**Atlantic RBCA**

**Guidelines for Laboratories Tier I and Tier II**

**Petroleum Hydrocarbon Methods**

**Version 3.1**

**May 2016**

## Disclaimer

This document was amended by the PIRI Analytical Laboratory Sub-committee in response to procedural changes recommended by CCME *Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment* (2016). Specifically, this revision incorporates the use of field preservation of soil samples for VPH Analysis as a best practice.

This document provides guidelines for the analysis of Petroleum Hydrocarbons in water and soil as part of Atlantic RBCA site remediation methodology. It is not intended to be a detailed laboratory procedure, but rather to outline required and performance-based elements of any method used.

# Acknowledgements

This Version 3.1 document was based on the Version 3.0 document and was prepared and edited by the Atlantic PIRI Laboratory Sub-Committee consisting of the following representatives James MacDonald (AGAT Laboratories, Dartmouth, NS), Alan Stewart (Maxxam Analytics, Bedford, NS) Bruce Phillips (Research and Productivity Council, Fredericton, NB) and Roland Gaudet (New Brunswick Department of Environment). Feedback and guidance was provided by Rita Mroz (Environment & Climate Change Canada, Dartmouth, NS).

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# 1.0 Method Overview

The Atlantic RBCA petroleum hydrocarbon method consists of two procedures:

1. A Tier I method involving an initial evaluation to assess whether the benzene, toluene, ethylbenzene and xylene(s) (BTEX) and/or total petroleum hydrocarbon (TPH) concentration minus BTEX has exceeded a *generic* risk-based screening level. This procedure reports the volatile petroleum hydrocarbons (C6-C10) including BTEX (VPH analysis), the extractable hydrocarbons (>C10-C32) (EPH analysis) as well as the modified TPH (sum of C6-C32 less BTEX). Refer to Section 4.1 for the Tier I reporting format.
2. A Tier II method to assess site-specific risk conditions. As in the Tier I analysis, the procedure consists of a VPH analysis, an EPH analysis as well as the calculation of modified TPH. In the Tier II analysis, both the VPH and EPH ranges are subdivided into aromatic and aliphatic fractions and narrower carbon ranges are reported as well. Refer to Section 4.2 for the Tier II reporting format.

This document provides required elements for both methods, thereby helping to ensure inter- laboratory comparability. The methods are as closely aligned as possible to ensure the best possible data comparability and to enhance the efficiency of the sample preparation steps.

The Tier I and Tier II methods share the feature that they are each divided into two separate procedures, namely volatile (VPH) and extractable (EPH) petroleum hydrocarbon analyses:

* + For water samples, the VPH is obtained by direct purge and trap gas chromatography/mass spectrometry (GC/MS), headspace GC with a photoionization detector (PID)/flame ionization detector (FID) or headspace GC-FID/MS analysis of the sample. The EPH is partitioned into hexane and the extracts are measured by a GC-FID analysis.
  + For soil samples, the VPH is measured using a methanol extract of the soil followed by analysis by purge and trap GC/MS, headspace GC-FID/MS or headspace GC-PID/FID. The EPH is obtained by acetone:hexane extraction and GC-FID analysis. Because different Tier I criteria exist for soil for potable and non-potable ground water usage, laboratories may need to develop two Tier I methods: i) a "low level" method for BTEX and ii) a "standard" method.

The Tier II method differs from the Tier I method in that separate concentrations are reported for aromatic and aliphatic compounds. This is accomplished through the detailed steps of the data analysis using a GC/MS or a GC-FID/MS for VPH analysis. These guidelines do not permit the use of GC-PID/FID for Tier II evaluations. The EPH analysis for Tier II differs from Tier I in the processing of the hexane extract prior to GC-FID analysis. These procedures are elaborated in the text.

**Note:** Carbon number ranges are established based on gas chromatographic elution times of straight chain n-alkane standards. The elution time for hydrocarbons (both aliphatic and aromatic) is largely dependent on their boiling points (with the GC columns specified by this method). A C12 substituted aromatic may elute later than the n-C12 alkane due to boiling point and structural differences. Consequently, this compound would not be quantified in the same range as the alkanes having twelve carbon atoms, but rather within the >C12 - C16 range.

### Calibration Standards

In order to maximize inter-laboratory data comparability, two defined mixtures of compounds are used as the primary calibration standards. The Atlantic RBCA VPH and EPH standards contain the aliphatic and aromatic compounds listed in Appendix 1. These mixtures can also be used as retention time window-setting standards.

Alternatively, a shorter list of compounds can be used for calibration purposes. Equivalent results will be obtained. Details of this alternate approach are provided in Appendix 1.

### Surrogate Standards

The VPH analysis is monitored by addition of iso-butylbenzene as a surrogate, which also serves as a retention time marker. Iso-butylbenzene and dotriacontane are used as surrogates and retention time markers for the EPH analysis. Surrogate standard recoveries should fall within the limits specified in Table 1. Surrogate recoveries outside of the specified limits should be re-analysed, or appropriately qualified on analytical reports.

### Quality Control Standards

The Atlantic RBCA EPH standard is to be used to verify the quality control of the EPH fractionation procedure (i.e. column separation check mixture). Restek gasoline (or equivalent) is used as a QC standard for the VPH analysis and Restek diluent transformer oil (or equivalent) is used for the EPH analysis. The use of these products is recommended since they represent common environmental contaminants quantified by this method, and cover all three of the Tier I carbon ranges. See Section 6 for additional details.

**2.0 VOLATILE PETROLEUM HYDROCARBONS (VPH)**

### VPH Sample Collection/Preparation

Note: All apparatus should be cleaned prior to use.

Soil: Samples received at the laboratory for analysis are to be field preserved with methanol. This involves the client taking a representative sample mass (5g or 10g sample) using a commercially available sampling device (eg. Terracore) and transferring to a 40 mL purge and trap vial containing 10 mL of Purge and Trap grade methanol. Alternate methods may also be used (eg. Encore type sampler) but the client must confirm the lab is able to process samples collected in this manner.

The following notation must appear on the Laboratory Analytical report for any sample that is not field preserved for VPH analysis.

**“*Sample(s)(note samples) were not field preserved for VPH when received at the laboratory. Analytical results for VPH parameters should be regarded as minimum values.”***

Water: Samples should be collected in 40 mL purge and trap vials and preserved in the field [0.2 g of sodium bisulphate per 40 mL vial or equivalent. (e.g. pH < 2 (2 drops\*1 concentrated HCl per 40 mL vial); copper sulphate (2 drops\*[[1]](#footnote-1) of a 10% solution))]. It may be beneficial to use sample bottles that are pre-charged with the necessary preservative. No air space should remain in the vials. Sampling in duplicate or triplicate is advised to allow for dilutions if needed and for QC purposes. A known volume of iso-butylbenzene surrogate (dissolved in methanol) is added prior to analysis.

### Purge & Trap and Headspace

Laboratories are free to establish the operating conditions for their purge & trap and headspace methods, providing that they can meet quality assurance criteria (Section 6). Specific conditions have not been set for parameters related to the purge and trap concentrator. A Supelco J trap (or equivalent) is probably the most suitable type of trap, as it allows the use of large amounts of methanol (up to approximately 2 mL in 40 mL of water).

### GC Conditions

Only DB-1, DB-5, or DB-624 (or other manufacturers’ equivalent) capillary columns are permitted for VPH analysis. Note that elution order differences exist between the phases, but these have no effect when the iso-butylbenzene surrogate is used as a retention time marker.

Specifically, DB-624 and thick film DB-5 columns exhibit the retention order n-C10 < 1,2,4- trimethyl benzene < iso-butylbenzene, while DB-1 and thin film DB-5 columns have the elution order 1,2,4-trimethyl benzene < n-C10 < iso-butylbenzene. Integration to just before the start of

the iso-butylbenzene surrogate peak ensures that 1,2,4-trimethyl benzene is included in the same

range as n-C10 in either case.

### MS Conditions

For analysis by Purge and Trap GCMS, a scan range of m/z 40 to at least m/z 200 must be used to ensure that total response factors (RFs) (and Tier I total volatile RFs) are representative. This is because the single component total ion current (TIC) responses for aliphatics are much more similar to the TIC responses for aromatics when the m/z 41, 43 aliphatic ions are included in the scan.

Note: Typical VOC analytical procedures have scans to m/z 45 in order to exclude carbon dioxide (m/z 44) and argon (m/z 40) background. Scanning to m/z 40 causes these background ions to be detected, raising the chromatographic baseline, but the advantages outweigh this disadvantage.

If a FID is used to determine total volatiles in the C6-C10 range, the MS may be operated in selected ion monitoring mode for the BTEX determination as required.

### Analysis with GC-PID-FID

As an alternative to GC/MS, GC-PID-FID may be used to measure VPH for Tier I assessments, where the PID is used to measure the concentrations of BTEX. PIDs are prone to interference from aliphatic compounds and it is recommended that samples detected for BTEX be reanalysed by GC/MS to confirm the validity of the data. A 9.6 eV lamp can be used to reduce the interference but a great deal of sensitivity is lost compared to the more common 10.0 to 10.6 eV lamps. GC/MS or GC/MS/FID must be used for Tier II VPH analyses.

### Definitions of VPH Target Analytes

The following compounds and ranges are determined as part of VPH analyses:

|  |  |
| --- | --- |
| **Tier I** | **Tier II** |
| **Benzene** | **Benzene** |
| **Toluene** | **Toluene** |
| **Ethylbenzene** | **Ethylbenzene** |
| **Xylenes** | **Xylenes** |
| **C6 - C10 Hydrocarbons** | **Aromatic >C8 - C10 Aliphatic C6 - C8 Aliphatic >C8 - C10** |

Ranges quoted refer to all compounds of a given type which have retention times within the boundaries given. Descriptors such as C6, C8, etc. refer to the retention times of the normal hydrocarbons n-hexane, n-octane, etc. Descriptors such as >C8 refer to all compounds eluting after, but not including, C8. If a descriptor does not have a > or < sign, then that n-alkane is included in the range.

The starting point of the iso-butylbenzene surrogate peak defines the limits of all retention time ranges ending in C10. For all practical purposes the end point of the C10 or 1,2,4- trimethylbenzene peak (depending on the GC column being used) is the starting point of the iso- butyl benzene peak and the C6 - C10 range is measured accurately using this approach.

### Integration and Calibration of VPH Target Compounds

The BTEX compounds are calibrated as target compounds with an expected retention time (plus or minus an acceptance range). For GC/MS analysis, a quantification ion and one qualifying ion (which must fall within an acceptable relative abundance range) or >80% match to calibration reference spectra are used to confirm identity. For GC-PID, BTEX concentrations are measured using the PID chromatogram.

The Atlantic RBCA VPH standard is used as primary calibration standard for all BTEX compounds. Thus all BTEX calibration curves may be derived from one standard.

For GC/MS, quantification and qualifier ions are as follows:

|  |  |  |
| --- | --- | --- |
| Compound | Quant. Ion, m/z | Qual. Ion, m/z |
| Benzene | 78 | 77 |
| Toluene | 91 | 92 |
| Ethylbenzene | 91 | 106 |
| Xylene(s) | 91 | 106 |

**Note 1:** For compound identification, the relative abundance acceptance range for the qualifying ion should be set at ± 20 % relative deviation (or less) from the expected relative abundance (± 30

% is permissible for responses < 5 times the reporting limit). Each laboratory should determine the expected relative abundance of the qualifying ions, as mass spectrometer temperature and scan parameters can influence them. Relative abundance values from reference spectra (such as NIST or Wiley library spectra) should be considered as approximate only.

**Note 2:** The retention time of a peak must not be more than ± 2% relative standard deviation from the expected retention time in order for the response to be assigned to the target compound. Retention times must be verified at least once each day that analysis is performed and updated as necessary.

**Note 3:** Xylene(s) refers to the sum of all three isomers (note Atlantic RBCA VPH standard requires only o- and p- isomers with the m- isomer being optional).

**Note 4**: Methyl t-Butyl Ether (MTBE) in water and soil may also be determined using the GC/MS method provided the instrumentation has been properly calibrated with this compound. The appropriate quantification and qualifier ions are 73 and 57 respectively.

### Integration and Calibration of VPH Hydrocarbon Ranges

* + 1. **VPH - Tier I C6 - C10 Range (GC/MS)**

Determine the Response Factor (RF) for the Total Purgeable C6 - C10 Hydrocarbons by integration of the TIC of all 12 components in the Atlantic RBCA VPH standard (4 n-alkanes +

BTEX + 3 other aromatics). Begin integrating from just before the start of the n-C6 peak and ending just before the start of the iso-butylbenzene surrogate peak. (Note the restrictions on scan range outlined in 2.4 MS Conditions). To obtain the RF, divide the TIC area by the sum of the concentrations of all 12 components.

Hence RF = Total Area of 12 Compounds

Summed concentrations of all 12 compounds

For samples, calculate the C6-C10 Hydrocarbon concentration using the formulas in Section 4.3. See Appendix 2 for an example chromatogram showing the VPH standard and integration ranges.

### VPH - Tier I C6 - C10 Range (GC/PID/FID or GC/MS/FID)

Determine the Response Factor (RF) for the Total Purgeable C6 - C10 Hydrocarbons by integrating (using baseline hold) the FID chromatogram of all 12 components in the Atlantic RBCA VPH standard (4 n-alkanes + BTEX + 3 other aromatics (trimethylbenzenes)). Begin integrating from just before the start of the n-C6 peak and ending just before the start of the iso- butylbenzene surrogate peak. To obtain the RF, divide the area by the sum of the concentrations of all 12 components. For samples, calculate the C6-C10 Hydrocarbon concentration using the formulas in Section 4.3.

### VPH - Tier II Aromatic >C8 - C10 Range

Integrate m/z 78, 91, 104, 105, 106, and 120 extracted MS ion chromatograms beginning just after the end of the n-C8 peak and ending just before the start of the iso-butylbenzene surrogate peak. Sum all of these areas. Determine an average RF by dividing the summed area by the total concentration of the standard aromatic components in this range (sum of ethyl benzene, p-xylene, o-xylene, 1-methyl-3-ethyl benzene, 1,3,5-trimethyl benzene, and 1,2,4-trimethyl benzene concentrations).

For samples, calculate the Aromatic >C8 - C10 concentration using the formulas in Section 4.3.

### VPH - Tier II Aliphatic Ranges

Because there are too many selected ions that are needed to adequately capture all possible aliphatic compounds, the aliphatic ranges are calculated from total hydrocarbon concentration less the applicable aromatic concentrations.

For Tier II analysis, determine two separate Response Factors (RF) for the Total Purgeable C6 - C8 and >C8 - C10 Hydrocarbons. For the first range, begin integrating the Atlantic RBCA VPH standard from just before the start of the n-C6 peak and end just after the n-C8 peak. For the second range, integrate the chromatogram from just after the n-C8 peak to just before the start of the iso-butylbenzene surrogate peak. To obtain the RFs, divide the TIC areas by the sum of the concentrations of the components in each range.

Note: If analysis is carried out on a GC/MS system, integrate the TIC. If a GC-FID/MS is used in SIM mode, integrate the FID trace.

These RFs are used differently in the C6 - C8 and >C8 - C10 ranges. In the first case, if a GC/MS has been used for analysis, the C6-C8 Aliphatic concentration is obtained by dividing the TIC area of all peaks in the range *excluding* benzene and toluene by the C6 - C8 Total RF. (Note, however, that benzene and toluene are included in the calculation of the C6 - C8 RF).

If data analysis is done using a GC-FID/MS, then the Total C6-C8 is calculated using the FID data. The C6-C8 Aliphatic concentration is then determined by subtracting the Benzene and Toluene concentrations obtained from the MS. (See Section 4.3 for details of the calculations).

In the second case, due to the larger number of aromatic peaks in the >C8 - C10 range, the approach of using TIC areas with selected components excluded is not practical. Thus, the >C8 - C10 Aliphatic concentration is obtained by calculating the Total >C8 - C10 Hydrocarbon concentration (TIC area of the range divided by the >C8 - C10 Total RF) and subtract the Total Aromatic >C8 - C10 concentration from the MS (Section 2.8.3). (See Section 4.3 for details of the calculations).

If data analysis is done using a GC-FID/MS, then the Total >C8-C10 is calculated using the FID data. The >C8 - C10 Aliphatic concentration is then determined by subtracting the Total Aromatic

>C8 - C10 concentration obtained from the MS. (See Section 4.3 for details of the calculations).

**3.0 EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)**

### EPH Sample Preparation

Soil: Soil samples should be collected in glass jars with minimal headspace, capped with Teflon lined lids and kept cold. A well-mixed portion of soil (e.g. 5 to 10 g) is placed into a 40 mL P&T vial and a known volume of iso-butylbenzene/dotriacontane surrogate (dissolved in dichloromethane) is added. A known volume (e.g. 10 to 15 mL) of 50:50 (v/v) acetone:hexane is added and the sample is mixed by vigorous shaking. Extraction times must be evaluated to ensure full recovery of the EPH using actual samples from the field.

The sample must be fully dispersed after the shaking period. Samples that are not fully dispersed using this procedure (i.e. hard clays) should be extracted first by vigorous shaking with acetone only. The hexane is then added and the samples are vigorously shaken once again.

A portion of the extract is then washed with deionized water to remove the acetone and concentrate the organics in the hexane layer. The volume of water used should be at least 5 times the volume of acetone being removed.

Water: Water samples should be collected in 250 mL or 1 L glass bottles fitted with Teflon lined caps and preserved in the field. Preservation with sodium bisulphate is preferred (pH <2), but other options may be acceptable [(~0.5 mL concentrated HCl per 250 mL); or copper sulphate (1 mL of a 10% solution in 250 mL)]. Unless the client specifies otherwise, the sample should be decanted prior to extraction and a comment flag added to the report if the sample contains more than 5% (v/v) sediment (visual examination).

The water is acidified to pH<2 (0.4 – 0.5 mL concentrated HCl per 250 mL), spiked with a small volume (e.g. 100 or 200 L) of iso-butylbenzene/dotriacontane surrogate standard (dissolved in dichloromethane) and extracted by mixing with n-hexane. Extraction conditions must be validated to ensure quantitative recovery of the EPH. The extract may be concentrated under nitrogen at room temperature to a known volume in order to achieve detection limit criteria.

### EPH Aromatic/Aliphatic Fractionation

The primary acceptance criterion for column separation of the aromatic and aliphatic EPH fractions is demonstration of separation of the components of the Atlantic RBCA EPH standard (with iso-butylbenzene added) with less than 20 % carryover of any compound into the alternate fraction. This should be demonstrated on a once per sample batch basis as part of method QC. Note: Since the Atlantic RBCA EPH standard contains a significant fraction of dichloromethane in the solvent, a 1 in 100 dilution of this standard in hexane (i.e. 10 µg/mL of each component) is recommended for use.

Laboratories may use silica gel or alumina to perform the column separation method provided QC criteria are met. The exact analytical requirements to achieve proper separation are left to the individual laboratories to determine. An example method using silica gel is provided here:

* Prepare silica gel columns by placing a glass wool plug and 7 mL of activated silica gel into a glass chromatography column. Add 1 mL of sodium sulphate to the top of the column.
* Wash the prepared silica gel column twice with n-hexane and transfer 1 mL of sample extract onto the silica gel column. Elute the sample with small volumes of hexane and collect the eluent from the column. Add the minimum volume of hexane required to elute all of the aliphatic components.
* Remove the sample collection tube and replace it with a new tube. Elute the column with small volumes of 50/50 (v/v) dichloromethane/acetone until all of the aromatic components have been removed from the column.
* Concentrate the aromatic and aliphatic extracts under nitrogen at room temperature to a known volume sufficient to achieve the required reporting limit criteria. Analyse the extracts separately by capillary column GC-FID.

### EPH GC Conditions

Only DB-1 and DB-5 (or other manufacturers' equivalent) capillary columns are permitted for this analysis. A flame ionization detector (FID) is used to detect and quantify the components.

### Definitions of EPH Target Analytes

The ranges determined as part of EPH Tier I and Tier II analyses are provided below. Ranges quoted refer to all compounds of a given type which have retention times within the boundaries given. Descriptors such as C12, C16, etc. refer to the retention times of the normal hydrocarbons n-dodecane, n-hexadecane, etc. Descriptors such as >C21 refer to all compounds eluting after, but not including, C21. If a descriptor does not have a > or < sign, then that n-alkane is included in the range.

The integration of >C10 begins just after the end of the iso-butylbenzene surrogate peak. This compound elutes just after decane and is not included in the >C10 - C32 ranges. The C10 descriptor is retained for simplicity.

The integration of the >C21 - C32 ends just prior to the start of the C32 peak. This single component is also used as a surrogate and it is not included in the >C21 - C32 range. Again, the C32 descriptor is retained for simplicity.

|  |  |
| --- | --- |
| **Tier I** | **Tier II** |
| **>C10 – C16 Hydrocarbons**  **>C16 – C21 Hydrocarbons**  **>C21 - C32 Hydrocarbons** | **Aromatic >C10 - C12 Aromatic >C12 - C16 Aromatic >C16 - C21 Aromatic >C21 - C32**  **Aliphatic >C10 - C12 Aliphatic >C12 - C16 Aliphatic >C16 - C21 Aliphatic >C21 - C32** |

### Integration and Calibration of EPH Tier I Ranges

Determine the Response Factor (RF) by integrating (using baseline hold) the FID chromatogram of the components in the Atlantic RBCA EPH standard (mixture of n-alkanes + PAHs - see Appendix). Begin integrating just after the end of the iso-butylbenzene peak until just after the end of the C16 peak. Divide the FID area in the >C10 – C16 range by the sum of the concentrations of the components in the >C10 – C16 range to obtain the >C10 – C16 extractable RF.

Integrate the range beginning just after the C16 peak until just after the end of the C21 peak – this is the >C16-C21 hydrocarbon range. Divide the FID area in the >C16 – C21 range by the sum of the concentrations of the components in this range to obtain the >C16 – C21 extractable RF.

Then integrate from just after the end of the C21 peak to just before the start of the C32 peak. Divide the FID area by the sum of the concentrations of all components in the >C21 - C32 range to obtain the >C21 - C32 extractable RF.

To calculate total hydrocarbon concentration for a specific range, determine the total area of the FID chromatogram for the carbon number range and divide it by the RF for that range. An example chromatogram showing the integration ranges used is given in Appendix 3.

### Integration and Calibration of EPH Tier II Aromatic and Aliphatic Ranges

Integrate the FID chromatograms for the aromatic fractions beginning just after the end of the iso- butylbenzene surrogate peak to just after the end of the C12 peak, (>C10 - C12). Then integrate from that point to just after the end of the C16 peak (>C12 - C16) and similarly for the C21 (>C16 - C21) and C32 peaks (>C21 - C32). Determine an average RF within each aromatic range by dividing the area in each range by the total concentration of the standard aromatic components within each range. To calculate the total aromatic concentration for any given range, determine the total area of the FID chromatogram for the retention time range of interest and divide this value by the RF established for the range.

Repeat the above procedure for the aliphatic fractions using the aliphatic standard components within each range. (Alternatively, response factors may be derived from the average of aromatic and aliphatic compounds in each range, and the same RF used for calculation of both fractions, provided that the instrument response factors for aromatics and aliphatics are quite similar.)

### Return to Baseline at C32

Labs reporting data using this method must indicate whether the chromatogram has returned to baseline in the analytical report. Samples that have not reached baseline at C32 may require additional analysis. ***For the purposes of this method samples are considered to have returned to baseline if the area from C32-C36 is less than 10% of the area from C10-C32.*** In some cases, it may be possible for the chromatogram to have returned to baseline without meeting this criterion. In such cases where it the chromatogram has obviously returned to baseline, it is acceptable to indicate on the analytical report that the sample has returned to baseline.

**4.0 CALCULATIONS AND REPORTING**

For both Tier I and Tier II soil samples, The analytical report must clearly specify any soil samples that are submitted to the lab without being field preserved. The comment format shall be:

***“Sample(s)(note samples) were not field preserved for VPH when received at the laboratory. Analytical results for VPH parameters should be regarded as minimum values.”***

### Tier I Reporting Format

Report the following analytes and surrogates for Tier I analyses (mg/L for waters; mg/kg (dry weight basis) for soils, and state % moisture).

|  |  |
| --- | --- |
| Benzene | |
| Toluene | |
| Ethylbenzene | |
| Xylenes | |
| C6 - C10 Hydrocarbons | |
| >C10 – C16 Hydrocarbons | |
| >C16 – C21 Hydrocarbons | |
| >C21 - C32 Hydrocarbons | |
| Modified TPH – Tier I |  |
| Return to Baseline at C32 | (Yes/No) |
| % Rec. iso-butylbenzene – VPH | |
| % Rec. iso-butylbenzene – EPH | |

% Rec. n-dotriacontane – EPH

Notes:

* + 1. Xylenes refers to the total of o-, m-, and p- isomers
    2. C6 - C10 Hydrocarbons does not include BTEX

3. Modified TPH – Tier I = (C6 - C10) + (>C10 - C16) +(>C16 – C21) + (>C21 - C32)

(does not include BTEX)

### Tier II Reporting Format

Report the following analytes and surrogates for Tier II analyses (mg/L for waters; mg/kg (dry weight basis) for soils, and state % moisture):

|  |
| --- |
| Benzene Toluene Ethylbenzene Xylenes |
| Aromatic >C8 - C10 Aromatic >C10 - C12 Aromatic >C12 - C16 Aromatic >C16 - C21 Aromatic >C21 - C32 |
| Aliphatic C6 - C8 Aliphatic >C8 - C10 Aliphatic >C10 - C12 Aliphatic >C12 - C16 Aliphatic >C16 - C21 Aliphatic >C21 - C32 |
| Modified TPH - Tier II  Return to Baseline at C32 (Yes/No) |
| % Rec. iso-butylbenzene – VPH  % Rec. iso-butylbenzene – EPH  % Rec. n-dotriacontane – EPH |

Notes:

* + 1. Xylenes refers to the total of o-, m-, and p- isomers
    2. Aromatic >C8 - C10 does not include ethylbenzene or xylenes
    3. Modified TPH - Tier II = sum of all aliphatic + aromatic ranges (does not include BTEX)

### Calculations

Response factors are defined as area per unit concentration. For simplicity, a modified response factor RFmay be used which is simply the 1/RF.

RF= 1 = Summed concentrations of all 12 compounds RF Total Area of 12 Compounds

This simplifies calculation of concentration to the form in Section 4.3.1

### VPH in Water

For all individual compounds and ranges, calculate the concentration in the water sample as follows:

Concentration (mg/L) = Area \* RF\* DF

Where: Area = the appropriate integrated area of the peak or range (see 2.7 or 2.8)

RF = the appropriate modified response factor of the peak or range (see 4.3) DF = the dilution factor, if required.

Note that standard concentrations must be expressed in mg/L of water.

### Tier I

Tier I C6 - C10 Hydrocarbons = [Total C6-C10 Purgeables] – [BTEX]

### Tier II

Tier II C6-C8 and >C8-C10 ranges:

Aliphatic C6 – C8 = [Total C6 – C8]\* – [B] – [T]

Aromatic >C8 - C10 = [Total Aromatic >C8 - C10] – [E] – [X] Aliphatic >C8 - C10 = [Total >C8 - C10]\* – [Total Aromatic >C8 - C10]

= [Total >C8 - C10]\* – [Aromatic >C8 - C10] – [E] – [X]

\* Use total from GC-FID trace when operating mass spectrometer in SIM mode otherwise use MS trace.

### VPH in Soil

In the case of soil samples, results must be expressed on a dry weight basis. The measured instrumental concentration must be converted to a soil concentration. Factors to be considered include the wet weight of soil analysed, the percent moisture, the volume of methanol used for extraction and analysis and the dilution effect caused by moisture in the soil mixing with the methanol used for extraction. Calculate concentrations in dry soil as follows:

Concentration (mg/kg) = Area \*RF\* Vol (water) \* Vol (total)

Vol (aliquot) \* Ww \* (100-%M)/100

Where: Area = Integrated area of the peak or range (see 2.7 or 2.8)

RF = Modified response factor of the peak or range (see 4.3)

Vol (water) = Volume of water solution (mL) which contains the extract aliquot (after dilution for analysis)

Vol (total) = Total Extract Volume in mL (= Methanol added to soil + water extracted).

= Vol (methanol added to the soil sample) + [Ww \* %M/100 ÷ 1 g/mL]

%M = Percent moisture determined from a separate aliquot of soil

Vol (aliquot) = Volume of extract (methanol + entrained water, mL) taken for dilution and analysis

Ww = Wet weight (g) of sample extracted (the term (100-%M)/100 corrects this to equivalent dry weight)

Note that standard concentrations must be expressed in mg/L of water.

### Tier I

Tier I C6 - C10 Hydrocarbons = [Total C6-C10 Purgeables] – [BTEX]

### Tier II

Tier II C6-C8 and >C8-C10 ranges:

Aliphatic C6 – C8 = [Total C6 – C8]\* – [B] – [T]

Aromatic >C8 - C10 = [Total Aromatic >C8 - C10] – [E] – [X] Aliphatic >C8 - C10 = [Total >C8 - C10]\* – [Total Aromatic >C8 - C10]

= [Total >C8 - C10]\* – [Aromatic >C8 - C10] – [E] – [X]

\* Use total from GC-FID trace when operating mass spectrometer in SIM mode otherwise use MS trace.

### EPH in Water

For all ranges, calculate the concentration in the water sample as follows: Concentration (mg/L) = Area \* RF\* Vol (extraction)\*Vol (final) \* DF

Vol (recovered) \* Vol (sample)

Where: Area = Integrated area of the range (see 3.5 or 3.6)

RF = Modified Response factor of the range (see 4.3) Vol (final) = Final volume of extract (mL)

Vol (sample) = Volume of water extracted (mL)

Vol (extraction) = Volume of extraction solvent added to the sample. Vol (recovered) = Amount of extraction solvent recovered.

DF = Dilution factor, if required.

Note that standard concentrations must be expressed in µg/mL of hexane.

### EPH in Soil

In the case of soil samples, results must be expressed on a dry weight basis. The measured instrumental concentration must be converted to a soil concentration. Factors to be considered include the wet weight of soil analysed, the percent moisture and the volume of hexane (the acetone is removed by water washing) used for extraction. Calculate concentrations in dry soil as follows:

Concentration (mg/kg) = Area \*RF\* Vol (extraction) \* Vol (final) DF

Vol (recovered)\*Ww \* (100-%M)/100

Where: Area = Integrated area of the range (see 3.5 or 3.6)

RF = Modified response factor of the range (see 4.3)

Vol (extraction) = Volume (mL) of hexane added to the soil (not volume of hexane:acetone)

Vol (final) = Final volume of the extract

Vol (recovered) = Amount of extraction solvent recovered.

DF = Dilution factor, if required.

Ww = Wet weight (g) of sample extracted (the term (100-%M)/100 corrects this to equivalent dry weight)

%M = Percent moisture determined from a separate aliquot of soil Note that standard concentrations must be expressed in µg/mL of hexane.

### Modified TPH

In order to compare analysis results with the Atlantic RBCA lookup tables, Total Petroleum Hydrocarbons must be reported as “Modified TPH”, that is, TPH less BTEX. Thus,

Tier I Modified TPH = (Total C6 - C10) + (>C10 – C16) + (>C16 – C21) + (>C21 - C32) - (BTEX)

Tier II Modified TPH = sum of all aliphatic + aromatic ranges (does not include BTEX)

### Surrogate Recovery

Percent recoveries of surrogates are to be calculated and included on the final report.

**5.0 PETROLEUM HYDROCARBON RESEMBLANCE COMMENTS**

The terms "Gas", "Diesel / #2" and "#6 Oil" appear along with corresponding modified TPH values in the Tier I look up table. The modified TPH (C6 - C32 less BTEX) concentration in the sample is compared to the values found in this table and the nature of the contaminant on the site determines whether the Gas, Diesel / #2 or #6 Oil value is used. For example, if the principal product contaminating the site is gasoline, then the Gas criteria are used. Analytical reports from laboratories must accurately specify the nature of the detected contaminants.

To ensure data comparability between laboratories, the following resemblance comments are commonly used to describe the type(s) of petroleum contamination detected. It should be noted that this process of assigning a petroleum source type to the observed contamination is subjective and the identification is not always definitive.

### Gasoline

Characteristics of gasoline include a boiling range that ends at approximately C10 - C12, with most of the mass fraction being in the C6 - C10 range; the presence of the BTEX compounds; the presence of C3- and C4- alkyl substituted benzenes and the presence of additives such as methyl- tertiary-butyl ether (MTBE, detectable by purge and trap analysis of water). If gasoline contamination is suspected, the sample chromatogram should be directly compared to a solution of gasoline analysed under the same conditions as the sample. Based on this comparison, the following resemblance comments could be made:

GASOLINE FRACTION. This indicates close similarity to the gasoline standard both in terms of the constituent compounds and their approximate relative ratios. Note, however, that significant differences exist between manufacturers, grades, and seasons of production, so this comment should be applied in a very general way.

WEATHERED GASOLINE. This indicates that some of the gasoline constituents have been partially or entirely removed relative to the fresh gasoline standard. Typical weathering patterns include relatively low (or absent) volatile constituents (i.e. an apparent increase in the relative amount of the heavier compounds) due to evaporation; selective removal of the more water- soluble (BTEX) constituents by water washing or microbial action, etc.

ONE PRODUCT IN GAS RANGE. This indicates that the hydrocarbon product elutes primarily within the C6 - C10 range, but it contains considerably different constituents from gasoline or very unusual relative ratios. Examples of this type of contamination would be petroleum-based cleaning solvents, aviation gas and refinery process streams.

### Diesel Fuel/Furnace Oil

Diesel fuel, in this context, refers to a general class of petroleum distillate fuels. In fact, a large number of variations exist (diesel #1, diesel #2, home heating oil, marine diesel, etc.) which are not treated separately here.

In general, diesel fuel corresponds to a boiling range of approximately C8 to C24, or higher, with most of the mass fraction in the C10 - C21 range (note that some BTEX may also be present). It is characterized in the GC-FID analysis by a prominent “hump” of unresolved compounds underlying a series of individually resolved compounds that includes the n-alkanes and some highly specific branched alkanes. These “biomarkers” include pristane (prominent peak just after n-C17), phytane (peak just after n-C18), nor-pristane (elutes between n-C16 and n-C17) and farnesane (elutes between n-C14 and n-C15). These biomarkers are excellent indicators of the presence of petroleum-derived products, even if other features are not present.

Following direct comparison of sample contamination to a reference chromatogram of diesel analysed under the same conditions, the following comments may be applied:

FUEL OIL FRACTION. This indicates close similarity to the diesel standard both in terms of the constituent compounds and their approximate relative ratios. Note, however, that the different types of distillate fuels have different boiling ranges (i.e., n-alkane at beginning and end), different maximum points for the “hump” of unresolved compounds, and differences in the most abundant n-alkane. As a result, this comment should be applied in a very general fashion.

WEATHERED FUEL OIL FRACTION. This indicates that some of the fuel oil constituents have been partially or entirely removed relative to the fresh fuel oil standard. Typical weathering patterns include relatively low (or absent) volatile constituents (i.e. an apparent narrowing and shift of the maximum point of the “hump” towards the heavier compounds) due to evaporation; selective removal of the n-alkanes by microbial action, etc.

ONE PRODUCT IN FUEL RANGE. This indicates that the hydrocarbon product elutes primarily within the C10 - C21 range, but that it contains considerably different constituents from diesel or very unusual relative ratios. An example of this type of contamination would be very heavily weathered diesel fuel that has lost all identifying features or a relatively low boiling mineral oil.

### #6 Fuel Oil/Lubricating Oil

In general, these oils are distillate products with heavier boiling ranges than diesel fuel (mainly in the C21 - C32 range). The heavy fuel oils generally exhibit an unresolved “hump” of a large number of compounds, which may begin well before C21 and end after C32. They also have resolved features such as n-alkanes, but pattern matching of these oils can be very difficult due to relatively wide boiling ranges.

Lubricating Oils, in contrast to heavy fuel oils, have few or no individually resolved peaks (n- alkanes are partially or totally removed), and may have relatively narrow boiling ranges. A large number of possible products exist (motor oils, gear oils, mineral oils, etc.) and these can have considerably different boiling ranges.

Because specific identification of heavy oils is very difficult, and because no additional information is needed to apply the look up tables, the following comment should be applied in all cases where a product is present:

LUBE OIL FRACTION. This indicates close similarity to lube oil standards that elute primarily in the C21 - C32 range.

### Mixtures

In the case where more than one type of contamination is present, the best estimate of its composition should be given in the comment, for example: “WEATHERED FUEL OIL FRACTION, LUBE OIL FRACTION” or “ONE PRODUCT GAS/FUEL RANGE”.

Mixtures are sometimes difficult to evaluate and, as a consequence, can be the cause of differences of opinion between analysts.

### No Resemblance

In the case where the chromatographic trace does not resemble available reference products or the chromatographic trace is indicative of a material that is non-petrogenic in origin, the term “NO RESEMBLANCE” should be used.

### Unidentified Compounds or Unknown Peaks

In some cases, a relatively small number of compounds or peaks may be observed which do not appear to be similar to distillate products (no “hump”, n-alkanes or biomarkers) or other known petroleum products. The following comment should be used:

UNIDENTIFIED COMPOUND(S) (or UNKNOWN PEAK(S)) IN THE C6 - C10 (or C10 - C21 or

C21 - C32) RANGE(S). This comment indicates that the contamination observed is definitely not petrogenic in nature. An example of the use of this comment would be the presence of fatty acids derived from vegetation or other chemical contaminants such as plasticizers or PAHs.

Note: In cases where there is likely to be a significant contribution to the modified TPH due to the presence of non-petrogenic hydrocarbons, silica gel clean-up may remove some chromatographic interferences. Labs should refer to the procedure outlined in the CCME PHC method or other relevant method. A notation must appear on the analytical report when silica gel has been used to treat samples.

**6.0 QUALITY ASSURANCE AND QUALITY CONTROL**

### General and Tier I QA/QC

* + 1. All response factors from initial calibration curves for individual components and ranges must have a relative standard deviation of 15%. Alternatively, a correlation coefficient criterion (e.g. 0.995 or better) may be established. Five-point curves are recommended.

Calibration curves must be verified when prepared through the use of second source standards. Commercially available BTEX and PAH mixtures can be used in this application. Continuing calibration standards must be run at least every 12 hours of GC run time. The responses of individual components and ranges must be within ± 30% of the calibration curves.

Because individual component standards are used for calibration, the linear ranges determined for the standard concentrations are not directly applicable to petroleum product concentrations. As a result, a sample response should be considered outside the linear range when the height of any peak in the sample is greater than the height of the highest standard. In these cases, the sample should be diluted and reanalysed.

* + 1. Method blanks shall be prepared on a once-per batch basis (up to 20 samples per batch) for all analyses. Blank levels must be less than reporting limits, otherwise the analysis must be repeated or the reporting limit raised to the blank level. GC sequences should contain a method blank or solvent blank for every 5 to 10 sample injections.
    2. Method detection limits for ranges should be determined as part of initial method validation using low concentrations of petroleum products, not the individual component standards used for calibration.
    3. Each laboratory shall maintain a standard operating procedure with detailed descriptions of the particulars of the method as routinely applied. This documentation must also include method validation data, including statements of linearity, precision, accuracy, and method detection limits.
    4. Sample duplicates should be prepared on a once per batch basis (up to 20 samples per batch). The Relative Percent Difference (RPD) is calculated as follows:

RPD = (Abs (Result A – Result B) x 100) /Average (A+B).

The relative percent difference acceptance criteria are provided in Table 1 and are applicable to duplicate samples having concentrations > 5 times the reporting limit.

* + 1. Matrix Spikes or Blank Spikes (Process Spikes) should be prepared on a once per batch basis (up to 20 samples per batch) using the gasoline or transformer oil QC standards. Recovery of the products must be within the range specified in Table 1.

Individual labs must determine the area percentage of gasoline eluting within the C6 – C10 range through a GC-FID analysis of an appropriate gasoline standard in the absence of a solvent peak (e.g. headspace analysis). This percentage (typically 50 – 70%) is then used to establish the concentration of gasoline present in the C6-C10 range. Alternatively, laboratory derived acceptance criteria can be established based upon historical analysis data. Samples that do not meet the acceptance criteria should be prepared once again and reanalysed.

Matrix spike percent recoveries are calculated as follows:

Abs (conc. spiked sample – conc. unspiked sample) x 100 Spiked concentration

Matrix Spike acceptance limits apply to samples having a native (unspiked) concentration

< 2 times the spiking level. For example, in soils, if the spiking concentration = 1000 mg/kg, the matrix spike acceptance criteria would only apply if the unspiked sample concentration was < 2000 mg/kg.

* + 1. For all samples, recovery of the iso-butylbenzene and n-dotriacontane surrogates should be in the range specified in Table 1. Alternatively, laboratory derived acceptance criteria can be established based upon historical analysis data. Samples that do not meet the acceptance criteria should be prepared once again and reanalysed.

### Tier II EPH Column Fractionation QA/QC

* + 1. Prepare a 1 in 100 dilution of the Atlantic RBCA EPH standard (i.e. 10 µg/mL of each component) in hexane as a column fractionation check standard. In addition, include iso- butylbenzene in this solution, as under certain conditions the separation efficiency of alkylbenzenes may be significantly different from those of the PAH compounds in the Atlantic RBCA EPH standard.
    2. On a once-per batch basis, verify that all of the aliphatic and aromatic components of the column fractionation check standard (diluted Atlantic RBCA EPH standard plus iso- butylbenzene) are separated in to their respective fractions with no more than 20% carryover into the opposite fraction.
    3. All of the aliphatic and aromatic components of the column fractionation check standard should be recovered in the range of 70% to 130% of the expected concentration.
    4. For all samples, recovery of the iso-butylbenzene and n-dotriacontane surrogates should be in the range specified in Table 1 in the aromatic and aliphatic fractions, respectively.

Table 1

### Data Quality Criteria for Atlantic RBCA Hydrocarbon Analysis

|  |  |
| --- | --- |
| **VPH Water** |  |
| Blank Spike Recovery | 70-130 % |
| Surrogate Recovery (Isobutylbenzene) | 70-130 % |
| Matrix Spike Recovery | 70-130 % |
| Laboratory Duplicate Results (RPD) | 40% |

|  |  |
| --- | --- |
| **VPH Soil** |  |
| Blank Spike Recovery | 60-140 % |
| Surrogate Recovery (Isobutylbenzene) | 60-140 % |
| Matrix Spike Recovery | 30-130 % |
| Laboratory Duplicate Results (RPD) | 50% |

|  |  |  |
| --- | --- | --- |
| **EPH Water** | Tier I | Tier II |
| Blank Spike Recovery | 70-130 % | 60-130 % |
| Surrogate Spike Recovery (Isobutylbenzene, n-Dotriacontane) | 70-130 % | 60-130 % |
| Matrix Spike Recovery | 70-130 % | 60-130 % |
| Laboratory Duplicate Results (RPD) | 40% | 40 % |

|  |  |  |
| --- | --- | --- |
| **EPH Soil** | Tier I | Tier II |
| Blank Spike Recovery | 60-140 % | 60-130 % |

|  |  |  |
| --- | --- | --- |
| Surrogate Spike Recovery (Isobutylbenzene, n-Dotriacontane) | 60-140 % | 60-130 % |
| Matrix Spike Recovery | 30-130 % | 30-130% |
| Laboratory Duplicate Results (RPD) | 50% | 50 % |

**7.0 SAMPLE HOLDING TIMES**

### Water samples

* + - BTEX / C6 – C10 (preserved to pH < 2 or with sodium bisulphate or equivalent): Samples to be refrigerated (1 to 6°C) and analysed within 14 days after sampling.
    - >C10 – C32 (preserved to pH < 2 or with sodium bisulphate or equivalent): Samples to be refrigerated (1 to 6°C) and extracted within 14 days after sampling. Extracts to be refrigerated (1 to 6°C) and analysed within 40 days of preparation.

### Soil samples:

* + - BTEX / C6 – C10: Methanol field preserved soil samples must be refrigerated (1 to 6°C) and analysed within 28 days of collection. Samples which are not field preserved must be refrigerated and extracted within 72 hours of receipt at lab (or sooner to meet 7 day hold time) or 7 days of collection, whichever is less. Any samples that are not field preserved must be identified and the notation in Section 2.1 must appear on the Analytical Report.
    - >C10 – C32: Samples to be refrigerated (1 to 6°C) and extracted within 14 days. Extracts to be refrigerated (1 to 6°C) and analysed within 40 days of preparation.

### REFERENCES

* + - ATLANTIC RBCA (Risk-Based Corrective Action) Version 3.0 For Petroleum Impacted Sites in Atlantic Canada, User Guidance, revised January 2015.
    - Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier I Method, Canadian Council of Ministers of the Environment Inc., 2001.
    - Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 1 – Guidance Document and Volume 4 – Compendium of Analytical Methods for Contaminated Sites, Canadian Council of Ministers of the Environment, 2016.
    - Weisman, W. (ed.), Total Petroleum Hydrocarbon Criteria Working Group Series, Analysis of Petroleum Hydrocarbons in Environmental Media, Volume 1, Amherst Scientific Publishers. Amherst, Massachusetts, 1998.
    - Potter, Thomas L. and Simmons, K.E., Total Petroleum Hydrocarbon Criteria Working Group Series, Volume 2, Composition of Petroleum Mixtures, Amherst Scientific Publishers. Amherst, Massachusetts, 1998.
    - Massachusetts Department of Environmental Protection, Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), January 1998.
    - Method for Determination of Gasoline Range Organics, American Petroleum Institute Publication, Revision 5, 1992.
    - Method for Determination of Diesel Range Organics, American Petroleum Institute Publication, Revision 3, 1992.
    - Method for Characterization of Petroleum Hydrocarbons in Soil, American Petroleum Institute Publication, Revision 1, 1992.
    - USEPA SW846 Method 8260B, Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS), Revision 2, 1996.
    - USEPA SW846 Method 8015B, Nonhalogenated Organics Using GC/FID, Revision 2, 1996.
    - USEPA SW846 Method 5030, Purge and Trap for Aqueous Samples, Revision 2, 1996.
    - USEPA SW846 Method 5035, Closed-System Purge and Trap and Extraction for Volatile Organics in Soil and waste Samples, Revision 0, 1996.

### APPENDIX 1

**Atlantic RBCA Standards**

|  |  |  |
| --- | --- | --- |
| **Volatiles (in methanol)** |  | **Extractables (in hexane/DCM - 85%/15%)** |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Aromatic** | **Aliphatic** |  | **Aromatic** | **Aliphatic** |
|  |  |  |  |  |
| Benzene | Hexane (C6) |  | Naphthalene | Decane (C10) |
| Toluene | Heptane (C7) |  | Acenaphthene | Dodecane (C12) |
| Ethylbenzene | Octane (C8) |  | Anthracene | Hexadecane (C16) |
| o-Xylene | Decane (C10) |  | Chrysene | Heneicosane (C21) |
| p-Xylene |  |  | Benzo[a]pyrene | Octacosane (C28) |
| 1-Methyl-3-ethylbenzene |  |  |  | Dotriacontane (C32) |
| 1,2,4-Trimethylbenzene |  |  |  |  |
| 1,3,5-Trimethylbenzene |  |  |  |  |

Note: The VPH standard may also include m-Xylene at the same concentration as p-Xylene. If this is the case, the total number of compounds in the VPH standard would equal 13 instead of 12.

Any subsequent calculations would need to account for this.

**Alternate Approach:** Because the FID analysis produces nearly equal responses for aliphatic and aromatic compounds within a particular range, fewer compounds can be used to calibrate the FID for EPH. The following compounds at a minimum are to be used for EPH calibration: C21. acenaphthene, and benzo[a]pyrene.

If these compounds are used, the areas of C21 and acenaphthene are used to calibrate the >C10-C16 and >C16-C21 ranges for Tier I analysis, and the >C10-C12, >C12-C16, >C16-C21 ranges for Tier II analysis.

The C21 and benzo[a]pyrene areas are used to calibrate the >C21-C32 range in Tier I and II analysis.

Stock alkane mixes would then need to be used for retention time marking if the complete PIRI standard is unavailable.

**Example Chromatogram showing VPH Integration Range**



**Example Chromatogram showing EPH Integration Range**



1. \* - assumes 20 drops per mL. [↑](#footnote-ref-1)