calibration check(s):</td>
<td>( \leq 20% )</td>
<td>( &gt; 20% )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### APH ANALYTICAL RESULTS

<table>
<thead>
<tr>
<th>Internal Standards:</th>
<th>Client ID</th>
<th>Lab ID</th>
<th>Date Collected</th>
<th>Date Received</th>
<th>Date Analyzed</th>
<th>Pre-sample vacuum (field)</th>
<th>Post-sample vacuum (field)</th>
<th>Lab receipt vacuum</th>
<th>Dilution Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS Tuning Standard:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>in. Hg</td>
<td>in. Hg</td>
<td>in. Hg</td>
<td></td>
</tr>
<tr>
<td>Target APH Analytes &amp; Hydrocarbon Ranges</td>
<td>Reporting Limit</td>
<td>Sample Results</td>
<td>Sample Results</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \mu g/m^3 )</td>
<td>( \mu g/m^3 )</td>
<td>( \mu g/m^3 )</td>
<td>( ppb v/v )</td>
<td>( ppb v/v )</td>
<td>( ppb v/v )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl tertiary butyl ether (MTBE)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m- &amp; p- Xylenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_5-C_8 ) Aliphatic Hydrocarbons</td>
<td>( 1,2 )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_9-C_{12} ) Aliphatic Hydrocarbons</td>
<td>( 1,3 )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_9-C_{10} ) Aromatic Hydrocarbons</td>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

1. Hydrocarbon range data from total ion chromatogram excluding any internal/tuning standards eluting in that range
2. \( C_5-C_8 \) aliphatic hydrocarbons exclude the concentration of Target APH Analytes eluting in that range
3. \( C_9-C_{12} \) aliphatic hydrocarbons exclude concentration of Target APH Analytes eluting in that range AND concentration of \( C_9-C_{10} \) aromatic hydrocarbons
16.4 **APPENDIX 4: RECOMMENDED SOP FOR CLEANING, CERTIFICATION, AND CALIBRATION OF APH AIR SAMPLING EQUIPMENT**

16.4.1 Canister Cleaning

All canisters must be certified clean and verified as leak free prior to being used for sampling.

**Recommended Equipment and Supplies**

- Flow Manifold – For attaching canisters and conveying flow during evacuation and flushing.

- Flushing Gas Source – Ultra zero air or UHP Nitrogen (compressed cylinder or on-site source) with appropriate cleaning media in line to ensure gas cleanliness.

- Roughing Pump – For initial evacuation stage.

- High Vacuum Pump – For final evacuation. Alcatel or equivalent molecular drag recommended. Alternatively, a non-oil equivalent pump may be used.

- Controls/Gauges:
  - Control valves or solenoids for enacting cycles.
  - Electronic gauges for measuring rough pressures (in psia or mm Hg) and fine pressure values (millitorrs).
  - Rough vacuum/pressure gauges used for field pressure and vacuum measurements.

- Humidification Device – Fixture or device to add humidity to canisters and flushing gas during cleaning and batch certification. Water should be deionized double distilled or HPLC grade.

- Canister Heaters – Heating belts or ovens for heating canisters to 100 degrees C to enhance removal of organic compounds.
• Laboratory Notebook/Log Book – Used to record dates and canister conditioning actions and certifications. Canisters last use must be tracked.

Recommended Procedures

• Empty all canisters to ambient pressure and attach to the manifold. Make sure that there are no leaks. This can be performed in one of two ways:
  
o Pressurize canisters with ultra zero air or UHP nitrogen to 30 psig. The canister pressure cannot vary by more than ±2 psig over a 24 hour period.

  o Apply vacuum pimp to the manifold to reduce manifold pressure. The system is leak free if the vacuum prior to cleaning is less than 500 mtorr.

• Evacuate canisters to at least 1 torr (1 mm Hg).

• Pressurize with humidified UHP nitrogen or ultra zero air up to 30 psig. Activate heating source during cleaning cycle.

• Repeat above two steps (evacuating and pressurizing). Note cycle numbers and ensure that a minimum of three cleaning cycles are completed. On the final cycle, turn off heating source and pump down with high vacuum pump to a maximum of 0.05 mm Hg (50 mtorr). This vacuum would correspond to 30 in. Hg. Close canister sampling valve prior to turning off high vacuum pump or placing the system in a standby mode.

• Remove treated canisters from the manifold. A properly evacuated canister should have a canister pressure of ≤ 0.05 mm Hg (50 mtorr; vacuum of 30 in. Hg).

Associated canister sampling equipment (e.g., flow controllers, critical orifice assemblies) should also be deemed clean and appropriate for use prior to sampling. Cleaning techniques may vary between laboratories but all procedures will include backflushing with humidified ultra zero air or UHP nitrogen. All flow controllers will be calibrated by the laboratory such that a small amount of vacuum (approximately 5 in. Hg) will remain in the canister at the end of sampling.

Recommended Equipment Certification Procedures

Batch or individual canister certification may be required depending on the requirements of the testing program.
Batch Canister Certification

- After the cleaning process is completed, a minimum of one canister per batch must be tested. A batch size of up to 20 canisters is allowed.

- Remove the canister from the manifold that exhibited the highest levels of contamination prior to cleaning (according to the analytical results). Pressurize the canister to a maximum of 30 psig with humidified ultra zero air or UHP nitrogen and analyze as a Laboratory Method Blank. Record in a laboratory notebook the serial number of this canister used for batch certification. If any of the APH target analytes or hydrocarbon range concentrations are detected at a concentration greater than one-half of their respective RLs, the entire batch of canisters must be rejected and recleaned. If three consecutive certifications fail, system maintenance is required.

- If the batch certification canister passes certification, batch canisters should be held for 24 hours uncapped prior to issue for field use. The vacuum in each canister should be rechecked prior to release for field use. The acceptance criterion for the “stored” canister vacuum is ≥ 28 in. Hg. Canisters not meeting this criterion must be retained for leak repair and not released for field use.

- At a minimum, the following information regarding canister certification should be permanently recorded and retained for a minimum of 5 years:
  
  - Processing Date
  - Canister Serial Number
  - Canister Volume (liters)
  - Serial Number for Canister used for Batch Certification
  - Post-cleaning Vacuum (in. Hg)
  - Results of the Certification Analysis

Individual Canister Certification

- After the cleaning process is completed, each canister from the batch must be tested.
- Remove each canister from the manifold. Pressurize the canister to a maximum of 30 psig with humidified ultra zero air or UHP nitrogen and analyze as a Laboratory Method Blank. Record in a laboratory notebook the serial number of the canisters being certified. If any of the APH Target analytes or hydrocarbon range concentrations are detected at a concentration greater than one-half of their respective RLs, the individual canister must be recleaned and re-certified.

- If the individual canister passes certification, it must be reevacuated and held for 24 hours uncapped prior to issue for field use. The vacuum in each canister should be re-checked prior to release for field use. The acceptance criterion for the “stored” canister vacuum is \( \geq 28 \text{ in. Hg} \). Canisters not meeting this criterion must be retained for leak repair and not released for field use.

- At a minimum, the same information listed above for Batch Canister Certification should be permanently recorded and retained for a minimum of 5 years.

Certification procedures associated with canister sampling equipment (e.g., flow controllers, critical orifice assemblies) will vary between laboratories. If certification is required, the data user must request this from the laboratory when ordering the sampling equipment.

### 16.4.2 Flow Controller Calibration

Flow controllers may be calibrated by either simulating a vacuum on the outlet side of the flow controller (the end that attaches to the canister) or by applying positive pressure to the inlet side of the flow controller. Using a NIST-traceable primary standard flow calibrator (e.g., BIOS Dry-Cal), the flow rate of air passing through the flow controller is measured. The flow rate may be adjusted by changing the size of the critical orifice used and/or performing coarse/fine adjustments on the flow controller itself. Specific procedures will vary depending on the model flow controller that is used.

The NIST-traceable primary standard flow calibrator is a mass flow meter used to accurately measure flow rates of 0 to 200 cubic centimeters per minute. This device must be constructed of inert materials. These flow calibrators must be calibrated at least annually using a certified volumetric measuring device (soap film or equivalent) and an accurate stopwatch.

The flow controller’s calibration must be verified prior to sample collection by the laboratory. Upon receipt of the canister and associated flow controller back at the laboratory, a post-sampling
calibration verification must be performed and the relative percent difference (RPD) between the initial and post sampling calibration calculated.

\[
\text{RPD} = \frac{|F_f - F_i|}{(F_i + F_f)/2} \times 100
\]

\( F_i = \text{Pre-sampling Flow Rate} \)

The flow calibration and associated sample collection interval are considered valid if the RPD is \(\leq 20\). If the RPD is \(>20\), re-sampling may be required to achieve data quality objectives. If the “elevated RPD” sample is analyzed, a notation must be provided in the laboratory narrative documenting the “compromised RPD” flow rate value. The flow controller RPD is one line of evidence in the proper collection of samples for APH analysis. If the canister vacuum is acceptable after sampling and the flow controller RPD is outside of the acceptance criteria, data quality is not adversely affected.
APPENDIX 5: APH METHOD CALCULATIONS

This Appendix provides, (1) example RRF calculations for APH aliphatic and aromatic ranges and the target analyte Benzene based on multi-point calibration data, and (2) example calculations of sample concentrations for APH aliphatic and aromatic ranges and the target analyte Benzene based on the calculated RRFs, simulated area counts, and other sample-specific data. The APH Method Analytical Flow Chart is shown in Figure 5-1.

Example Calculations

Refer to information found on Tables 5-1 through 5-4. An APH Method Calculation Worksheet in Microsoft Excel format using the analytical data presented in Tables 5-1 through 5-4 is available on the APH Method web page.

Equation 1: Relative Response Factor for Target APH Analytes

RRFs are calculated for each APH Target analyte using the area response of the analyte’s characteristic ion, its true concentration, the area response of the associated internal standard’s characteristic ion, and its concentration, using Eq. 1.

RRF calculated for Benzene, Calibration Level 1, using data found in Tables 5-2 and 5-3:

\[
RRF_{Benzene} = \frac{(A_{EC} \times C_I)}{(A_{EI} \times C_C)}
\]

Where:
- \(A_{EC} = 3556\) area count of the primary quantitation ion for Benzene (m/e 78)
- \(C_I = 37 \mu g/m^3\) concentration of internal standard (IS2)
- \(A_{EI} = 143419\) area count of the primary quantitation ion for the associated internal standard (m/e 114)
- \(C_C = 2 \mu g/m^3\) concentration of Benzene, Calibration Level 1

\[
RRF_{Benzene} = \frac{(3556 \times 37)}{(143419 \times 2)}
\]

\[
RRF_{Benzene} = 0.4587
\]
Equation 2: Relative Response Factor for C₅-C₈ Aliphatic Hydrocarbons

The RRF for the C₅-C₈ Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range and their total ion area counts.

RRF calculated for C₅-C₈ Aliphatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3.

\[
RRF_{\text{Range}} = \frac{(A_T)(C_I)}{(A_{EI})(C_T)}
\]

Where:
- \(A_T = 18097\) total ion area count of C₅-C₈ Aliphatic range (six aliphatic components)
- \(C_I = 37\) µg/m³ concentration of internal standard (IS2)
- \(A_{EI} = 143419\) area count of the primary ion for the associated internal standard (m/e 114)
- \(C_T = 12\) µg/m³ total concentration of C₅-C₈ Aliphatic range, Calibration Level 1 (six aliphatic components)

\[
RRF_{\text{Range}} = \frac{(18097)(37)}{(143419)(12)}
\]

\[RRF_{\text{Range}} = 0.3891\]

Equation 3: Relative Response Factor for C₉-C₁₂ Aliphatic Hydrocarbons

The RRF for the C₉-C₁₂ Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range and their total ion area counts.

RRF calculated for C₉-C₁₂ Aliphatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3:

\[
RRF_{\text{Range}} = \frac{(A_T)(C_I)}{(A_{EI})(C_T)}
\]

Where:
- \(A_T = 32296\) total ion area count of C₉-C₁₂ Aliphatic range (six aliphatic components)
- \(C_I = 38\) µg/m³ concentration of internal standard (IS3)
- \(A_{EI} = 316020\) area count of the primary ion for the associated internal standard (m/e 117)
- \(C_T = 12\) µg/m³ total concentration of C₉-C₁₂ Aliphatic range, Calibration Level 1 (six aliphatic components)

\[
RRF_{\text{Range}} = \frac{(32296)(38)}{(316020)(12)}
\]

\[RRF_{\text{Range}} = 0.3236\]

16-10
**Equation 4: Relative Response Factor for C₉-C₁₀ Aromatic Hydrocarbons**

The RRF for the C₉-C₁₀ Aromatic range is calculated using a summation of the m/e 120 and m/e 134 extracted ion area counts for the APH aromatic components eluting within this range (see Table 3a of the method).

RRF calculated for C₉-C₁₀ Aromatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3:

\[
RRF_{Range} = \frac{(A_T) \times (C_T)}{(A_{EI}) \times (C_I)}
\]

Where:
- \( A_T = 54343 \) summation of extracted ion area counts (m/e 120 + m/e 134: five aromatic components)
- \( C_I = 38 \) ug/m³ concentration of internal standard (IS3)
- \( A_{EI} = 316020 \) area count of the primary ion for the associated internal standard (m/e 117)
- \( C_T = 10 \) ug/m³ total concentration of C₉-C₁₀ Aromatic range, Calibration Level 1 (five aromatic components)

\[
RRF_{Range} = \frac{(54343) \times (38)}{(316020) \times (10)}
\]

**Equation 5: Percent Relative Standard Deviation**

For each target compound and range a percent relative standard deviation (%RSD) is calculated from the RRFs generated for each point of the curve using equation 5 below.

**Example: Benzene from Table 5-1:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cal 1</th>
<th>Cal 2</th>
<th>Cal 3</th>
<th>Cal 4</th>
<th>Cal 5</th>
<th>Cal 6</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.4587</td>
<td>0.5119</td>
<td>0.5167</td>
<td>0.4679</td>
<td>0.5540</td>
<td>0.5083</td>
<td>0.5029</td>
<td>0.03490</td>
</tr>
</tbody>
</table>

\[
\%RSD_{Benzene} = \left[ \frac{(SD_{n-1})}{(AVG_X)} \right] \times 100
\]

Where:
- \( \%RSD = \) percent relative standard deviation
- \( SD_{n-1} = 0.03490 \) standard deviation (n-1 degrees of freedom)
- \( AVG_x = 0.5029 \) mean response factor from the initial calibration

\[
\%RSD_{Benzene} = \left( \frac{0.03490}{0.5029} \right) \times 100
\]

\[
\%RSD_{Benzene} = 6.9
\]
Equation 7: Percent Difference

Calculate a percent difference for Benzene in a continuing calibration standard having a calculated RRF of 0.4769:

\[
\% D_{\text{Benzene}} = \frac{[(R_{FC}) - (R_{FI})]}{[(R_{FI})] \times 100}
\]

Where:
\( %D \) = percent difference
\( R_{FC} = 0.4769 \) response factor from the continuing calibration
\( R_{FI} = 0.5029 \) mean response factor from the initial calibration
\( %D_{\text{Benzene}} = \frac{[(0.4769) - (0.5029)]}{[(0.5029)]} \times 100 \)
\( %D_{\text{Benzene}} = -5.2 \)

Equation 8: Dilution Factor for Pressurization of Subatmospheric Samples

\[
DF = \frac{(P_f + 14.7)}{(P_i = 14.7)}
\]

Where:
\( P_i \) = pressure reading of canister prior to pressurization (in psig)
\( P_f \) = pressure reading of canister after pressurization (in psig)
\( DF \) = dilution factor

Note: To convert from in. Hg to psig: \( \text{psig} = \text{in. Hg} \times 0.491159 \)

Example Canister Dilution Calculation Final Pressure >0

\( P_i = -2.5 \) in. Hg = -1.28 psig
\( P_f = 10 \) psig
\( DF = (10 + 14.7) / (-1.28 + 14.7) \)
\( DF = 1.84 \)

Example Canister Dilution Calculation Final Pressure <0

\( P_i = -2.5 \) in. Hg = -1.28 psig
\( P_f = -0.5 \) in. Hg = -0.246 psig
\( DF = (-0.246 + 14.7) / (-1.28 + 14.7) \)
\( DF = 1.08 \)
Equation 9: Calculation of Sample Results in µg/m³: Target Analyte (Benzene)

Calculate a final µg/m³ concentration for Benzene using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250 L):

\[
\text{µg} / \text{m}^3_{\text{Benzene}} = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF
\]

Where:
- \( A_x = 60285 \) area count of the primary ion for Benzene (m/e 78)
- \( C_{IS} = 37 \) µg/m³ concentration of internal standard (IS2)
- \( A_x = 115082 \) area count of the primary ion for the associated internal standard (m/e 114)
- \( RRF_{avg} = 0.5029 \) average RRF for benzene
- \( DF = 1.0 \) dilution factor

\[
\text{µg} / \text{m}^3_{\text{Benzene}} = [(60285) * (37)] / [115082] * 0.5029] * 1.0
\]
\[
\text{µg} / \text{m}^3_{\text{Benzene}} = 38.5
\]

Equation 11: Calculation of Sample Results in µg/m³: C₅-C₈ Aliphatic Range

Calculate a preliminary µg/m³ concentration for C₅-C₈ Aliphatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250 L):

\[
\text{µg} / \text{m}^3_{\text{Aliphatic}} = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF
\]

Where:
- \( A_x = 823563 \) total ion area count of all peaks eluting within this range (excluding internal standard areas)
- \( C_{IS} = 37 \) µg/m³ concentration of internal standard (IS2)
- \( A_{IS} = 115082 \) area count of the primary ion for the associated internal standard (m/e 114)
- \( RRF_{avg} = 0.4177 \) average RRF for C₅-C₈ Aliphatic range
- \( DF = 1.0 \) dilution factor

\[
\text{µg} / \text{m}^3_{\text{Aliphatic}} = [(823563) * (37)] / [115082] * 0.4177] * 1.0
\]
\[
\text{µg} / \text{m}^3_{\text{Aliphatic}} = 634
\]

Calculate a final µg/m³ concentration for C₅-C₈ Aliphatic range using data found in the Sample Data Table 5-4:
Final C₅-C₈ Aliphatic range µg/m³ concentration = (Preliminary µg/m³ concentration) – (concentrations of target analytes which elute within the C₅-C₈ Aliphatic range)

Final C₅-C₈ Aliphatic range µg/m³ concentration = (634 µg/m³) – (concentrations of MTBE, benzene, toluene, ethylbenzene, xylenes)

Final C₅-C₈ Aliphatic range µg/m³ concentration = (634 µg/m³) – (44.5 + 38.5 + 37.7 + 41.0 + 78.0 + 37.9 µg/m³)

Final C₅-C₈ Aliphatic range µg/m³ concentration = 356 µg/m³

**Equation 11: Calculation of Sample Results in µg/m³: C₉-C₁₀ Aromatic Range**

Calculate a final µg/m³ concentration for C₉-C₁₀ Aromatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250 L):

\[
\mu g / m^3_{\text{Aromatic}} = \frac{(A_x) * (C_{IS})}{(A_{IS}) * (RRF_{avg})} * DF
\]

Where:
- \(A_x = 3217570\) summation of extracted ion area counts (m/e 120 + m/e 134) eluting within range
- \(C_{IS} = 38 \, \mu g/m^3\) concentration of internal standard (IS3)
- \(A_{IS} = 289465\) area count of the primary ion for the associated internal standard (m/e 117)
- \(RRF_{avg} = 0.8187\) average RRF for C₉-C₁₀ Aromatic range
- \(DF = 1.0\) dilution factor

\[
\mu g / m^3_{\text{Aromatic}} = \frac{(3217570) * (38)}{(289465) * (0.8187)} * 1.0
\]

\[
\mu g / m^3_{\text{Aromatic}} = 516
\]

**Equation 12: Calculation of Samples Results in µg/m³: C₉-C₁₂ Aliphatic Range**

Calculate a preliminary µg/m³ concentration for C₉-C₁₂ Aliphatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250L):

\[
\mu g / m^3_{\text{Aliphatic}} = \frac{(A_x) * (C_{IS})}{(A_{IS}) * (RRF_{avg})} * DF
\]

Where:
- \(A_x = 1971741\) total ion area count of all peaks eluting within this range (excluding BFB)
- \(C_{IS} = 38 \, \mu g/m^3\) concentration of internal standard (IS3)
A_{IS} = 289465 area count of the primary ion for the associated internal standard (m/e 117)

\[ \text{RRF}_{\text{avg}} = 0.3677 \] average RRF for C_{9}-C_{12} Aliphatic range

\[ \text{DF} = 1.0 \] dilution factor

\[ \mu g/m^3_{\text{Aliphatic}} = \frac{[(1971741) \times (38)]/[(289465) \times (0.3677)] \times 1.0}{\mu g/m^3_{\text{Aliphatic}}} = 704 \]

Calculate a final \( \mu g/m^3 \) concentration for C_{9}-C_{12} Aliphatic range using data found in the Sample Data Table 5-4:

Final C_{9}-C_{12} Aliphatic range \( \mu g/m^3 \) concentration = (Preliminary \( \mu g/m^3 \) concentration) – (concentrations of naphthalene and C_{9}-C_{10} Aromatics)

Final C_{9}-C_{12} Aliphatic range \( \mu g/m^3 \) concentration = \( 704 \mu g/m^3 \) – \( 38 + 516 \mu g/m^3 \)

Final C_{9}-C_{12} Aliphatic range \( \mu g/m^3 \) concentration = \( 150 \mu g/m^3 \)

**Equation 13: Percent Recovery**

From information found in Table 5-4 (Sample Data Table), calculate a percent recovery for Benzene having a true, or spiked concentration of 40 \( \mu g/m3 \).

\[ \% R_{\text{Benzene}} = [(C_{\text{found}})/(C_{\text{true}})] \times 100 \]

Where:
\( \%R \) = percent recovery
\( C_{\text{found}} \) = 38.5 concentration of the analyte or range (\( \mu g/m^3 \))
\( C_{\text{true}} \) = 40 true concentration of the analyte or range (\( \mu g/m^3 \))

\[ \% R_{\text{Benzene}} = [(38.5)/(40)] \times 100 \]

\( \% R_{\text{Benzene}} = 96 \)

**Equation 10: Conversion of \( \mu g/m^3 \) to ppbV**

To convert target analyte results from \( \mu g/m3 \) into ppbv, use the following equation. NOTE: this equation is not applicable to the hydrocarbon ranges.

\[ \text{ppbV}_{\text{Benzene}} = (\mu g/m^3)_{\text{Benzene}} \times \frac{24.45}{MW_{\text{Benzene}}} \]

Where:
\( \mu g/m^3_{\text{Benzene}} = 38.5 \)
\( MW_{\text{Benzene}} = 78.1 \)

\[ \text{ppbV}_{\text{Benzene}} = 38.5 \times \frac{24.45}{78.1} \]

\[ \text{ppbV}_{\text{Benzene}} = 12.05 \]
### TABLE 5-1: RELATIVE RESPONSE FACTORS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cal 1</th>
<th>Cal 2</th>
<th>Cal 3</th>
<th>Cal 4</th>
<th>Cal 5</th>
<th>Cal 6</th>
<th>Mean</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>3.7454</td>
<td>4.2517</td>
<td>3.8698</td>
<td>3.7343</td>
<td>4.0661</td>
<td>2.5931</td>
<td>3.7101</td>
<td>15.7</td>
</tr>
<tr>
<td>Methyl tertiary butyl ether (MTBE)</td>
<td>3.9877</td>
<td>5.0958</td>
<td>4.6380</td>
<td>4.4756</td>
<td>5.9072</td>
<td>5.0969</td>
<td>4.8669</td>
<td>13.5</td>
</tr>
<tr>
<td>Bromochloromethane (IS1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.4587</td>
<td>0.5119</td>
<td>0.5167</td>
<td>0.4679</td>
<td>0.5540</td>
<td>0.5083</td>
<td>0.5029</td>
<td>6.9</td>
</tr>
<tr>
<td>1,4-Difluorobenzene (IS2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.3663</td>
<td>0.3700</td>
<td>0.3991</td>
<td>0.3792</td>
<td>0.4910</td>
<td>0.4887</td>
<td>0.4157</td>
<td>14.1</td>
</tr>
<tr>
<td>Chlorobenzene-d5 (IS3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.9927</td>
<td>1.0447</td>
<td>1.1267</td>
<td>1.0705</td>
<td>1.0902</td>
<td>0.9343</td>
<td>1.0432</td>
<td>6.7</td>
</tr>
<tr>
<td>Xylene (m, p)</td>
<td>0.7869</td>
<td>0.8913</td>
<td>0.9613</td>
<td>0.9133</td>
<td>0.9041</td>
<td>0.7809</td>
<td>0.8730</td>
<td>8.4</td>
</tr>
<tr>
<td>Xylene (o)</td>
<td>0.7809</td>
<td>0.8473</td>
<td>0.9138</td>
<td>0.8682</td>
<td>0.9504</td>
<td>0.8417</td>
<td>0.8671</td>
<td>6.8</td>
</tr>
<tr>
<td>4-Bromofluorobenzene (BFB)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.4234</td>
<td>0.2969</td>
<td>0.3203</td>
<td>0.3043</td>
<td>0.3681</td>
<td>0.3530</td>
<td>0.3443</td>
<td>13.8</td>
</tr>
<tr>
<td>C₅-C₈ Aliphatic Hydrocarbons</td>
<td>0.3891</td>
<td>0.4618</td>
<td>0.4662</td>
<td>0.4221</td>
<td>0.4073</td>
<td>0.3594</td>
<td>0.4177</td>
<td>10.0</td>
</tr>
<tr>
<td>C₉-C₁₂ Aliphatic Hydrocarbons</td>
<td>0.3236</td>
<td>0.3598</td>
<td>0.3881</td>
<td>0.3687</td>
<td>0.4018</td>
<td>0.3640</td>
<td>0.3677</td>
<td>7.3</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatics (m/e 120)</td>
<td>0.5452</td>
<td>0.6602</td>
<td>0.7121</td>
<td>0.6765</td>
<td>0.7895</td>
<td>0.6795</td>
<td>0.6772</td>
<td>11.7</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatics (m/e 134)</td>
<td>0.1082</td>
<td>0.1330</td>
<td>0.1435</td>
<td>0.1363</td>
<td>0.1668</td>
<td>0.1612</td>
<td>0.1415</td>
<td>14.9</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatic Hydrocarbons</td>
<td>0.6535</td>
<td>0.7932</td>
<td>0.8555</td>
<td>0.8128</td>
<td>0.9563</td>
<td>0.8406</td>
<td>0.8187</td>
<td>12.1</td>
</tr>
</tbody>
</table>
### 16.5.2 TABLE 5-2: CALIBRATION CURVE AREA COUNTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cal 1</th>
<th>Cal 2</th>
<th>Cal 3</th>
<th>Cal 4</th>
<th>Cal 5</th>
<th>Cal 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>6337</td>
<td>14664</td>
<td>36660</td>
<td>183300</td>
<td>980573</td>
<td>1854649</td>
</tr>
<tr>
<td>Isopentane</td>
<td>2223</td>
<td>7456</td>
<td>18640</td>
<td>93200</td>
<td>459196</td>
<td>1031595</td>
</tr>
<tr>
<td>Methyl tertiary butyl ether (MTBE)</td>
<td>6747</td>
<td>17575</td>
<td>43937</td>
<td>219688</td>
<td>1424596</td>
<td>3645385</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1391</td>
<td>3384</td>
<td>8460</td>
<td>42300</td>
<td>255744</td>
<td>761077</td>
</tr>
<tr>
<td>Bromochloromethane (IS1)</td>
<td>3553</td>
<td>36214</td>
<td>39788</td>
<td>41232</td>
<td>40515</td>
<td>60078</td>
</tr>
<tr>
<td>Benzene</td>
<td>3556</td>
<td>8201</td>
<td>20505</td>
<td>75025</td>
<td>489347</td>
<td>967332</td>
</tr>
<tr>
<td>1,4-Difluorobenzene (IS2)</td>
<td>143419</td>
<td>148189</td>
<td>146799</td>
<td>162114</td>
<td>172980</td>
<td>246302</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1788</td>
<td>5250</td>
<td>13125</td>
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## 16.5.3 TABLE 5-3: CALIBRATION STANDARD CONCENTRATIONS (µg/m³)

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<th>Cal 4</th>
<th>Cal 5</th>
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<td>500</td>
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<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
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<td>37</td>
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<td>C₉-C₁₀ Aromatics (m/e 134)</td>
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<tr>
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<td>2500</td>
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### TABLE 5-4: SAMPLE ANALYSIS DATA

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<th>Compound</th>
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<th>Area</th>
<th>ISTD µg/m³</th>
<th>Concentration µg/m³*</th>
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<td>1,3-Butadiene</td>
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<td>Methyl tertiary butyl ether (MTBE)</td>
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<td>Bromochloromethane (IS1)</td>
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*Sample aliquot volume = 0.250 L

### 16.5.5 FROM TABLE 4 OF METHOD. APH RANGE MARKER COMPOUNDS AND RANGE RETENTION TIMES

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<tr>
<th>Compound</th>
<th>Range Start RT</th>
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<td>C₅-C₈ Aliphatic Hydrocarbons</td>
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<td>C₉-C₁₀ Aromatic Hydrocarbons</td>
<td>17.474</td>
<td>29.174</td>
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FIGURE 5-1: AIR-PHASE HYDROCARBONS (APH) METHOD
ANALYTICAL FLOW CHART

GC/MS Tuning

APH Component Standards
Internal Standards IS1, IS2 and IS3
GC/MS Tuning BFB

Perform Initial Calibration

GC/MS

Target Analytes and Aliphatic
- Relative Retention Time (RRT) – Target Analytes
- Retention Time (Rt) Windows – Hydrocarbon Ranges
- Relative Response Factors (RRFs)
- Percent Relative Standard Deviation (%RSD)

Identify and Quantify

Area Counts

Total Ion

Total Area Counts
Of Extracted Ions

Quantify C₅-C₈ and C₉-C₁₂
Aliphatic Ranges

Quantify C₉-C₁₀

Analyze Method Blank

Daily GC/MS
16.7 APPENDIX 6: APH METHOD CALIBRATION AND ANALYSIS USING LINEAR REGRESSION

Use of linear regression is permissible to calculate the slope and y-intercept that best describes the linear relationship between APH target analytes or range concentrations and instrument responses.

Prepare APH Calibration Standards as described in Tables 3a and 3b at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 9.4. The APH marker compounds for the C₅-C₈ aliphatic, C₉-C₁₂ aliphatic and C₉-C₁₀ aromatic ranges are presented in Table 4.

Analyze each APH calibration standard following the procedures outlined in Section 9.4. Tabulate area response ratios (area of target analyte/ area of internal standard) against the concentration ratio (concentration of the target analyte/concentration of internal standard). These data are used to calculate a calibration curve for each target analyte (Equation 6-1). The correlation coefficient (r) of the resultant calibration curve must be greater than or equal to 0.99.

**Equation 6-1: Linear Regression: APH Target Analytes**

\[
\frac{A_S}{A_{IS}} \cdot \frac{C_{IS}}{} = a \cdot C_S + b
\]

Where:
- \(a\) = the calculated slope of the line
- \(b\) = the calculated y intercept of the “best fit” line
- \(C_S\) = Concentration of the target analyte (\(\mu\)g/m³)
- \(A_S\) = Area count of the primary (quantitation) ion for the analyte of interest
- \(C_{IS}\) = Concentration of associated internal standard (\(\mu\)g/m³)
- \(A_{IS}\) = Area count of the primary (quantitation ion) for the associated internal standard

A calibration curve may also be established for each aliphatic and aromatic hydrocarbon range of interest. Calculate the calibration curve for C₅-C₈ Aliphatic Hydrocarbons and C₉-C₁₂ Aliphatic Hydrocarbons using the total ion integration and sum of the individual peak areas of the APH components within each range. Calculate the calibration curve for the C₉-C₁₀ Aromatic Hydrocarbons using the sum of the 120 and 134 extracted-ion chromatograms within the designated window for the range. Tabulate the ratio of the summation of the peak areas to the area of the internal standard of all components in that fraction (i.e., C₅-C₈ Aliphatic Hydrocarbons, 6 components) against the ratio of the total concentration of the range to the
concentration of the internal standard. These data are used to calculate a calibration curve for each APH hydrocarbon range (Equation 6-2). The correlation coefficient (r) of the resultant calibration curve must be greater than or equal to 0.99.

Note: Do not include the area of BFB when determining the calibration curve for C₉-C₁₂ Aliphatic Hydrocarbons. Do not include the area of the three internal standards when determining the calibration curve for C₅-C₈ Aliphatic Hydrocarbons.

**Equation 6-2: Linear Regression: APH Aliphatic and Aromatic Hydrocarbon Ranges**

\[
\frac{A_T}{A_{IS}} C_{IS} = aC_T + b
\]

Where:
- \(a\) = the calculated slope of the line
- \(b\) = the calculated y intercept of the “best fit” line
- \(C_T\) = summation of the concentrations (µg/m³) of the six aliphatic APH components which elute within this range for C₅-C₈ or C₉-C₁₂ Aliphatic Hydrocarbons or summation of the concentrations of the five APH components which elute within this range for C₉-C₁₀ Aromatic Hydrocarbons
- \(A_T\) = total ion area of the six aliphatic APH components which elute within this range for C₅-C₈ or C₉-C₁₂ Aliphatic Hydrocarbons or summation of areas of the extracted ions 120 and 134 for five APH components which elute within this range for C₉-C₁₀ Aromatic Hydrocarbons

The concentration of a specific target analyte or hydrocarbon range may be calculated using linear regression analysis by applying Equation 6-3.

**Equation 6-3: Determination of APH Target Analyte and Hydrocarbon Range Concentrations using Linear Regression**

\[
\frac{A_x}{A_{IS}} C_{IS} = aC_T + b
\]

\[
\left( \frac{A_x}{A_{IS}} C_{IS} - b \right) \div a \times D = \text{Conc. Analyte or HC Range} \ (\mu g/m^3)
\]

where:
- \(A_x\) = Response for the analyte or hydrocarbon range in the sample. Units are in area counts for APH Target Analytes and the hydrocarbon ranges.
- \(D\) = Dilution factor; if no dilution was made, \(D = 1\), dimensionless
- \(a\) = Slope of the line for APH Target Analyte or hydrocarbon range
- \(b\) = Intercept of the line for APH Target Analyte or hydrocarbon range
At a minimum, the working calibration curve must be verified every 24 hours prior to the analysis of samples to verify instrument performance and linearity. If the Percent Drift (% Drift) for more than one compound varies from the predicted response by more than ±30 or if the % Drift for any one compound is greater than 50, as determined using Equation 6-5, a new five-point calibration must be performed for that analyte.

**Equation 6-5: Percent Drift**

\[
\% \text{Drift} = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100
\]