

ANALYTICAL METHOD 7 ***FOR CONTAMINATED SITES***

Aliphatic/ Aromatic Separation of Extractable Petroleum
Hydrocarbons in Solids or Water by Silica gel
Fractionation

Prepared pursuant to Section 64 of the
Contaminated Sites Regulation under the
Environmental Management Act

Approved: _____

Version 2.1

EMS Method Code:*****

Revision Date: Sept 2001

Silica Gel Fractionation of Extractable Petroleum Hydrocarbons

1. Parameters and Analyte Codes

Aliphatic Extractable Petroleum Hydrocarbons _(nC10-nC19) in water	Analyte	Code:
Aliphatic-EPH _{W10-19}		
Aromatic Extractable Petroleum Hydrocarbons _(nC10-nC19) in water	Analyte	Code:
Aromatic-EPH _{W10-19}		
Aliphatic Extractable Petroleum Hydrocarbons _(nC10-nC19) in solids	Analyte	Code:
Aliphatic-EPH _{S10-19}		
Aromatic Extractable Petroleum Hydrocarbons _(nC10-nC19) in solids	Analyte	Code:
Aromatic-EPH _{S10-19}		
Aliphatic Extractable Petroleum Hydrocarbons _(nC19-nC32) in water	Analyte	Code:
Aliphatic-EPH _{W19-32}		
Aromatic Extractable Petroleum Hydrocarbons _(nC19-nC32) in water	Analyte	Code:
Aromatic-EPH _{W19-32}		
Aliphatic Extractable Petroleum Hydrocarbons _(nC19-nC32) in solids	Analyte	Code:
Aliphatic-EPH _{S19-32}		
Aromatic Extractable Petroleum Hydrocarbons _(nC19-nC32) in solids	Analyte	Code:
Aromatic-EPH _{S19-32}		

2. Analytical Method

Aliphatic/Aromatic fractionation by Silica Gel adsorption column chromatography.

Refer to specific EPH methods for instrumental analysis procedures:

Extractable Petroleum Hydrocarbons in Solids by GC-FID, July 1999, version 2.1 (1).

Extractable Petroleum Hydrocarbons in Water by GC-FID, July 1999, version 2,1 (2).

3. Introduction

This method is used in conjunction with Ministry of Water, Land and Air Protection (MWLAP) methods for Extractable Petroleum Hydrocarbons in Solids and Water by GC-FID.

The method uses silica gel to physically separate the components of Extractable Petroleum Hydrocarbons (EPH) based on their polarities, producing two “fractions” for further analysis: an aliphatic fraction and an aromatic fraction. Each of these fractions is then analyzed by GC-FID using the same procedures as for EPH₁₀₋₁₉ and EPH₁₉₋₃₂ in solids or water. Highly polar sample components are irreversibly retained on the silica gel, and are not analyzed. Thus, for a given EPH boiling point fraction, the sum of the aliphatic and aromatic EPH results should be less than or equal to the unfractionated EPH result (within the range of normal analytical variability).

The method can be used as a means to distinguish between naturally occurring and petroleum based hydrocarbons, based on the premise that most naturally occurring hydrocarbons are polar, and so will be irreversibly retained by silica gel. Examples of polar naturally occurring hydrocarbons include humic acids, fatty acids, and resin acids. Note that some naturally occurring compounds with medium polarities may elute partially or completely in the aromatic fraction as described by this method.

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 the sample.

This method contains numerous prescribed (required) elements, but it is otherwise a Performance Based Method (PBM). Prescriptive elements are included where necessary to maintain consistency of results among laboratories. The Ministry of Water, Land and Air Protection encourages method innovations and supports the performance based methods approach, but recognizes that the application of performance based methods to method-defined aggregate parameters like Extractable Petroleum Hydrocarbons is somewhat limited.

Refer to the EPH methods for solids and water for further information about the use and applicability of EPH parameters. Note that unlike the LEPH and HEPH parameters, PAHs are not subtracted from the Aliphatic and Aromatic EPH parameters.

4. Method Summary

Iso-octane sample extracts from the appropriate EPH method are separated into aliphatic and aromatic fractions using a 7 gram column of 100% activated silica gel. The aliphatic fraction is eluted with hexane. The aromatic fraction is eluted with 50% DCM in hexane. The resulting extracts are concentrated and analyzed by the appropriate EPH

analysis procedure.

5. Matrix

This method requires that sample extracts be prepared in an appropriate aliphatic solvent (iso-octane is strongly recommended).

Sample matrices to which this method is applicable, when used with the appropriate EPH method, include the following:

Soil

Sediment

Marine Sediment

Fresh Water

Waste Water

Marine Water

6. Interferences and Precautions

Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. All of these should be routinely monitored and demonstrated to be free of interferences under the conditions of the routine analysis of method blanks.

Sample extracts must be introduced to the silica gel column in an appropriate aliphatic solvent (iso-octane is strongly recommended). The presence of residual polar solvents (e.g., DCM, toluene, acetone) in sample extracts may cause some aromatic compounds to elute in the aliphatic fraction.

Keep the silica gel column fully wetted and below the solvent level throughout this procedure. Air pockets within the column can create selective paths through the column which can influence component retention.

For a 7g silica gel column, sample extracts containing more than approximately 200mg of petroleum hydrocarbons may overload the retention capacity of the column, and should be diluted prior to fractionation.

Never heat silica gel above 160°C, since it can oxidize at higher temperatures. If Procedure Blanks indicate contamination problems, silica gel can be solvent extracted prior to use.

7. Health and Safety Precautions

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.

8. Sample Collection and Preservation

Refer to the appropriate EPH method for specific details on sample collection and preservation.

Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

9. Apparatus

9.1 Glassware and Support Equipment

25-30 cm x 10 mm i.d. glass chromatography columns with 250mL reservoir

Teflon stop-cocks for above

Kuderna-Danish Concentrator system (or rotary evaporator)

250 mL Kuderna-Danish (KD) flasks (or round bottom flasks)

Nitrogen blowdown system

Micro-syringes

Oven (Capable of 130°C)

100 mL Graduated cylinders

50 mL beakers

Glass extract vials and GC autosampler vials with Teflon-lined lids

Balance (sensitive to at least 0.1 grams)

10. Reagents and Standards

10.1 Reagents

Use analytical grade or better for all reagents.

Silica gel, 60-120 mesh, baked at 130°C for a minimum of 16 hours

Dichloromethane (DCM)

Hexane and/or Pentane

Iso-octane (2,2,4-trimethyl-pentane)

Sodium sulfate, Anhydrous

Glass wool, silanized

10.2 Calibration Standard Stock Solution

Prepare a Calibration Standard Stock Solution in DCM containing 1,000 ug/mL

of each of decane (nC10), dodecane (nC12), hexadecane (nC16), nonadecane (nC19), eicosane (nC20), dotriacontane (nC32), naphthalene, phenanthrene, and pyrene. This mixture may be purchased commercially or prepared from neat standards. Ensure all components are fully dissolved before use. Warm the solution and/or place in an ultrasonic bath if necessary to re-dissolve any precipitated components. Store refrigerated at $(4 \pm 4)^{\circ}\text{C}$.

10.2.1 EPH Fractionation Performance Check Solution

Prepare a 50 ug/mL EPH Performance Check Solution in iso-octane by diluting the 1,000 ug/mL Calibration Standard Stock Solution. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at $(4 \pm 4)^{\circ}\text{C}$.

11. Quality Control (QC)

11.1 General QC Requirements

Each laboratory that uses this method is required to follow a formal, internally documented Quality System, as outlined in CAN/CSA-Z753 (3). Required and recommended QC elements are described within this section.

Samples are prepared in a set that is referred to as a preparation batch, and are analyzed by GC in a set that is referred to as an analysis batch. Only QC related to preparation batches are discussed within this method.

If any of the specified acceptance criteria for Procedure QC cannot be met for the analysis of a given sample, then the data reported for that sample must be appropriately qualified.

QC requirements are described for each of the EPH₁₀₋₁₉ and EPH₁₉₋₃₂ parameters. If this method is used to report only one of these parameters, then only those QC criteria that are relevant to that parameter need be satisfied.

11.2 Procedure QC

Procedure QC samples must begin from the start of a given procedure (i.e. this fractionation procedure) and must be carried through to the end of the analysis component of the appropriate method so that numerical results may be generated. They are intended to measure average procedure performance over time, and to control procedure performance under a statistical process control model.

11.2.1 Procedure Blank

OPTIONAL¹ - Recommended frequency of 1 per preparation batch of no more than 50 samples. Procedure Blanks help to identify whether the fractionation process may be a source of contamination. If a Procedure Blank result is above a Reported Detection Limit for a sample within a preparation batch, the data report for that sample must be qualified (it may be acceptable to increase the Reported Detection Limit of affected sample results to a level above that of the Procedure Blank result).

- 1 If the Method Blank for a sample being fractionated by this procedure is not also carried through the fractionation procedure, then the analysis of a Procedure Blank is required.

Prepare a Procedure Blank by processing 1.0 mL of iso-octane through the fractionation process, and analyze together with samples processed in the same preparation batch.

11.2.2 EPH Fractionation Performance Check Spike

OPTIONAL² - Recommended frequency of 1 per preparation batch of no more than 50 samples. EPH Fractionation Performance Check Spikes evaluate whether the aliphatic / aromatic fractionation is occurring as expected.

Prepare an EPH Fractionation Performance Check Spike by processing 1.00 mL of the EPH Fractionation Performance Check Solution through the fractionation process, and analyze together with samples processed in the same preparation batch.

Calculate the recovery of each component of the mixture by quantitation against the appropriate component of the EPH Calibration Standard (i.e. calculate naphthalene against naphthalene). Calculate aromatic component recoveries from the aromatic fraction, and calculate aliphatic component recoveries from the aliphatic fraction.

The recovery of each component should normally be between 85% and 115% for nC13 through nC32, and between 70% and 115% for nC10, nC12, and naphthalene. No more than 5% of any of the compounds in the EPH Instrument Performance Check Standard may elute in the wrong fraction (i.e., less than 5% of any aromatic component should be found in the aliphatic fraction, and less than 5% of any aliphatic component should be found in the aromatic fraction).

- 2 If the EPH Method Performance Spike for a sample being fractionated by this procedure is not also carried through the fractionation procedure, then the analysis of an EPH Fractionation Performance Check Spike is required, using the same acceptance criteria.

11.3 Method QC

Method QC samples are carried through all stages of sample preparation and measurement. They are intended to measure average method performance over time, and to control method performance under a statistical process control model.

For all samples processed through this fractionation procedure, their corresponding Method Blanks and EPH Method Performance Spikes should, where possible, be carried through the fractionation procedure as well. If not, then a Procedure Blank and/or EPH Fractionation Performance Check Spike must be analyzed instead.

12. Sample Preparation Procedure

12.1 Silica Gel Column Preparation Procedure

Bake 60-120 mesh silica gel at 130°C for 16 hours or more, using a beaker or glass dish covered with aluminum foil. Remove the beaker from the oven, place in a desiccator, and allow to cool.

Assemble a 25-30 cm x 10 mm i.d. chromatography column with a glass wool plug inserted just above the Teflon stopcock. Close the stopcock. Add a few mL of DCM to the column and remove any air bubbles from the glass wool.

Weigh (7.0 ± 0.2) grams of 100% activated 60-120 mesh silica gel into a 50 mL beaker. Immediately add enough DCM to cover the silica gel. Swirl the solution to create a slurry. Pour the slurry into the column. Rinse the beaker with 5 mL aliquots of DCM until all the silica gel has been transferred to the column.

Add a 1 cm layer of anhydrous sodium sulphate to the top of the silica gel. Open the stopcock and drain excess DCM from the column until the top of the sodium sulphate is just reached.

Add 40.0 mL hexane or pentane to the column. Elute to waste. When solvent reaches the top of the column packing turn off stopcock.

12.2 Sample Fractionation Procedure

Ensure sample extract is prepared in an aliphatic solvent (iso-octane recommended).

If a sample extract is expected to contain more than approximately 200 mg of petroleum hydrocarbon material, dilute it prior to fractionation to prevent overloading the adsorption capacity of the silica gel.

Quantitatively add the sample extract (or a quantitative fraction of the extract) to the top of the column. The total volume of extract introduced to the column should not exceed 2.0 mL. Open the stopcock and elute to waste until the solvent reaches the top of the column material.

Rinse the extract vial with two portions of 0.5 mL of hexane. Open the stopcock and elute to waste until the solvent reaches the top of the column material.

Place a KD collection flask (or round bottom flask) below the column. Add (25 \pm 1) mL of hexane or pentane to column, open the stopcock and begin collecting the aliphatic fraction (F1). Turn off the stopcock when the solvent reaches the top of the packing. [Note: If naphthalene is found to partially elute in F1 of the EPH Fractionation Performance Check Spike, the elution volume for F1 may be reduced.]

Place a second KD collector flask (or round bottom flask) below the column. Add (40 \pm 2) mL of 50:50 DCM:Hexane or 50:50 DCM:Pentane to the column, open the stopcock and collect the aromatic fraction (F2). Collect this fraction until the column is completely drained.

Add 1 mL (or more) iso-octane to each flask to act as a keeper solvent for volatile analytes during the solvent removal step (prevents accidental total evaporation of solvent). If the sample extract was initially prepared in iso-octane prior to fractionation, it may not be necessary to add more iso-octane to the aliphatic fraction (F1).

Concentrate each extract to an accurate final volume of 1.00 mL using the Kuderna-Danish concentrator (or rotary evaporator) and a nitrogen blowdown system. Average error in the final volume must be no greater than 3%. Dilutions or larger final extract volumes may be appropriate for higher level samples.

Never concentrate the final extract to below 0.5 mL, or severe losses of volatile components may result.

If extracts have been stored in a refrigerator, warm them to room temperature and mix gently before dispensing them into GC autosampler vials.

13. Analysis Procedure

Transfer a portion of the extract to a GC autosampler vial and analyze by GC/FID following the procedures specified in the appropriate ministry EPH method. Store remaining extract at 4°C for at least 40 days in case re-analysis is required.

Report EPH results for Fraction 1 (Aliphatics) as:

F1-Aliphatic Results	EPH 10-19 Fraction	EPH 19-32 Fraction
Water Samples	Aliphatic-EPH _{W10-19}	Aliphatic-EPH _{W19-32}
Sediment Samples	Aliphatic-EPH _{S10-19}	Aliphatic-EPH _{S19-32}

Report EPH results for Fraction 2 (Aromatics) as:

F2-Aromatic Results	EPH 10-19 Fraction	EPH 19-32 Fraction
Water Samples	Aromatic-EPH _{W10-19}	Aromatic-EPH _{W19-32}
Sediment Samples	Aromatic-EPH _{S10-19}	Aromatic-EPH _{S19-32}

14. Method Validation

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

14.1 Initial Verification of EPH Fractionation Efficiency

Before proceeding with further validation steps, verify that the method as used meets the fractionation efficiency requirements outlined below by performing at least one EPH Fractionation Performance Check Spike (see section 11.2.2).

The recovery (average recovery if multiple spikes are performed) of each component must be between 85% and 115% for nC16 through nC32, including phenanthrene and pyrene, and between 70% and 115% for nC10, nC12, and naphthalene.

No more than 5% of any of the compounds in the EPH Instrument Performance Check Standard may elute in the wrong fraction (i.e., no more than 5% of any aromatic component may be found in the aliphatic fraction, and no more than 5% of any aliphatic component may be found in the aromatic fraction).

14.2 Method Detection Limits

Apply the MDL=s determined during method validation of the applicable ministry EPH method as the MDL=s for the aliphatic and aromatic EPH parameters (see below).

Table 1. EPH MDL=s to be applied to Aliphatic/Aromatic EPH parameters

Fractionated EPH parameter:	Code	Use MDL for
Aliphatic-EPH ₁₀₋₁₉ in water	Aliphatic-EPH _{W10-19}	EPH ₁₀₋₁₉ in water

Aromatic-EPH ₁₀₋₁₉ in water	Aromatic-EPH _{W10-19}	EPH ₁₀₋₁₉ in water
Aliphatic-EPH ₁₉₋₃₂ in water	Aliphatic-EPH _{W19-32}	EPH ₁₉₋₃₂ in water
Aromatic-EPH ₁₉₋₃₂ in water	Aromatic-EPH _{W19-32}	EPH ₁₉₋₃₂ in water
Aliphatic-EPH ₁₀₋₁₉ in solids	Aliphatic-EPH _{S10-19}	EPH ₁₀₋₁₉ in solids
Aromatic-EPH ₁₀₋₁₉ in solids	Aromatic-EPH _{S10-19}	EPH ₁₀₋₁₉ in solids
Aliphatic-EPH ₁₉₋₃₂ in solids	Aliphatic-EPH _{S19-32}	EPH ₁₉₋₃₂ in solids
Aromatic-EPH ₁₉₋₃₂ in solids	Aromatic-EPH _{S19-32}	EPH ₁₉₋₃₂ in solids

14.3 Reporting Detection Limits

A Reporting Detection Limit is defined as the detection limit for an analytical parameter that is reported to a client or end-user of the data.

Ensure that Reporting Detection Limits are below any regulatory criteria values or regulatory standards specified by MWLAP or other applicable regulatory body.

14.4 Accuracy and Precision

Refer to the applicable MWLAP EPH method. No single laboratory or interlaboratory data was generated for this method from the 1998 ministry interlaboratory study.

The accuracy and precision of this fractionation procedure may be estimated by analyzing replicate EPH Fractionation Performance Check Spikes, and assessing average component recoveries and the standard deviations of those recoveries.

15. Use of Alternative Methods

This method contains several prescribed and required elements which may not be modified. These requirements are necessary due to the nature of aggregate parameters like Extractable Petroleum Hydrocarbons, where many components are calculated against a single calibration reference standard. This method has been specifically designed to minimize the relative bias among responses of common EPH components, and among EPH water and solids 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 below.

15.1 Prescribed Elements

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

- Every laboratory that uses this method, whether modified or not, must validate the method (as used) following the protocols described in section 14.1.
- “REQUIRED” QC elements from section 11 must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.
- Maximum holding time of refrigerated extracts prior to fractionation is 40 days after extraction. Where holding times are exceeded, data must be qualified.
- A minimum weight of 5g of silica gel per 5-20 grams of wet sediment extracted must be used as the adsorption medium. Proportionately smaller quantities of silica gel may be used if only a portion of the extract is fractionated (e.g. 1g silica gel to fractionate one-fifth of the total extract). Commercially prepared silica cartridges are acceptable only if a successful equivalence test has been performed and all method validation requirements have been met.
- The sample extract must be dissolved in an aliphatic solvent (iso-octane is recommended) prior to being loaded on the silica gel column. If traces of polar solvents are present in the extract, ensure that the corresponding EPH Fractionation Performance Check Spike or Method Performance Check Spike is dissolved in an identical solvent to demonstrate that the effectiveness of the fractionation is not compromised.
- The elution solvent for the aliphatic fraction (F1) must be a low-boiling aliphatic solvent (e.g., hexane or pentane).
- The elution solvent for the aromatic fraction (F2) must be composed of 50% DCM and 50% of a low-boiling aliphatic solvent (e.g. hexane or pentane).
- Use of a low volatility “keeper” solvent is required during solvent concentration steps (iso-octane is recommended).

15.2 Performance Based Method Changes

This is a Performance Based Method. Unless prohibited in section 15.1 or elsewhere, 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 thoroughly describe any revised or alternate methods used at any time following the initial adoption of this method by MWLAP. This information must be available in the event of audit by the ministry.

Pay particular attention to the results of EPH Fractionation Performance Check Spikes (section 11.2.2), since this check evaluates the aliphatic / aromatic fractionation process. Any modified method that cannot achieve the performance requirements of this QC check is not equivalent to the reference method.

15.2.1 Modifications Where Equivalence Testing is Not Required

Except where expressly disallowed in section 15.1 or elsewhere, or where included in section 15.2, changes to the following components of this method are permitted if all specified quality control requirements of the method are achieved:

- Apparatus (section 9)
- Reagents and Standards (section 10)
- Sample Preparation Procedure (section 12)

The required QC elements contained within this method are deemed sufficient to identify potential biases introduced by permitted minor modifications within these sections.

15.2.2 Modifications Where Equivalence Testing is Required

Except where expressly disallowed in section 15.1 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:

- Use of commercially prepared silica gel cartridges (refer to section 12.1).
- Use of less than the specified elution volumes for F1 and F2 (refer to section 12.2).

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 sample extracts. Tests for bias (mean accuracy) and precision are required. Only one equivalence test is required to satisfy usage of this method for both solids and waters.

The equivalence test criteria must be satisfied for all of the analytes listed below:

Aliphatic-EPH_{W10-19} or Aliphatic-EPH_{S10-19}

Aromatic-EPH_{W10-19} or Aromatic-EPH_{S10-19}

Aliphatic-EPH_{W19-32} or Aliphatic-EPH_{S19-32}

Aromatic-EPH_{W19-32} or Aromatic-EPH_{S19-32}

For any method that includes a modification that requires equivalence testing, a detailed report that demonstrates equivalence to the reference method by the procedure described below must be available to clients and to MWLAP on request.

15.2.2.1 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:

- i) *At least one appropriate Sample or Product Extract**. The sample or product extract must be selected such that it can be used to effectively validate the fractionation process. The extract must contain both EPH₁₀₋₁₉ and EPH₁₉₋₃₂ at ≥ 3 times the laboratory's routinely reported detection limits (≥ 5 times DL is recommended), AND must contain significant and detectable levels of aliphatic and aromatic components. Ideally, the extract should also contain significant levels of naturally occurring polar organics like humic or fatty acids. Spiked extracts of natural samples may be particularly useful for this purpose. The sample or extract must be analyzed in triplicate (at minimum) by both the reference method and the modified method. Appropriate sample or product types for this procedure may include:

- Petroleum-contaminated peat sample.

- Peat sample spiked with diesel.
- Bunker fuel.

*ii) At least one soil / sediment Reference Material extract*³. While available, either of the two RMs analyzed within the 1998 ministry Hydrocarbon Round Robin are recommended to satisfy this requirement:

- Resource Technology Corporation RTC CRM 355-100
- National Research Council of Canada HS3B

Extracts for the selected Reference Material must be analyzed in triplicate (at minimum) by both the reference method and the modified method. If either of the above RMs are unavailable, any other soil or sediment reference material(s) containing both EPH₁₀₋₁₉ and EPH₁₉₋₃₂ at ≥ 3 times the laboratory's routinely reported detection limits may be substituted.

³ **Important:** For each sample extract type, all analyses by both methods should use sub-portions of the same extract! Ensure that a sufficient quantity of the extract is produced to achieve the required number of analyses.

For both (i) and (ii) above, compare the means obtained for each sample by the reference method and the modified method. For each sample, one of the following must be satisfied:

1. The means for each method must differ by less than 15% relative percent difference (RPD), where relative percent difference of X_1 and X_2 is defined as:

$$\text{RPD} = |(X_1 - X_2) / \text{mean}_{(X_1, X_2)}| * 100\%$$

OR,

2. The difference between the means for each method must not be statistically significant at the 95% confidence level, using a test for significance of the difference of two means, as described by John Keenan Taylor (7). This test is summarized in Appendix I.

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 datapoints (7).

15.2.2.2 Test for Precision of Modified Methods

Modified methods must demonstrate a reasonable level of precision on replicate analyses of either of the two sample types analyzed in section 15.2.2.1. Analyze a minimum of 8 replicates of either sample type.

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 (7).

The modified method must demonstrate a precision of $\leq 20\%$ relative standard deviation on all relevant EPH Aliphatic and Aromatic analytes.

16. References

- (1). British Columbia Ministry of Environment, Lands and Parks, July 1999, Extractable Petroleum Hydrocarbons in Solids by GC/FID, version 2.1.
- (2). British Columbia Ministry of Environment, Lands and Parks, July 1999, Extractable Petroleum Hydrocarbons in Water by GC/FID, version 2.1.
- (3). Canadian Standards Association, January 1995, Requirements for the Competence of Environmental Laboratories, CAN/CSA-Z753.
- (4). Massachusetts Department of Environmental Protection, January 1998, Method for the Determination of Extractable Petroleum Hydrocarbons (EPH).
- (5). Office of Solid Waste, US Environmental Protection Agency, December 1996, Method 3630C, Silica Gel Cleanup.
- (6). Laboratory and Systems Management, Environmental Protection Department, Ministry of Environment, Lands and Parks, Province of British Columbia, 1996, British Columbia Field Sampling Manual, Parts A & D.

(7). Laboratory Services, Environmental Protection Department, Ministry of Environment, Lands, and Parks, Province of British Columbia, 1994, British Columbia Environmental Laboratory Manual for the Analysis of Water, Wastewater, Sediment and Biological Materials, sections 2.17.3 and 2.17.5.

(8). John Keenan Taylor, 1990, Statistical Techniques for Data Analysis, Lewis Publishers, pages 75-78 and 98.

17. Disclaimer

Mention of trade names or commercial products does not constitute endorsement by the British Columbia Ministry of the Environment, Lands and Parks.

18. Acknowledgments

Mark Hugdahl and Scott Hannam of ALS Environmental developed and wrote this method.

The authors gratefully acknowledge the contributions of the Massachusetts Department of Environmental Protection (MADEP). Some components of this method were adapted from MADEP's "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" (4).

MWLAP thanks all laboratories, organizations and individuals that contributed to the development and review of this method, and who participated in the first ministry hydrocarbon round robin study in 1998.

Appendix I

Test for Determining the Significance of the Difference of Two Means

The following is a summary of a two-tailed test for determining whether two means are significantly different (at the 95% confidence level). Two cases are described in John Keenan Taylor's *Statistical Techniques for Data Analysis* (8). The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

This test is one of two options given in section 18.2.2.1 for determining the equivalence of any two datasets produced by the reference method and a modified method.

Step 1: Calculate the variance (V) for the respective means for datasets A and B:

$$V_A = s_A^2 / n_A$$

$$V_B = s_B^2 / n_B$$

where: s = the estimate of the standard deviation (in units of sample concentration, not %RSD)

n = the number of independent data points

Step 2: Calculate the *effective number of degrees of freedom, f*, to be used for selecting t when calculating U_Δ :

$$f = \frac{(V_A + V_B)^2}{\frac{V_A^2}{(n-1)} + \frac{V_B^2}{(n-1)}}$$

Round the calculated value for *f* to the nearest integer. Values below 10 are typical for smaller datasets.

Step 3: Calculate U_Δ , the uncertainty in the difference of the means:

$$U_\Delta = t \sqrt{(V_A + V_B)}$$

where: t = the student's t-variate for a 2-tailed dataset, at 95% confidence and *f* degrees of freedom.

Step 4: If the difference between the means is less than U_Δ , the *uncertainty* in the difference of the means, then there is no evidence that the two datasets are significantly different at the 95% confidence level.

