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

Parameters

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

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Codes
EPH_{s10-19}	100 mg/kg	LEPH F086
EPH_{s19-32}	100 mg/kg	HEPH F086

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

Analytical Method

Hexane-Acetone extraction - Gas Chromatography with Flame Ionization Detection (GC/FID).

Introduction

This method measures the aggregate concentration of Extractable Petroleum Hydrocarbons (EPH) in solids, divided into two boiling point ranges, each quantitated against eicosane (nC20). EPH_{s10-19} measures hydrocarbons that elute between nC10 and nC19 (b.pt. range of ~ 174-330˚C). EPH_{s19-32} 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

Solids samples are dried and Soxhlet extracted with 1:1 Hexane:Acetone. Extracts are concentrated and 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

Soil, sediment, marine sediment.

Interferences and Precautions

Contaminants present in solvents, reagents, sample containers, or sample processing equipment may cause interferences or yield artifacts. Test method conditions must be suitably monitored by routine analysis of method blanks.

This method does not differentiate naturally occurring hydrocarbons from petroleum based hydrocarbons, nor does it differentiate hydrocarbons from complex organics. Polar organics characteristic of natural sources (e.g. humic acid) 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.

Contamination by GC carryover can occur whenever high-level and low-level samples are sequentially analyzed. If possible, when an unusually concentrated sample is analyzed, it should be followed by an Instrument Blank to check for system cleanliness. Alternatively, low-level samples that follow such high level samples must be re-analyzed if carryover above Reported Detection Limits is suspected.

The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat all chemicals used in this method as a potential health hazard. To ensure your personal safety and the safety of co-workers, read and understand the Material Safety Data Sheets (MSDS) for all chemicals used.

Sample Handling and Preservation

Collect samples in glass wide-mouth jars with Teflon-lined lids.

No chemical preservation is recommended.

Stability

Holding Time: Maximum holding time prior to extraction is 14 days after sampling. 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.

Apparatus

Glassware and Support Equipment
250 mL beakers
Soxhlet extraction apparatus
Glass or cellulose thimbles
Kuderna-Danish Concentrator system (or rotary evaporator)
250 mL Kuderna-Danish (KD) flasks (or round bottom flasks)
Nitrogen Blowdown System
Micro-syringes
Glass extract vials and GC autosampler vials with Teflon-lined lids
Balance (sensitive to at least 0.01 grams)

Gas Chromatograph (GC)
A temperature programmable capillary gas chromatograph is required. A heated splitless or on-column inlet is recommended. The data station must be capable of storing and reintegrating chromatographic data and must allow integration of peak areas using a forced baseline projection.

Detector
A Flame Ionization Detector (FID) is required for the quantitation of $EPH_{s10\text{-}19}$ and

EPH_{s19-32}. The FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

Sample Introduction Mechanism
An autosampler capable of making 1 to 2 uL splitless or on-column injections is strongly recommended.

Chromatographic Column
The reference column for this method is a 30 meter, 0.32 mm internal diameter capillary column with a 0.25um coating of 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified.

Sample Extraction Procedure

Take an aliquot of each sample to perform an accurate moisture determination on the sample.

Minimize the time that samples are exposed to ambient temperatures during sub-sampling, in order to reduce potential losses of volatile components. It is recommended for samples to be sub-sampled, weighed, dried, and transferred to Soxhlet thimbles (with solvent) in very small batches, ideally one at a time. Where feasible, mix solid samples well before sub-sampling. For samples that cannot be mixed in-situ, take a representative sub-sample by combining portions of sample taken from top to bottom at several locations in the container (e.g. by combining several core samples).

Accurately weigh approximately 20 wet grams of sample into a beaker. To reduce sub-sampling variability, no less than 5 grams (wet weight) may be used, except where limited by available sample. For alternative non-Soxhlet extraction mechanisms (see Use of Alternative Methods section), smaller amounts may be used for highly contaminated samples where necessary to prevent difficulties with the extraction process, but the 5 gram minimum weight still applies for typical samples.

Mix the sample for a few seconds with enough diatomaceous earth to create a free flowing, homogenous mixture. Once dry, transfer the sample immediately to a Soxhlet thimble and place in a pre-cleaned Soxhlet body. Immediately add a few mL of hexane:acetone to the thimble to prevent loss of volatiles.

Note: Drying with diatomaceous earth is a rapid physical process, which is recommended over the traditional practice of chemical drying using anhydrous salts. Longer drying times needed for anhydrous salts, combined with heat from exothermic adsorption of water can cause loss of volatiles, particularly within the nC10-nC12 range. Drying with anhydrous salts is not recommended unless the time between drying and solvent extraction is minimized and carefully controlled. If samples are dried with anhydrous salts, a volatile surrogate (eluting before nC10) must be used, and must be added prior to the drying process.

Prepare appropriate and required Method QC samples as described in the Method QC section. Use 10 g of a clean soil/sediment matrix for the Method Blank and Diesel/Motor Oil Method Spike samples. Before spiking or extraction, add about 2.0 mL of reagent water to each to simulate samples that contain 20% moisture.

Extract the sample for 16 hours by Soxhlet using approximately 200 mL of 1:1 Hexane:Acetone. Ensure that each Soxhlet extractor cycles at 4-6 times per hour.

Allow the apparatus to cool. Add a few grams of sodium chloride to the round bottom flask, and mix well to dissolve the salt in any water that may be present in the flask. If water is present in the extract, the salt will cause it to separate into a distinct aqueous phase, driving dissolved acetone into the organic phase, and making the water easier to remove with anhydrous salts.

Transfer the extract through anhydrous sodium sulfate into a Kuderna-Danish collection flask (or round bottom flask). Rinse the Soxhlet body with several Hexane:Acetone rinses and add them to the flask.

Before solvent removal, add about 2 mL iso-octane to the sample extract to act as a keeper solvent for volatile analytes (to prevent total evaporation of the solvent).

Concentrate the extract to an accurate final volume of 5.00 mL using a Kuderna-Danish concentrator (or rotary evaporator) and a nitrogen blowdown system. Average error in the final volume must be no greater than 3%. Dilutions may be appropriate for higher level samples. Smaller final volumes may be required to reach lower detection limits.

Transfer a portion of the extract to a GC autosampler vial and analyze by GC/FID. Store remaining extract at ≤ 6˚C for at least 40 days in case re- analysis is required.

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:	iso-octane
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)

Reagents and Standards

Reagents

Hexane (mixture of isomers recommended)
Acetone (2-propanone)
Iso-octane (2,2,4-trimethyl-pentane)
Reagent water (organic free)

Diatomaceous earth drying reagent (e.g. Hydromatrix)
Sodium sulfate, anhydrous
Sodium chloride
Clean soil/sediment matrix (e.g. clean sand)*

***Note:** Prior to using this material within sample batches, analyze a Method Blank to ensure it does not introduce detectable levels of EPH. Oven bake before use if necessary

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: 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_{s10-19} + EPH_{s19-32} (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_{s10-19} and EPH_{s19-32}. 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 EPHs 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
Matrix Spike or Reference Material	1 per 20 samples (1 per batch minimum)	60-140% recovery
Laboratory Duplicates	1 per 20 samples (1 per batch minimum)	40% RPD
Surrogates	Required – every sample	60-140%**
Field QC		
Field Duplicates	Recommended	Not specified

* Duplicate DQOs apply above 5x Reported DL. Laboratories must report qualified data if 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 $EPH_{s10\text{-}19}$ and $EPH_{s19\text{-}32}$ 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 or iso-octane) 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 Reported 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.

If the calculated concentration of eicosane in the CVS varies by more than 15% from the expected target, then the calibration is suspect. Discrepancies must be corrected before any sample results for the analysis batch may be reported. Correction may require any or all of:

a) Re-analysis of Control Standard and/or Calibration Standard.
b) Re-preparation and re-analysis of Control Standard and/or Calibration Standard.
c) GC maintenance (if discrepancy is due to calibration non-linearity).

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 clean soil/sediment matrix. 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 a clean sediment/soil matrix (containing approximately 20% 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_{s10-19} and EPH_{s19-32} 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
REQUIRED. Frequency of 1 per preparation batch of no more than 20 samples is recommended or as per discretion of the laboratory. Prepare a Laboratory Duplicate by weighing a second aliquot of the soil sample for extraction. Laboratory Duplicates must be subjected to all sample preparation steps experienced by samples, including optional elements such as centrifugation.

Field Sample Replicates / Splits
RECOMMENDED. Frequency at the discretion of the laboratory and/or the end user of the data. Replicate samples by this method may be either Laboratory Sample Replicates or Field Sample Replicates/Splits, depending on whether the sub-samples originate from the same or different sample containers. No generic acceptance criteria are specified, since the source of variability may be shared among the sampling process, the laboratory method, and the samples themselves.

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").

Reference Material or Matrix Spike

Reference Material (RM) or Matrix Spike
REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Acceptance criteria are 60-140% of certified values (if available) or of laboratory defined targets if certified values are unavailable. Reference Materials must be wetted with reagent water to approximately 20% moisture prior to extraction.

While available, one (or both) of the following two RMs are recommended for use with this method:

NRC HS3B. A marine sediment from Halifax Harbour, produced by National Research Council of Canada, Halifax, Nova Scotia.

CRM 355-100 (TPH in Soil). A diesel-contaminated terrestrial soil, produced specifically for this method by Sigma-Aldrich (formerly Resource Technology Corporation).)

Single laboratory data and multiple laboratory consensus data for both the above RMs are presented in the Method Performance Data section.

Matrix Spikes using Diesel/Motor Oil spiking solution may be substituted if RMs are unavailable.

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_{s10-19} and EPH_{s19-32}

EPH_{s10-19} and EPH_{s19-32} 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_{s10-19} begins at the apex of the nC10 peak and ends at the apex of the nC19 peak.
b) EPH_{s19-32} 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_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32}:

EPH_{s10-19} (ug/g) = [$A_{(10-19)}$ ÷ RF_{nC20}] * [FV * Dil / DryWt]
EPH_{s19-32} (ug/g) = [$A_{(19-32)}$ ÷ RF_{nC20}] * [FV * Dil / DryWt]

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)
Dil = Dilution factor of sample extract (unitless)
DryWt = Dry weight of sample extracted (g)

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_s 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_s] of a Diesel / Motor Oil Reference Solution
This procedure describes how to calculate the *Actual EPH_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32} Concentrations are required within this method for the following purposes:

a) Determination of GC/FID linear range for EPH_{s10-19} and EPH_{s19-32} (calibration range).
b) Determination of EPH_{s10-19} and EPH_{s19-32} Instrument Detection Limits (IDLs).
c) Preparation of DL Check Standards and LCS Solutions.
d) Calculation of EPH_{s10-19} and EPH_{s19-32} targets for DL Check Standards and LCS Solutions.

Use the following procedure to calculate the *Actual EPH_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32}. 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:

$$\%\ EPH_{s10-19}\ \text{in DMO solution} = 100\% \times [EPH_{s10-19,\ measured}] / [DMO]$$
$$\%\ EPH_{s19-32}\ \text{in DMO solution} = 100\% \times [EPH_{s19-32,\ measured}] / [DMO]$$

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_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32} results for each solution using the procedure described in the Calculations section.

At the Limit of Reporting, EPH_{s10-19} and EPH_{s19-32} 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_{s10-19} and EPH_{s19-32}, using the procedure outlined in the British Columbia Environmental Laboratory Manual or a comparable reference.

Select a concentration for method spikes of DMO into clean sediment/soil matrix (of 20% moisture) that will result in extracts with concentrations of between one and three times the estimated IDLs for EPH_{s10-19} and EPH_{s19-32} (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_{s10-19} and EPH_{s19-32}.

Average recoveries of the MDL Method Spikes for EPH_{s10-19} and EPH_{s19-32} must be between 60 -140%. If this condition is not met, repeat the MDL determination at a higher spike level.

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= $DL_{EPH\ Total}$ * DryWt / FV * 1 / (%Total EPH fraction in DMO)

For Example, if:

$DL_{EPH\ Total}$ = (100 + 100) ug/g = Reported DL of EPH_{s10-19} + DL of EPH_{s19-32}
DryWt = 10 g = Dry weight of sample extracted
FV = 10 mL = Final Volume of extract
%EPH fraction in DMO = 0.8 = 80% (sum of EPH_{s10-19} and EPH_{s19-32})

Then DMO DL Std Concentration = 200 ug/g* 10g / 10mL * 1 / 0.8 = 160 ug/mL

Accuracy Requirement:
Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes at concentrations above ten times the MDL. Average accuracy must be between 80-120%.

Precision Requirement:
Laboratories must demonstrate method precision through repeat analysis of clean matrix spikes or reference materials at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <15% for each range (EPH_{s10-19} and EPH_{s19-32}).

Method Performance Data

Method performance data is presented for selected Reference Samples and for required QC components of the method. This data was compiled from the 1998 BCMELP Petroleum Hydrocarbon Round Robin Study, and from the Single Laboratory Validation Study, which was performed at the same time. Method Detection Limit data from the single laboratory data are also presented.

The single laboratory data presented here was generated using the instrument conditions described in GC Analysis Procedure section, except for minor differences in the GC oven temperature program.

EPH_S Instrument Performance Check Data: Multiple laboratory (Round Robin) data and single laboratory data for EPH_S Instrument Performance Checks are presented in Table I-1. These samples were analyzed as described in the Instrument Performance Check section.

Table I-1: EPHs Instrument Performance Check Data

	Round Robin Results			Single Lab Results		
Relative Response	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Decane (nC10)	6	0.98	6.3%	8	1.01	1.8%
Naphthalene	6	1.03	6.9%	8	1.07	1.3%
Dodecane (nC12)	4	0.98	3.1%	8	1.00	1.4%
Hexadecane (nC16)	7	0.99	2.8%	8	1.00	1.5%
Phenanthrene	7	1.05	4.6%	8	1.06	0.8%
Nonadecane (nC19)	7	1.00	0.8%	8	0.99	0.4%
Eicosane (nC20)	7	1.00	n/a	8	1.00	n/a
Pyrene	7	1.07	3.3%	8	1.08	1.3%
Benzo(a)pyrene	6	0.87	13.6%	8	0.92	1.8%
Triacontane (nC30)	5	0.90	17.2%	8	1.02	1.5%
Dotriacontane (nC32)	7	0.90	16.1%	8	1.00	1.3%

Method Detection Limit Data: The EPH_S Method Detection Limit data reported in Table I-2 was obtained from the 1998 Single Laboratory Validation Study, and was generated as described in Establishing Method Detection Limits section. The EPH_S target was determined by direct analysis of the spike solution. Please note that the data presented

demonstrates achievable MDLs; each laboratory must determine the MDLs that apply to their individual circumstances

Table I-2: EPH_S Method Detection Limits (Single Laboratory Data)

units = mg/kg	#1	#2	#3	#4	#5	#6	#7	#8	Mean	Std. Dev.	Target	Mean Recovery	MDL
EPH_{S10-19}	52.0	51.2	45.7	42.6	42.1	51.4	51.8	37.3	**46.8**	**5.7**	**44.6**	**105%**	**21**
EPH_{S19-32}	56.1	52.9	54.2	51.3	55.4	55.9	58.4	51.7	**54.5**	**2.4**	**51.7**	**105%**	**9.1**

EPH_S Reference Material Data

Multiple laboratory (Round Robin) data and single laboratory data for EPH_S Reference Materials are presented in Tables I-3 and I-4. Two different Reference Materials were analyzed. One is the TPH in Soil CRM 355-100, manufactured by Resource Technology Corporation. The other is HS3B, manufactured by the National Research Council of Canada. These samples were analyzed as described in Reference Materials section. PAH and calculated $LEPH_S$ and $HEPH_S$ results also presented for the same samples

Table I-3: EPHs Reference Material - RTC CRM 355-100

	Round Robin Results			Single Lab Results		
EPH Results (mg/kg)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
EPH_{S10-19}	6	3312	9.9%	8	3429	2.6%
EPH_{S19-32}	6	5038	17.7%	8	5284	1.9%
LEPHs	6	3302	9.9%	8	3417	2.6%
HEPHs	6	5038	17.7%	8	5283	1.9%
PAH Results (mg/kg)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Naphthalene	8	4.06	28.9%	8	4.47	4.9%
Phenanthrene	8	5.34	34.8%	8	6.87	4.5%
Pyrene	8	0.69	50.3%	8	0.75	1.9%
Benz(a)anthracene	4	0.11	55.5%	8	0.08	3.0%
Benzo(b)fluoranthene	3	0.04	20.8%	8	0.05	6.7%
Benzo(k)fluoranthene	3	0.02	75.8%	8	0.01	8.9%
Benzo(a)pyrene	3	0.05	32.8%	8	0.05	4.7%
Indeno(1,2,3-cd)pyrene	3	0.02	2.8%	8	0.02	3.0%
Dibenz(a,h)anthracene	3	0.01	10.8%	8	0.01	24.5%

Table I-4: EPHs Reference Material - NRC Canada HS3B

	Round Robin Results			Single Lab Results		
EPH Results (mg/kg)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
EPH_{S10-19}	5	385	18.0%	11	458	7.2%
EPH_{S19-32}	5	2745	26.6%	11	2456	4.0%
LEPHs	5	369	17.6%	11	439	7.2%
HEPHs	5	2707	26.6%	11	2411	4.0%
PAH Results (mg/kg)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Naphthalene	8	1.62	31.1%	11	1.82	5.2%
Phenanthrene	8	14.91	27.4%	11	17.56	6.1%
Pyrene	8	13.72	28.9%	11	15.75	2.1%
Benz(a)anthracene	8	5.85	35.6%	11	7.07	4.7%
Benzo(b)fluoranthene	8	6.50	43.5%	11	8.90	2.9%
Benzo(k)fluoranthene	8	3.25	41.1%	11	3.40	3.3%
Benzo(a)pyrene	8	3.79	28.8%	11	5.23	3.7%
Indeno(1,2,3-cd)pyrene	7	2.51	39.6%	11	3.99	2.5%
Dibenz(a,h)anthracene	7	0.57	50.2%	11	1.08	7.4%

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) Maximum holding time prior to extraction is 14 days after sampling. Maximum holding time for refrigerated extracts stored at ≤ 6˚C is 40 days. Where holding times are exceeded, data must be qualified.

d) The normal amount of sample extracted must not be less than 5 grams wet weight (see the Sample Extraction Procedure section).

e) If anhydrous salts are used to dry sediment samples prior to extraction, a volatile surrogate (eluting earlier than nC10) must be used, and must be added prior to the drying process.

f) 1:1 hexane:acetone solvent is required as the extraction solvent (mixtures of hexane isomers are recommended, which are typically composed of ~60-65% n-hexane).

g) A 16 hour Soxhlet extraction, or an alternative extraction process that is as rigorous as a 16 hour Soxhlet extraction is required. Accelerated Solvent Extraction (ASE) or Microwave Assisted Extraction (MAE) are recommended as viable and more productive and cost-effective alternatives to Soxhlet extraction (refer to Performance Based Method Changes section for further details on requirements for alternative extraction techniques).

h) Gas Chromatography with Flame Ionization Detection is required.

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

j) Eicosane (nC20) must be used as the calibration standard for EPH_{s10-19} and EPH_{s19-32}. A minimum 3 point averaged response factor (linear) calibration is required.

k) 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.

l) EPH_{s10-19} and EPH_{s19-32} method detection limits and Reported Detection Limits must be based on diesel / motor oil spikes (see the Establishing Method Detection Limits section).

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. Any modified method that cannot achieve the performance requirements of these QC checks is not equivalent to the reference method.

Modifications Where Equivalence Testing is Not Required
Except where expressly disallowed in the Use of Alternative Methods section or elsewhere, changes to the following components of this method are permitted if all specified quality control requirements of the method are achieved:

a) Apparatus.

b) Reagents and Standards.

c) Gas Chromatograph Conditions.

Modifications Where Equivalence Testing is Required
Except where expressly disallowed in the Prescribed Elements section or elsewhere, changes to the following components of this method are permitted, but only if the laboratory has conducted and documented a rigorous test for equivalence to the reference method.

Sample Extraction Procedure (see appropriate section)
An equivalence test for Sample Extraction Procedure modifications to this method involves a comparison of results from the modified method with results from the reference method for several appropriately selected samples. Tests for bias (mean accuracy) and precision are required.

Test for Bias of Modified Methods
Compare results from the modified method with results from the reference method for several appropriately selected samples. Both of the following sample types must be investigated:

a) at least five field samples (if necessary, field samples may be fortified with diesel/motor oil if equilibrated for at least 8 hours prior to analysis). Each sample must contain both EPH_{s10-19} and EPH_{s19-32} at ≥ 3 times the laboratory's routinely reported detection limits (≥ 5 times DL is recommended). Each sample must be analyzed in triplicate (at minimum) by both the reference method and the modified method. Samples must include:
    - one or more clay samples
    - one or more soil/sediment samples
    - one or more samples with >40% moisture

b) at least two soil / sediment Reference Materials. While available, the two RMs analyzed within the 1998 BCMELP Hydrocarbon Round Robin must be used to satisfy this requirement:
    - Sigma-Aldrich CRM 355-100
    - National Research Council of Canada HS3B

Each Reference Material must be analyzed in triplicate (at minimum) by both the reference method and the modified method.

For the two RMs above, results for the modified method may be compared either against the Single Laboratory Results (in the Method Performance Data section), against the Round Robin Results (*for CRM-355 RM only*, in the Method Performance Data section), or against in-house results generated by the reference method. Sample results from future Round Robin studies may also be used for equivalency comparisons where the study population is six or greater [d].

Note: 1998 Round Robin results for the HS3B RM may not be used for the equivalence comparison, due to the small study population for that sample of n=5.

If either of the above RMs are unavailable, any other soil or sediment reference material(s) containing both EPH_{s10-19} and EPH_{s19-32} at ≥ 3 times the laboratory's routinely reported detection limits may be substituted.

For both (a) and (b) above, compare the means obtained for each sample by the reference method and the modified method. For each sample, the means for each method must differ by less than 20% relative percent difference (RPD), where relative percent difference of X_1 and X_2 is defined as:

$$RPD = | (X_1 – X_2) / mean_{(X1, X2)} | \times 100\%$$

If results for one or more samples do not meet one of the above criteria, additional replicates of the same samples may be analyzed, with the tests applied to the larger populations. If necessary, either the Dixon or Grubbs outlier tests may be used to discard outlier data points [d].

Test for Precision of Modified Methods

Modified methods must demonstrate a reasonable level of precision on homogeneous Reference Materials. Analyze a minimum of 8 replicates of at least one Reference Material containing both EPH_{s10-19} and EPH_{s19-32} at ≥ 3 times the laboratory's routine Reported Detection Limit (≥ 5 times DL recommended).

Replicates may be either "within-run" or "between-run". Within-run replicates normally demonstrate better precision.

Where necessary, outlier data points may be discarded if they satisfy either the Dixon or Grubbs outlier tests [d].

For both EPH_{s10-19} and EPH_{s19-32}, the modified method must demonstrate a precision of ≤ 20% relative standard deviation.

References

a) US EPA Method 8015D, Nonhalogenated Organics Using GC/FID, Rev 4, June 2003.

b) Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method, CCME 2001.

Revision History

July 14, 2016	Revised to new format, eliminated Method Performance Check Spikes, added LCS and surrogate requirement, revised QC requirements, changed requirements around permitted drying techniques, changed equivalence test procedure to align more closely with Alberta Environment procedure for CCME PHC method. Effective date for this version: September 1, 2016.
Dec 31, 2000	Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; phrase 'Analyte Code' changed to 'Analyte Symbol'. Mandatory tests made bold. Former methods superseded. Reference to out of print manuals deleted.
July 1999	Finalization of present method based on results of a vetting round robin.
1998 - 1999	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee (now BCELTAC).
March 1997	Initial publication of Version 1.0 for EPH in Soil.

This method has been officially approved by the Director of Waste Management. It may be cited in Waste Management permits, approvals and orders, as well as legislated requirements.

Approval:_____ **Date:**_____