

## DRAFT Extractable Petroleum Hydrocarbons (EPH) in Water by GC/FID

**Parameters** Extractable Petroleum Hydrocarbons (nC10-nC19) in water  
Extractable Petroleum Hydrocarbons (nC19-nC32) in water

<b>Analyte Symbols and EMS Codes</b>	<b>Analyte Symbol</b>	<b>Approx MDL</b>	<b>EMS Code</b>
	EPH <sub>w10-19</sub>	0.25 mg/L	LEPH F065
	EPH <sub>w19-32</sub>	0.25 mg/L	HEPH F065

Note that the above EMS codes are not corrected for PAHs.

**Analytical Method** Hexane Micro-Extraction - Gas Chromatography with Flame Ionization Detection (GC/FID).

**Introduction** This method measures the aggregate concentration of Extractable Petroleum Hydrocarbons (EPH) in water, divided into two boiling point ranges, each quantitated against eicosane (nC20). EPH<sub>w10-19</sub> measures hydrocarbons that elute between nC10 and nC19 (b.pt. range of ~ 174-330°C). EPH<sub>w19-32</sub> measures hydrocarbons that elute between nC19 and nC32 (b.pt range of ~ 330-467°C).

The EPH parameters are precursors to the calculation of Light and Heavy Extractable Petroleum Hydrocarbons (LEPH and HEPH). Specified Polycyclic Aromatic Hydrocarbon (PAH) results are subtracted from EPH concentrations to arrive at LEPH and HEPH using the procedure outlined in the BC Lab Manual method "Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids or Water (LEPH & HEPH)".

Petroleum products that are captured by EPH have substantial components within the boiling point range of ~ nC10-nC32 (e.g. the majority of most diesel fuels, lubricating oils, greases, and waxes). Many petroleum products contain components within both the VH and EPH parameter ranges (e.g. kerosenes, jet fuels, and weathered gasolines). Heavy hydrocarbons with boiling points greater than nC32 are not captured by EPH.

In addition to quantitative numerical results, this method generates FID chromatograms that can sometimes be used to characterize the type of petroleum hydrocarbon mixture present in a sample.

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e. PAHs). However, the hexane extract produced by this method may be used for the analysis of PAHs by GC/MS if performance requirements are met.

**Method Summary** Water samples are extracted using hexane either directly within the sample container (standard procedure) or within a separatory funnel (alternate procedure). A single vigorous extraction using a small volume of hexane is normally conducted. Two extractions with a larger volume of hexane are used in circumstances where the standard extraction procedure is ineffective (samples with high solids, substantial NAPL presence, or samples that form difficult emulsions). A quantitative portion of the hexane extract is concentrated by evaporation if necessary to achieve detection limit requirements, and is analyzed by capillary column gas chromatography with flame ionization detection.

This is a Performance Based Method (PBM) with many prescriptive elements included where necessary to maintain consistency of results among laboratories.

This version of the EPH method was adopted in order to improve interlaboratory consistency and to more directly target non-polar organic compounds that comprise petroleum hydrocarbons.

**Matrix** Fresh water, wastewater, seawater.

**Interferences and Precautions**

Contaminants present in solvents, reagents, sample containers, or sample processing equipment may cause interferences or yield artifacts. Phthalate esters and silicones are common interferences for this test that can potentially be introduced from exposure to plastics or silicone rubber. Test method conditions must be suitably monitored by routine analysis of method blanks.

The hexane extraction solvent of this method is non-polar and specifically targets non-polar and aromatic hydrocarbons that compose crude oils and refined hydrocarbon products. Polar organics characteristic of natural source hydrocarbons are not specifically targeted, but high levels of polar organics may cause positive interferences. Interferences from polar compounds may be removed by silica gel cleanup if natural source hydrocarbons are believed to be at cause.

Pure petroleum samples are not applicable to the extraction and preservation components of this method, but may be analyzed by the EPH analytical procedures. Most middle-distillate or heavier petroleum products (diesels, oils, etc.) can simply be dissolved in hexane and analyzed by standard EPH analytical protocols.

**Sample Handling and Preservation**

Collect samples in amber glass bottles with Teflon-lined lids. 250 mL sample bottles are effective and are commonly used, but larger or smaller containers may be used depending on laboratory preference.

Preservation with ~ 1 gram / 250 mL sample with Sodium Bisulfate ( $\text{NaHSO}_4$ ) or with HCl or  $\text{H}_2\text{SO}_4$  (to  $\text{pH} \leq 2$ ) is recommended.

Where possible, groundwater samples should be collected such that they do not contain solids except where representative of the sample. Sampling staff are referred to the British Columbia Field Sampling Manual to minimize suspended solids in collected water samples.

For compliance purposes, this method requires the extraction and analysis of the total contents of each sample container, including hydrocarbons which may be present as Non-Aqueous Phase Liquid (NAPL), adsorbed to solids within the sample, or adsorbed to the surface of the sample container, with the exception that for the micro-extraction procedure, a small portion of sample may be removed and discarded to allow room for the hexane extraction solvent and for a mixing space. The recommended practice is for the laboratory to provide sample bottles with a "fill-to" line (avoids the need to remove a portion of sample).

**Stability**

**Holding Time.** Maximum holding time prior to extraction is 14 days after sampling if preserved, or 7 days after sampling if unpreserved. Maximum hold time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

**Storage Conditions:** Store samples at  $\leq 10^\circ\text{C}$  during shipment to lab, and at  $\leq 6^\circ\text{C}$  at the laboratory.

**Standard Micro-Extraction Procedure**

Inspect sample for solids or NAPL. The default micro-extraction procedure is not appropriate for samples containing a Non-Aqueous Phase Liquid (NAPL) beyond a trace surface sheen or for samples with high levels of solids (more than ~10% solids by volume). NAPL contributes error to the assumed volume of hexane extraction solvent. High levels of solids tends to cause emulsions, and may require additional solvent for effective extraction. The alternate Separatory Funnel extraction procedure is recommended for these types of samples.

Record observations if NAPL or solids are observed to be present.

Invert sample and shake well to mix contents, then immediately use a pipette to remove enough sample (taken from below the surface – do not pour) to allow room for hexane extraction solvent plus sufficient air space to accommodate effective mixing.

If sample was preserved, add just enough NaOH or KOH solution to counteract the acidity of the preservative (e.g. add 1.50 mL of 6N NaOH or equivalent per 1 gram of sodium

bisulfate). If PAHs will be concurrently extracted, it is recommended that pH is verified as  $\geq 7$  to ensure that ionizable nitrogen-containing PAHs like acridine and quinoline are in their neutral (solvent extractable) forms. Do not routinely add excess base if not necessary, because high hydroxide ion concentrations can cause emulsions in some samples. Adjustment of pH is optional if PAHs will not be concurrently extracted and analyzed.

Add at least one surrogate compound to all samples and QC using a 100% acetone solution. Surrogates highlight possible problems with analyses or with the extraction process (e.g. due to emulsions or excessive sediment loads). Use of a volatile surrogate that elutes slightly earlier than nC10 (e.g. 2-methylnonane or 2-bromobenzotrifluoride) is required as a check for evaporative losses if extract concentration steps are applied.

To each sample, add an exact amount of hexane extraction solvent (mixtures of hexane isomers are recommended over n-hexane due to cost). The amount of hexane extraction solvent used must be within a ratio of 20:1 to 30:1 for sample volume to hexane volume.

Cap, shake briefly, and vent any pressure build-up.

Apply vigorous mechanical shaking to extract samples with hexane extraction solvent for at least 30 minutes. Suitable mechanical shaking processes include wrist shakers, rapid tumblers ( $\geq 60$  rpm), paint shakers, and orbital or reciprocal platform shakers, where performance requirements can be met (on-axis rolling extractions are not permitted).

Allow phases to separate. Separate aqueous and hexane phases by centrifugation if necessary.

If required to meet detection limit requirements, transfer an exact portion of the hexane extract to a suitable glass vial for further evaporative concentration to an exact reduced final volume.

Store extracts at  $\leq 6$  °C.

**Alternate  
Separatory Funnel  
Extraction  
Procedure**

This procedure is provided as an alternative protocol for samples where the standard micro-extraction procedure may be ineffective. This procedure is recommended for samples containing a visibly distinct Non Aqueous Phase Layer (i.e.  $> \sim 1$  mL NAPL in a 250 mL sample, which would contribute to the hexane extraction solvent volume, causing error of  $>10\%$ ), or for samples containing solids exceeding  $\sim 10\%$  by volume, or for any samples that form emulsions that are difficult to separate.

When this procedure is required, conduct a Method Blank and an LCS by the same procedure, and add a comment to the laboratory report indicating that the alternate separatory funnel procedure was conducted.

Transfer the entire sample to a separatory funnel of suitable volume. If the micro-extraction is initially attempted, but is determined to be unsuitable (for any of the reasons described above), the entire sample may be transferred to a separatory funnel for completion of the extraction by this procedure.

If sample was preserved, add just enough NaOH or KOH solution to counteract the acidity of the preservative (e.g. add 1.50 mL of 6N NaOH or equivalent per 1 gram of sodium bisulfate). If PAHs will be concurrently extracted, it is recommended that pH is verified as  $\geq 7$  to ensure that ionizable nitrogen-containing PAHs like acridine and quinoline are in their neutral (solvent extractable) forms. Do not routinely add excess base if not necessary, because high hydroxide ion concentrations can cause emulsions in some samples. Adjustment of pH is optional if PAHs will not be concurrently extracted and analyzed.

Add at least one surrogate compound to all samples and QC using a 100% acetone solution. Surrogates highlight possible problems with analyses or with the extraction process (e.g. due to emulsions or excessive sediment loads). Use of a volatile surrogate that elutes

slightly earlier than nC10 (e.g. 2-methylnonane or 2-bromobenzotrifluoride) is required as a check for evaporative losses if extract concentration steps are applied.

To the original sample container, add hexane extraction solvent at a volume equal to approximately 10% of the sample volume. Shake the sample container well, and transfer contents to the separatory funnel. Shake the separatory funnel well to mix sample and hexane for at least 2 minutes.

Transfer water sample back to original sample bottle. Drain first hexane extraction layer to a collection flask through a funnel of sodium sulfate. Rinse sodium sulfate with hexane.

Transfer water sample back to separatory funnel. Repeat with a second extraction using an additional amount of hexane extraction solvent equal to approximately 10% of the sample volume. Shake the separatory funnel for at least 2 minutes.

Transfer water sample back to original sample bottle. Drain second hexane extraction layer to the collection flask through a funnel of sodium sulfate, rinse with hexane, and combine with hexane from first extraction.

If required to meet detection limit requirements, evaporatively concentrate the hexane extract to an exact reduced final volume.

Store extracts at  $\leq 6^\circ\text{C}$ .

#### **GC-FID Analysis**

Analyze sample extracts by GC-FID. Splitless inlets are recommended but on-column or other inlets may be used if QC and relative response requirements are met.

The chromatography software used must be capable of storing and integrating chromatographic data using a forced baseline projection or other means of integrating all signal above that of an instrument blank.

FID was chosen for this method because FID is the most universal detector for hydrocarbons and generates nearly equivalent response by weight or concentration for most hydrocarbons and other organic compounds (more so than any other detector).

Samples must be matrix-matched with calibration standards and QC samples in terms of the solvent used.

#### **Example GC-FID Conditions**

The following GC-FID conditions are provided as example only. Any conditions that can baseline resolve the solvent peak from nC10 and that meet specified QC and relative response requirements are acceptable. GC phase type must be 100% dimethylpolysiloxane.

Column:	100% dimethylpolysiloxane (e.g. DB-1), 30 m, 0.32 mm id, 0.25 $\mu\text{m}$ phase
Carrier Gas:	helium
Head pressure:	25 psi @ $65^\circ\text{C}$ (with column dimensions as specified)
Column flow:	6.8 mL/minute @ $65^\circ\text{C}$ (80 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	$300^\circ\text{C}$
Injection solvent:	hexane
Injection volume:	2 $\mu\text{L}$
Injection mode:	splitless or on-column
GC liner type:	4mm id splitless liner with glass wool
Inlet purge on time:	1.0 minute (splitless)
FID temperature:	$320^\circ\text{C}$
Oven program:	Initial Temp $65^\circ\text{C}$ (hold 2.0 minutes) $15^\circ\text{C}/\text{min}$ to $320^\circ\text{C}$ (hold 10 minutes)

## Standards

Ensure that all calibration standards and reference solutions are warmed to room temperatures and mixed well prior to use to ensure complete dissolution of all components. Store all standards refrigerated at  $\leq 6$  °C.

### Calibration Standard Stock Solution

Prepare or purchase a Calibration Standard Stock Solution containing decane (nC10), nonadecane (nC19), eicosane (nC20), and dotriacontane (nC32). A concentration of 1,000 mg/L in hexane is recommended.

### Calibration Standards

Prepare a minimum of 3 levels of Calibration Standards in hexane, each containing decane (nC10), nonadecane (nC19), eicosane (nC20), dotriacontane (nC32), and all selected surrogate compounds. Concentrations of 20, 50, and 250  $\mu\text{g/mL}$  in hexane are recommended.

### Calibration Verification Standard

Prepare a Control Standard containing eicosane (nC20) in hexane at 50  $\mu\text{g/mL}$  or near the mid-point of the calibration. It must be prepared from a source independent from the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions).

### Diesel / Motor Oil (DMO) Stock Solution

Prepare a stock solution of 1:1 diesel #2 : motor oil (non-synthetic SAE30 or 10W30) in hexane by weight (e.g. weigh 1.25 g of diesel #2 and 1.25 g motor oil into a 25 mL volumetric flask to make a 100,000 mg/L solution). Record the source of the diesel and motor oil used. Retain additional quantities of these spiking materials for future use, because new target concentrations must be determined whenever new sources are used. Note that the nominal concentration of diesel + motor oil (i.e. the weight/volume of diesel + motor oil) is not exactly equal to the concentration of  $\text{EPH}_{\text{w}10-19} + \text{EPH}_{\text{w}19-32}$  (the nominal concentration may be higher).

### Diesel / Motor Oil (DMO) Spiking Solution

Dilute the DMO Stock Solution by a factor of 5x into acetone to prepare a 20,000 mg/L DMO Spiking Solution (used for LCS and Method Validation purposes). Motor Oil is practically insoluble in pure acetone, but the DMO mixture is soluble at this concentration in 4:1 acetone:hexane.

### Detection Limit Check Standard

Dilute the DMO Stock Solution to prepare a Detection Limit (DL) Check Standard in hexane. Prepare the standard at a concentration that is approximately equal to the extract concentration that corresponds to the Reporting Detection Limits for  $\text{EPH}_{\text{w}10-19}$  and  $\text{EPH}_{\text{w}19-32}$ . This standard is required for Initial Calibration QC.

## Quality Control

All required calibration and QC components of this method are summarized in the table below. Each of these components is described in detail in this section.

Summary of EPHw QC and Calibration Requirements		
QC Component	Minimum Frequency	Data Quality Objectives
<b>Instrument Performance QC</b> Instrument Performance Check	Daily at beginning of each analysis batch, repeated at least every 24 hours.	Relative response ratios must be 0.7-1.3 for nC10/nC20 and nC32/nC20.  nC10, nC19, nC32 retention times $\pm 0.2$ mins of initial calibration

<b>Calibration QC and Verification</b>		
RSD of nC20 Response Factor	Each initial calibration	≤ 15% RSD
Instrument Blank	1 per initial calibration	< Reported Detection Limit (before background correction)
Calibration Verification Standard	1 per initial calibration	Within 15% of expected concentration.
Detection Limit Check Standard	1 per initial calibration	50 – 150% of EPH targets.
Continuing Calibration Verification	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	nC20 within 15% of initial calibration nC10, nC19, nC32 retention times ± 0.2 mins of initial calibration
<b>Method QC</b>		
Method Blank	1 per 20 samples (1 per batch minimum)	< Reported Detection Limit.
Laboratory Control Sample (Diesel/Motor Oil Method Spike)	1 per 20 samples (1 per batch minimum)	70-130% recovery
Laboratory Duplicates	Not applicable due to whole sample analysis	Not applicable
Surrogates	add to every sample	60-140%*
<b>Field QC</b>		
Field Duplicates	Recommended	Not specified
* Surrogate DQOs do not apply when samples contain high levels of hydrocarbons that interfere with the measurement of the surrogate. Non-measurable surrogate recoveries due to interference does not indicate a data quality issue.		

## Instrument Performance QC

### Instrument Performance Check

REQUIRED. Perform this check at least daily, at the beginning of each analysis batch, and repeat at least every 24 hours. The Instrument Performance Check is used to:

- Measure and control relative response ratios of EPH components,
- Determine retention time windows for EPH integration ranges, and
- Confirm resolution of decane (nC10) from the solvent peak.

The Instrument Performance Check ensures that GC/FID response factors throughout the EPH boiling point range are roughly equal, which is important for interlaboratory consistency.

Compute the relative response ratios (by peak area) for nC10/nC20 and for nC32/nC20, to ensure they fall with the acceptance criteria of 0.7 – 1.3. If these response ratios are not met, associated sample data is suspect and corrective action is required. Loss of response of any of the compounds in the mixture may indicate that GC maintenance is necessary.

Check retention times for nC10, nC19, and nC32 retention time markers. After each initial calibration, update retention times used for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> integrations if new retention times differ significantly from last update (e.g. by more than 0.05 minutes for the example GC program).

Within a run, confirm that nC10, nC19, and nC32 retention times are stable. Establish lab-specific acceptance criteria for allowable retention time drift, up to a maximum deviation of ± 0.2 minutes from retention times of the initial calibration. Substantial retention time drifting

normally indicates a GC inlet leak, which requires correction and re-analysis of affected samples.

## Calibration QC

### Instrument Blank (IB)

REQUIRED. Minimum 1 per initial calibration. Inject a solvent blank to the GC system using the injection solvent (e.g. hexane) to establish the chromatographic baseline and to ensure its suitability. Compute an Instrument Blank concentration using typical sample calculation factors. The resulting concentration must be below the Reporting Detection Limit.

### Calibration Verification Standard (CVS)

REQUIRED. Minimum 1 per Initial Calibration. CVS must contain nC20, prepared independently from calibration standards (at least from alternate stock solutions). Acceptance criteria is +/- 15% of target, for a mid-concentration standard.

### Detection Limit Check

REQUIRED. Minimum 1 per initial calibration. The sensitivity of the GC-FID system at the Reporting Detection Limit must be verified regularly using a low level solution of DMO. Acceptance criteria is 50-150% of targets.

### Continuing Calibration Verification (CCV)

REQUIRED. Minimum every 12 hours and at end of analysis batch if > 6 hrs from previous check. Use a mid-level nC20 calibration standard as CCV. Verify that retention times of nC10, nC19, and nC32 fall within the lab-specified acceptance range, as defined under the Instrument Performance Check (to a maximum of  $\pm 0.2$  mins from initial calibration retention times).

## Method QC

### Method Blank (MB)

REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Prepare a Method Blank using organic-free reagent water.

### Laboratory Control Sample (LCS)

REQUIRED. Minimum 1 per 20 samples. Prepare a Diesel / Motor Oil LCS by fortifying organic-free reagent water with an accurate volume of a DMO Spike Solution, which should be prepared at a concentration at least 10x the laboratory's reported detection limit. The LCS solution must be spiked from a solution of at least 80% acetone.

Determine targets for  $EPH_{w10-19}$  and  $EPH_{w19-32}$  by directly analyzing several replicates of the DMO Spike Solution diluted to a concentration equal to the target final extract concentration for the method.

### Laboratory Duplicates

NOT APPLICABLE. Laboratory Duplicates are not possible with this method, since the entire contents of each sample are consumed with each analysis.

### Surrogate Compounds

REQUIRED. At least one Surrogate Compound is required. If extract concentration steps are applied within the method, a volatile Surrogate Compound (eluting earlier than nC10) must be used (e.g. methyl-nonane or 2-bromobenzotrifluoride). Surrogate(s) must be added to each sample in acetone solution prior to extraction. Surrogates that elute outside the EPH retention time range are recommended so that there is no need to subtract them from integrated EPH peak areas.

Positive interferences from high concentration volatile hydrocarbons in a sample may sometimes preclude the accurate measurement of FID surrogates. This does not indicate a data quality issue, and no action is required in this circumstance. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (e.g. report "n/a").

**Calibration &  
Analysis  
Procedure**

**Field Duplicates**

RECOMMENDED. DQOs depend on sampling techniques and project objectives and are unspecified by this method.

**Initial Calibration**

A minimum 3 point linear average response factor (not linear regression) calibration against eicosane (nC20) is required for this method. Calibration standard concentrations of 20, 50, and 250 µg/mL are recommended.

For each analysis batch, verify that the GC system is performing adequately by conducting all checks specified in the Instrument Performance QC section.

For each point in the multi-point nC20 calibration, calculate a Response Factor (RF) for eicosane (nC20):

$$RF_{nC20} (\text{mL}/\mu\text{g}) = \text{nC20 area} / [\text{nC20}] (\mu\text{g}/\text{mL})$$

Average the Response Factors for all calibration levels to obtain an Averaged Response Factor for nC20,  $RF_{nC20, \text{Avg}}$

The relative standard deviation of the Response Factors must be < 15% in order to be considered acceptable.

**Ongoing Verification of Calibration (Verification Standards)**

After initial calibration, the Response Factor of nC20 must be verified, at minimum, after every 12 hours of continuous operation, by re-analysis of a Calibration Standard. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

A calibration remains valid as long as the nC20 Response Factor remains within 15% of the average Response Factor from the initial calibration (for a mid-level CVS).

**Integration of Total Areas for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub>**

EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> are defined to include all GC-FID peaks eluting between decane (nC10) and dotriacontane (nC32). Determine the total integrated peak area of each EPH range, where:

- a) EPH<sub>w10-19</sub> begins at the apex of the nC10 peak and ends at the apex of the nC19 peak.
- b) EPH<sub>w19-32</sub> begins at the apex of the nC19 peak and ends at the apex of the nC32 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch.

Peak integration must include all peaks, whether resolved or not, that are above the chromatographic baseline, as established by instrument blanks within the analysis batch.

Automated software integrations of EPH areas must be visually verified, and must be manually corrected where integration error appears to exceed approximately 2%.

Both EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> are quantitated against eicosane (nC20) using a linear averaged response factor calibration.

If any surrogate compound(s) utilized elute within the EPH range of nC10 – nC32, then the contribution to EPH of those surrogates must be excluded or subtracted from EPH results.



Use the following equations to calculate  $EPH_{w10-19}$  and  $EPH_{w19-32}$ :

$$EPH_{w10-19} (\text{ug/mL}) = [ A_{(10-19)} \div RF_{nC20} ] * [ FV * ECF * Dil / Vol ]$$

$$EPH_{w19-32} (\text{ug/mL}) = [ A_{(19-32)} \div RF_{nC20} ] * [ FV * ECF * Dil / Vol ]$$

where:

$A_{(10-19)}$  = Total area between nC10 and nC19 for the sample chromatogram.

$A_{(19-32)}$  = Total area between nC19 and nC32 for the sample chromatogram.

$RF_{nC20}$  = Average Response Factor for nC20 standard (mL/ug)

FV = Final Volume of extract (mL)

ECF = Extract Concentration Factor (post-extraction, unitless)

Dil = Dilution factor of sample extract (unitless)

Vol = Volume of sample extracted (mL)

### **Dilution Requirement for High Level Sample Extracts**

All valid sample analyses must lie within the validated linear range of the GC/FID system, based on initial validation. Any samples that exceed the validated linear range must be diluted and re-analyzed.

## **Method Validation Requirements**

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate EPH results for unknown samples.

### **Initial Verification of Relative Response Requirements**

Before proceeding with further validation steps, verify that the GC-FID method meets the relative response requirements of the method by performing the Instrument Performance Check (see the Instrument Performance QC section).

### **Calculation of Actual [EPH] of a Diesel / Motor Oil Reference Solution**

This procedure describes how to calculate the *Actual  $EPH_{w10-19}$  and  $EPH_{w19-32}$  Concentrations* for solutions of 1:1 Diesel / Motor Oil (DMO) where only the nominal weight/volume concentration of the DMO solution is explicitly known. *Actual EPH Concentrations* of a petroleum product solution can only be measured experimentally.

*Actual  $EPH_{w10-19}$  and  $EPH_{w19-32}$  Concentrations* are required within this method for the following purposes:

- Determination of GC/FID linear range for  $EPH_{w10-19}$  and  $EPH_{w19-32}$  (calibration range).
- Determination of  $EPH_{w10-19}$  and  $EPH_{w19-32}$  Instrument Detection Limits (IDLs).
- Preparation of DL Check Standards and LCS Solutions.
- Calculation of  $EPH_{w10-19}$  and  $EPH_{w19-32}$  targets for DL Check Standards and LCS Solutions.

Use the following procedure to calculate the *Actual  $EPH_{w10-19}$  and  $EPH_{w19-32}$  Concentrations* of a DMO Stock Solution:

- Prepare a reference solution of 1:1 Diesel : Motor Oil from the DMO Stock Solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for  $EPH_{w10-19}$  and  $EPH_{w19-32}$ . A nominal DMO concentration of at least 2,000  $\mu\text{g/mL}$  is recommended for this purpose (for the example GC conditions provided). This concentration is referred to in the example below as [DMO].
- Perform a minimum of 3 replicate analyses of the DMO solution from above using the selected GC-FID method conditions.

- c) Calculate the percentage that each EPH range represents of the total DMO concentration:

$$\begin{aligned}\% \text{ EPH}_{w10-19} \text{ in DMO solution} &= 100\% \times [\text{EPH}_{w10-19, \text{measured}}] / [\text{DMO}] \\ \% \text{ EPH}_{w19-32} \text{ in DMO solution} &= 100\% \times [\text{EPH}_{w19-32, \text{measured}}] / [\text{DMO}]\end{aligned}$$

where [DMO] = nominal concentration of Diesel / Motor Oil stock solution ( $\mu\text{g DMO / mL}$ )

**Note:** The sum of the percentages of each EPH fraction in a 1:1 Diesel : Motor Oil mixture is typically about 80-90%, because some components of DMO may fall outside the nC10 – nC32 boiling point range.

- d) To calculate the *Actual EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> Concentrations* of other dilutions of the same DMO source, multiply the nominal DMO concentration of the solution by the percentages determined above.

### **Establish Instrument Calibration Working Range and Estimated IDLs**

Establish the linear working range of the GC-FID system for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> using a series of dilutions of the DMO Stock Solution prepared in hexane. Analyze DMO solutions at concentrations ranging from below the estimated Instrument Detection Limit to above the estimated maximum calibration concentration in approximately 2-fold increments. For the example GC-FID conditions provided, the following solution concentrations are recommended as an approximate guide: 100, 200, 500, 1,000, 2,500, 5,000, 10,000, and 20,000  $\mu\text{g/mL}$  of DMO. Calculate EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> results for each solution using the procedure described in the Calculations section.

At the Limit or Reporting, EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> should be measurable at 50-150% of the expected concentration.

Any samples whose EPH responses exceed the upper limit of the validated linear range must be considered over-range, and must be diluted and re-analyzed.

### **Establishing Method Detection Limits**

Determine the Method Detection Limits (MDLs) at the 99% confidence level for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub>, using the procedure outlined in the British Columbia Environmental Laboratory Manual or a comparable reference.

Select a concentration for method spikes of DMO into organic-free reagent water that will result in extracts with concentrations of between one and three times the estimated IDLs for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> (as determined above). Prepare, extract, and analyze at least 8 method spikes at this concentration as per the method.

Calculate the Method Detection Limit (MDL) at the 99% confidence level for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub>.

Average recoveries of the MDL Method Spikes for EPH<sub>w10-19</sub> and EPH<sub>w19-32</sub> must be between 60 -140%. If this condition is not met, repeat the MDL determination at a higher spike level.

It is not required to formally validate an MDL for the alternate separatory funnel extraction procedure, since this procedure is required for samples that are generally high in EPH. The Reported Detection Limit for the separatory funnel procedure must be validated with each use by the analysis of a Method Blank by the same procedure.

### **Determination of DL Check Standard Concentration and EPH Targets**

Determine the nominal concentration of DMO in hexane to be used in the DL Check Standard as follows:

$$\text{DMO DL Std Conc} = \text{DL}_{\text{EPH Total}} * \text{Vol} / \text{FV} * \text{ECF} / (\% \text{Total EPH fraction in DMO})$$

For Example, if:

$DL_{EPH\ Total} = (0.25 + 0.25) \text{ mg/L} = \text{Reported DL of } EPH_{w10-19} + \text{DL of } EPH_{w19-32}$

Vol = 250 mL = Volume of sample extracted

FV = 10 mL = Final Volume of extract

ECF = 4 = Extract Concentration Factor (post-extraction, unitless)

%EPH fraction in DMO = 0.8 = 80% (sum of  $EPH_{w10-19}$  and  $EPH_{w19-32}$ )

Then DMO DL Std Concentration =  $0.50 \text{ mg/L} * 250\text{mL} / 10\text{mL} * 4 / 0.8 = 62.5 \text{ mg/L}$

**Accuracy and Precision**

For this method, a minimum of 18 Laboratory Control Samples prepared from 1:1 DMO must be used to assess accuracy and precision, as follows:

- a) 6 LCS samples (3 mid level & 3 high level) using Deionized Water.
- b) 6 LCS samples (3 mid level & 3 high level) using Lake Water or Groundwater.
- c) 6 LCS samples (3 mid level & 3 high level) using Seawater.

Determine LCS targets using Actual  $EPH_{w10-19}$  and  $EPH_{w10-19}$  Concentrations of the DMO solution as described above. The minimum accuracy requirement for Initial Validation is an average recovery of 85-115%. The minimum precision requirement for Initial Validation is a Relative Standard Deviation of  $\leq 15\%$ .

It is not required to formally validate the accuracy and precision of the alternate separatory funnel extraction procedure, since this procedure is required only for rare exceptional samples. Accuracy and precision for the separatory funnel procedure must be validated with each use by the analysis of an LCS by the same procedure.

**Use of Alternative Methods**

This method contains many prescribed and required elements that may not be modified. These requirements are necessary due to the nature of empirical (method-defined) aggregate parameters like EPH, where diverse mixtures are calculated against single component reference standards. This method has been specifically designed to minimize relative bias among responses of common Extractable Petroleum Hydrocarbon components, and among test results generated by different laboratories.

Modification or omission is not permitted to anything described within the method text as "required" or preceded by the word "must". Most of the prescribed requirements of the method are summarized in the Prescribed Elements section.

**Prescribed Elements**

Laboratories that report data for regulatory purposes may not alter any method conditions listed in this section without prior written permission from BC MOE:

- d) Specified Method Validation requirements must be met.
- e) All elements from Quality Control sections must be completed as specified, and must meet specified acceptance criteria, or sample data must be qualified.
- f) Sample Handling and Preservation guidelines must not be modified.
- g) Extraction with hexane is required (mixtures of hexane isomers are recommended, which are typically composed of ~60-65% n-hexane). The ratio of sample volume to hexane must be between 20:1 and 30:1 for the micro-extraction procedure.
- h) A minimum agitation time of 30 minutes is required for the micro-extraction procedure using vigorous mechanical shaking (e.g. by wrist shaker, rapid tumbler at  $\geq 60$  rpm, paint shaker, orbital or reciprocal platform shaker, or automated separatory funnel shaker, but not by on-axis rolling extraction).
- i) A comment must be added to reports to indicate where the use of the specified alternate separatory funnel hexane extraction procedure was necessary.
- j) If required, removal of sample to make room for hexane extraction solvent and air space must be conducted by pipette or other device from the sub-surface, without pouring, and

immediately following inversion and mixing of the sample. No more than 25% of the total volume of the sample may be removed.

- k) For BC MOE compliance purposes, the entire sample as submitted must be extracted and analyzed (except as described above). If test results are not for compliance purposes and if test results are clearly qualified on reports, samples with high solids or that are multi-phasic may be physically separated into aqueous or solids or NAPL phases with the phase(s) of interest tested as dictated by the client of the laboratory.
- l) Gas Chromatography with Flame Ionization Detection is required.
- m) GC column must be a capillary column, with 100% dimethylpolysiloxane stationary phase (e.g. DB-1, HP-1, RTX-1 or equivalent).
- n) Eicosane (nC20) must be used as the calibration standard for  $EPH_{w10-19}$  and  $EPH_{w19-32}$ . A minimum 3 point averaged response factor (linear) calibration is required.
- o) GC calibration standard must be prepared in the same solvent as sample extracts, unless equivalence (within 2%) can be demonstrated for component responses and retention times of Instrument Performance Checks in alternative injection solvents.
- p)  $EPH_{w10-19}$  and  $EPH_{w19-32}$  method detection limits and Reporting Detection Limits must be based on diesel / motor oil spikes (see the Establishing Method Detection Limits section).

Any samples whose EPH responses exceed the upper limit of the validated linear range must be considered over-range, and must be diluted and re-analyzed.

#### **Performance Based Method Changes**

This is a Performance Based Method. Unless prohibited in the Prescribed Elements section or where instructions are prefaced by the words "required" or "must", modifications to this method are permitted, provided that the laboratory possesses adequate documentation to demonstrate an equivalent or superior level of performance. Laboratories that modify this method must achieve all specified Quality Control requirements, and must maintain on file the Standard Operating Procedures that describe any revised or alternate methods used.

The Instrument Performance Check requirements of this method are designed to identify and prevent potential sources of instrument and method biases.

#### **References**

- i) US EPA Method 3511, Organic Compounds in Water by Microextraction, Revision 0, Nov 2002.
- ii) US EPA Method 8015C, Nonhalogenated Organics by Gas Chromatography, Revision 3, February 2007.

#### **Revision History**

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|--------------|--|
| Mar 6, 2015  | Revised to change method from DCM extraction to hexane micro-extraction to more selectively target petroleum hydrocarbon contaminants and to ensure inter-laboratory consistency. Usage of a surrogate was made mandatory, and a volatile surrogate must be used if extract concentration steps are applied (including silica gel cleanup steps). Method Performance Spikes were replaced with Laboratory Control Samples (diesel / motor oil) as QC requirement. Maximum batch size changed from 50 to 20 samples as per industry standard practice. Calibration changed to minimum 3 point linear by average response factor with narrower 15% CCV requirement. DQOs were added for Instrument Blanks and for retention time monitoring. Preservatives and hold times were updated to reflect recent BC updates. |
| April 2007   | Revision of hold times and preservation requirements.  |
| Dec 31, 2000 | SEAM codes replaced by EMS codes. Out of print reference deleted. Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; Mandatory tests made bold.  |
| July 1999    | Finalization of method (revised by ALS under contract to BC MOE) based on results of round robin vetted by BCLQAAC.  |
| March 1997   | Initial publication of v1.0 of Volatile Petroleum Hydrocarbons in Solids.  |