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

Parameters

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

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Analyte Codes	EMS Method Code
EPH_{w10-19}	250 ug/L	LEPH	EPH3
EPH_{w19-32}	250 ug/L	HEPH	EPH3

***Refer to EMS Parameter Dictionary on the ministry website for current EMS codes.

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_{w10-19} measures hydrocarbons that elute between nC10 and nC19 (b.pt. range of ~ 174-330˚C). EPH_{w19-32} 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 directly from within the original sample container. A single extraction using a small volume of hexane is conducted using vigorous mechanical agitation. Modified procedures are provided for circumstances where the standard extraction procedure may be ineffective (samples with high solids, or with observed presence of Non-Aqueous Phase Liquids (NAPL), either light (LNAPL) or dense (DNAPL). 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 the 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 used in 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 sources are not specifically targeted, but high levels of polar organics may cause positive interference and bias. Most biases 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 ($NaHSO_4$) or with HCl or H_2SO_4 (to pH ≤ 2) is recommended.

Where possible, groundwater samples should be collected in such a manner 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 ***entire 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, except that a small portion of sample may be removed and discarded to allow room for the hexane extraction solvent and for mixing space (for the micro-extraction procedure). The recommended practice is for the laboratory to provide sample bottles with a “fill-to” line (which 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 ≤ 10˚C during shipment to lab, and at ≤ 6˚C at the laboratory. Store extracts refrigerated or in a freezer at ≤ 6˚C.

Sample Inspection and Selection of Appropriate Procedure

Inspect sample and note on sample extraction records if the presence of a visibly distinct Non-Aqueous Phase Layer (NAPL) and/or solids are observed.

If NAPL and/or solids are observed, estimate and record the approximate quantities of NAPL and/or solids in the sample, and measure the total volume of the sample contents for data calculation purposes.

For samples containing visibly distinct NAPL or more than approximately 10% solids by volume, follow the modified procedures below. Otherwise, refer to the Standard Micro-Extraction Procedure, which is applicable to the majority of water samples.

Standard Micro-Extraction Procedure

Unless sufficient space already exists, invert sample and shake well to mix contents, then immediately use a glass pipette to remove enough sample (taken from below the surface – do not pour) to allow for the hexane extraction solvent and for a consistent air space (of at least 4% of the container volume). Accurately measure the volume of the sample that is to be extracted.

If sample was preserved, add NaOH or KOH solution to neutralize the acidity of the preservative (e.g. add ~1.5 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 to be ≥ 7 to ensure that ionizable nitrogen-containing PAHs like acridine and quinoline are in their neutral (solvent extractable) forms, to prevent the necessity for re-extractions in case N-PAH surrogate recoveries do meet meet acceptance criteria. 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 samples by addition of a 100% acetone surrogate 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.

Add an exact amount of hexane extraction solvent into the original sample container (mixtures of hexane isomers or n-hexane are allowed). 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 the vessel tightly to ensure no leakage occurs during extraction.

Apply vigorous mechanical shaking to extract the sample with hexane, in its original sample container, for 30 minutes or more. Suitable mechanical shaking processes include wrist shakers, rapid tumblers (≥ 60 rpm), paint shakers, and high speed orbital or reciprocal platform shakers, where performance requirements can be met (on-axis rolling extractions are not permitted).

Allow the hexane and water phases to separate. Separate by centrifugation if necessary. Transfer a portion of the hexane extract to a glass vial.

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

Modified Extraction Procedure for Samples Containing NAPL

This modified procedure is required for samples observed to contain a visibly distinct Non Aqueous Phase Layer (NAPL), which may contribute to the hexane extraction solvent volume.

Measure the total volume of sample contents (including NAPL and/or solids volume) for data calculation purposes. Estimate and record the approximate volume (in mL) of NAPL in the sample.

Invert sample and shake well, then transfer the entire contents of the sample container to a clean separatory funnel.

If sample was preserved, neutralize with NaOH or KOH solution as per the Standard Micro-Extraction Procedure.

Add at least one surrogate compound to all samples and QC samples using a 100% acetone surrogate solution.

For a 250 mL sample, add approximately 10 mL of hexane extraction solvent to the sample container (for other containers sizes, add hexane equal to ~4% of the container volume). Mix well, and transfer the hexane to the separatory funnel. Repeat the container rinse with a second portion of hexane of similar volume to ensure quantitative transfer of all NAPL from the sample container to the separatory funnel.

Manually extract the sample once only by shaking vigorously for 2 minutes.

Allow the hexane and water phases to separate. Discard the aqueous phase. Drain the hexane extraction solvent layer to a collection flask through a funnel containing anhydrous sodium sulfate. Rinse the sodium sulfate with additional hexane for quantitative transfer.

Dilute or concentrate the entire hexane extract to a known and accurate final volume.

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

Modified Extraction Procedure for Samples With High Solids

The standard micro-extraction procedure may be inappropriate for samples containing high levels of solids, which may cause emulsions; additional solvent may be necessary for effective extraction. Use the modified procedure described here for samples containing more than ~10% solids by volume, or where the standard procedure becomes ineffective due to the presence of solids. With this procedure, the sample is split into two portions (one portion primarily water, and one portion primarily solids), which are extracted separately, with equal fractions of their extracts combined prior to analysis.

Measure the total volume of sample contents (including solids) for data calculation purposes. Also estimate and record the volume of solids in the sample in mL or as a percentage of the total sample volume.

Allow solids in the sample to settle, then decant the majority of the aqueous phase into a new clean sample bottle for extraction, leaving enough room for hexane and adequate mixing.

Extract the water portion of the sample as per the standard micro-extraction procedure. Extraction surrogates should be added only to the water portion of the sample. Verification or adjustment of the pH of the solids portion is not necessary or required.

Determine the volume of hexane to be used for extraction of the solids, which should be approximately equal to the estimated volume of the solids (more hexane may be used if necessary). Accurately add the determined volume of hexane extraction solvent to the solids portion of the sample, in its original sample container. Cap the vessel tightly to ensure no leakage during extraction. Record the volume of hexane used for extraction of the solids portion.

Apply vigorous mechanical shaking to extract the solids portion of the sample with hexane for 30 minutes or more. Retrieve as much of the hexane extraction solvent as is practical, and collect in a glass vial.

When the extractions of the water and solid portions are complete, combine equal fractions of the extracts from each portion. For example, combine one-half of the extract from the water portion with one-half of the extract from the solids portion. For data calculation purposes, use the sum of the two extraction volumes as the final extract volume.

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

High Solids Method Example:

A water sample was received, which contained a total volume of 260 mL, with approximately 10% solids by volume.

Water Portion: ~ 234 mL of water was extracted with 10.0 mL hexane
Solids Portion: ~ 26 mL of wet solids was extracted with 30.0 mL of hexane

Half of the water portion extract (5.00 mL) was combined with half of the solids portion extract (15.0 mL). The combined 20.0 mL extract portion represents an effective 40.0 mL final extract volume for the entire sample. 10.0 mL of the combined extract was evaporatively concentrated to 1.00 mL prior to analysis, which represents an Extract Concentration Factor of 10x.

For data calculation purposes, the following variables were used (refer to Calibration and Analysis Procedure section for further details):

- *Sample Volume (Vol): 260 mL*
- *Final Volume of extract (FV): 40.0 mL*
- *Extract Concentration Factor, post-extraction (ECF): 10.0 (unitless)*

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 an 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 µm phase
Carrier Gas:	helium
Head pressure:	25 psi @ 65˚C (with column dimensions as specified)
Column flow:	6.8 mL/minute @ 65˚C (80 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	300˚C
Injection solvent:	hexane
Injection volume:	2 µL
Injection mode:	splitless or on-column
GC liner type:	4 mm id splitless liner with glass wool
Inlet purge on time:	1.0 minute (splitless)
FID temperature:	320˚C
Oven program:	Initial Temp 65˚C (hold 2.0 minutes) 15˚C /min to 320˚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 ≤ 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 µg/mL in hexane are recommended.

Calibration Verification Standard (CVS)
Prepare a Control Standard containing eicosane (nC20) in hexane at 50 ug/mL or near the mid-point of the calibration. The CVS must be prepared from a source independent from the Calibration Standard.

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 EPH_{w10-19} + EPH_{w19-32} (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 Reported Detection Limits for EPH_{w10-19} and EPH_{w19-32}. 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***
Instrument Performance QC 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 ± 0.2 mins of initial calibration

Calibration QC and Verification		
RSD of nC20 Response Factor	Each initial calibration	≤ 15% RSD
Instrument Blank	1 per initial calibration and every 24 hours	< 2x Reported Detection Limit (for absolute EPH fraction areas converted to concentrations)
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
Method QC		
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%**
Field QC		
Field Duplicates	Recommended	Not specified

* DQOs apply at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met.

** Surrogate DQOs do not apply when samples contain high levels of hydrocarbons that interfere with the measurement of the surrogate. Non-measureable 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:

a) Measure and control relative response ratios of EPH components,
b) Determine retention time windows for EPH integration ranges, and
c) 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_{w10-19} and EPH_{w19-32} 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 and every 24 hours. 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 effective Instrument Blank concentration from its absolute EPH fraction areas using typical sample calculation factors. The resulting EPH concentrations for the IB must be below 2x the Reporting Detection Limit. Instrument Blank EPH fraction areas may then be subtracted from corresponding sample EPH fraction areas as described in the Calibration & Analysis Procedure.

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 Reported 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 ± 0.2 min 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. Method Blanks must be subjected to all sample preparation steps experienced by samples, including optional elements such as centrifugation.

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 $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ 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").

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

Calibration & Analysis Procedure

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} (mL/µg) = nC20 area / [nC20] (µg/mL)

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

The Relative Standard Deviation (RSD) 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_{w10-19} and EPH_{w19-32}
EPH_{w10-19} and EPH_{w19-32} 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_{w10-19} begins at the apex of the nC10 peak and ends at the apex of the nC19 peak.
b) EPH_{w19-32} 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 (correction for instrument blank background may done using column compensation or by peak area subtraction, or both).

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_{w10-19} and EPH_{w19-32} 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} (ug/mL) = [$A_{(10-19)}$ ÷ RF_{nC20}] * [(FV * Dil) / (Vol * ECF)]
EPH_{w19-32} (ug/mL) = [$A_{(19-32)}$ ÷ RF_{nC20}] * [(FV * Dil) / (Vol * ECF)]

where:
$A_{(10-19)}$ = Total area between nC10 and nC19 for the sample chromatogram (after subtraction of Instrument Blank C10-19 area, if applicable).
$A_{(19-32)}$ = Total area between nC19 and nC32 for the sample chromatogram (after subtraction of Instrument Blank C19-32 area, if applicable).
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:

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

a) Prepare a reference solution of 1:1 Diesel : Motor Oil from the DMO Stock Solution at a concentration at least 10x greater than the estimated Instrument Detection Limits for EPH_{w10-19} and EPH_{w19-32}. A nominal DMO concentration of at least 2,000 µg/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.

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

$$\%\ EPH_{w10\text{-}19}\ \text{in DMO solution} = 100\% \times [EPH_{w10\text{-}19,\ measured}] \ /\ [DMO]$$
$$\%\ EPH_{w19\text{-}32}\ \text{in DMO solution} = 100\% \times [EPH_{w19\text{-}32,\ measured}] \ /\ [DMO]$$

where:
[DMO] = nominal concentration of Diesel / Motor Oil stock solution (µg 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.

c) To calculate the *Actual $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ 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 $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ 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 µg/mL of DMO. Calculate $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ results for each solution using the procedure described in the Calculations section.

At the Limit or Reporting, $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ should be measureable at 50-150% of the expected concentration.

Any samples whose EPH responses exceed the upper limit of the validated linear range must are 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 $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$, using the procedure outlined in the British Columbia Environmental Laboratory Manual.

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 $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ (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 $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$.

Average recoveries of the MDL Method Spikes for $EPH_{w10\text{-}19}$ and $EPH_{w19\text{-}32}$ 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 modified extraction procedures for samples with NAPL or high solids, since these procedures are required for samples that are generally high in EPH. For the modified procedures, use the Reported Detection Limits for the standard micro-extraction procedure, but increased for any higher dilution

factors used.

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:

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

For Example, if:
$DL_{EPH\ Total}$ = (0.25 + 0.25) mg/L = Reported DL of EPH_{w10-19} + 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 mg/L* 250mL / 10mL * 4 / 0.8 = 62.5 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_{w19-32}. 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 ≤ 15%.

It is not required to formally validate the accuracy and precision of the modified procedures for NAPL or high solids, since these procedures represent only slight modifications of the standard micro-extraction procedures, and are required only for rare and exceptional samples.

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". 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:

a) Specified Method Validation requirements must be met.
b) All elements from Quality Control sections must be completed as specified, and must meet specified acceptance criteria, or sample data must be qualified.
c) Sample Handling and Preservation guidelines must not be modified.
d) 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 standard micro-extraction procedure.
e) Except when validated as described below in the Performance Based Method Changes section, a minimum agitation time of 30 minutes is required using vigorous

mechanical shaking (e.g. by wrist shaker, rapid tumbler at ≥ 60 rpm, paint shaker, orbital or reciprocal platform shaker, or automated separatory funnel shaker, but not by on-axis rolling extraction).

f) A comment or qualifier must be added to reports to indicate where the use of the modified extraction procedure for high solids or NAPL was used.

g) 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 20% of the total volume of the sample may be removed.

h) During the extraction process, a minimum air volume of 4% of the volume of the sample container must exist to permit effective mixing during the extraction process. Depending on the shape of the sample container, a larger air space may promote improved extraction efficiency.

i) 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.

j) Gas Chromatography with Flame Ionization Detection is required.

k) GC column must be a capillary column, with 100% dimethylpolysiloxane stationery phase (e.g. DB-1, HP-1, RTX-1 or equivalent).

l) 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.

m) GC calibration standards 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.

n) 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 are 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 most potential sources of instrument and method biases.

Laboratories that invoke exceptionally high powered mechanical shaking techniques may validate an extraction time shorter than 30 minutes, to a minimum of 15 minutes, by conducting the following validation procedure:

a) Identify a suitable soil reference material containing petroleum hydrocarbons within the EPH 10-19 range (pertaining to LEPHw, as regulated under the CSR). If prepared by fortification of a soil material with hydrocarbons, the RM must have been prepared at least one week prior to the validation experiment.

b) Prepare a minimum of 6 test samples containing 1.00 +/- 0.02 grams of the soil RM in ~ 250 mL of deionized water, prepared in typical sample collection bottles (for different sized bottles, use the same proportion of solids : water).

c) Add preservative to all test samples and equilibrate test samples for at least 16 hours prior to extraction.

d) Extract 3 samples for 60 minutes using the standard micro-extraction method and extract 3 samples using the proposed shorter extraction time (both sets of samples must use the same mechanical shaking apparatus).

e) A shorter extraction time (to a minimum of 15 minutes), may be used if the average of the 3 samples extracted for the shorter time demonstrates EPH10-19 results that are at least 75% of the average of the results for the 3 samples extracted for 60 minutes.

Note that the study described above is considered to be representative of near worst-case conditions for interlaboratory variability, since it measures the extraction efficiency of solids. This method achieves quantitative recovery of dissolved phase EPH components from waters.

References

a) US EPA Method 3511, Organic Compounds in Water by Microextraction, Revision 0, Nov 2002.

b) US EPA Method 8015D, Nonhalogenated Organics by Gas Chromatography, Revision 4, June 2003.

Revision History

Sept 15, 2017	Corrected formula error with ECF in Calibration and Analysis section. EMS method and analyte codes added.
Nov 30, 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 and minimum frequency were added for Instrument Blanks and for retention time monitoring. Preservatives and hold times were updated to reflect recent BC updates. Effective date: Jan 4, 2016.
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 (now BCELTAC).
March 1997	Initial publication of v1.0 of Volatile Petroleum Hydrocarbons in Solids.