BRITISH COLUMBIA
Ministry of Water,
Land & Air Protection

ANALYTICAL METHOD 10 FOR CONTAMINATED SITES

Silica Gel Cleanup of Extractable Petroleum Hydrocarbons

Prepared pursuant to Section 53 of the
Contaminated Sites Regulation under the
Waste Management Act

Approved: _____ _____
Director of Waste Management Date

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Silica Gel Cleanup of Extractable Petroleum Hydrocarbons

Organics

Version 1.0

EMS Method Code:********
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1. Parameters and Analyte Codes

Extractable Petroleum Hydrocarbons$_{(nC10\text{-}nC19)}$ in water (Silica-gel treated) = $EPH_{W10\text{-}19(sg)}$
Extractable Petroleum Hydrocarbons$_{(nC19\text{-}nC32)}$ in water (Silica-gel treated) = $EPH_{W19\text{-}32(sg)}$
Extractable Petroleum Hydrocarbons$_{(nC10\text{-}nC19)}$ in solids (Silica-gel treated) = $EPH_{S10\text{-}19(sg)}$
Extractable Petroleum Hydrocarbons$_{(nC19\text{-}nC32)}$ in solids (Silica-gel treated) = $EPH_{S19\text{-}32(sg)}$

2. Analytical Method

EPH extracts are treated using a column of activated silica gel to remove polar co-extractants.

Refer to specific EPH methods for instrumental analysis procedures:

Extractable Petroleum Hydrocarbons in Solids by GC-FID, July 1999, version 2.1 ref. [1].
Extractable Petroleum Hydrocarbons in Water by GC-FID, July 1999, version 2.1 ref. [2].

3. Introduction

This method describes an optional silica gel column cleanup procedure that may, under appropriate circumstances, be used in conjunction with the BC WLAP methods for Extractable Petroleum Hydrocarbons in Solids and Water by GC-FID.

The cleanup is intended as a means to exclude bionic organics from quantitative EPH results, based on the premise that most naturally occurring hydrocarbons are polar, and so will be irreversibly retained by activated silica-gel. Examples of biogenic organics include lipids, plant oils, tannins, lignins, animal fats, proteins, humic acids, fatty acids, and resin acids.

It is important to consider that the silica gel cleanup is not selective to the removal of only

biogenic organics. Silica gel will remove non-biogenic organics if they are sufficiently polar (e.g. some bacterial metabolites of petroleum hydrocarbons; typically alcohols, aldehydes, and acids ref. [3]). Non-polar or slightly polar biogenic components (e.g. some plant waxes) will not be removed by silica gel.

After cleanup, extracts are analyzed by GC-FID using the same procedures as for EPH_{10-19} and EPH_{19-32} in solids or water.

In addition to quantitative numerical results, this method generates a GC-FID chromatogram that can sometimes be used to characterize the type of petroleum hydrocarbons present in a sample.

This procedure is closely related to the EPH Silica Gel Fractionation Method (Method 7: Silica Gel Fractionation of Extractable Petroleum Hydrocarbons, Sept 2001, version 2.1 ref.[4]). The fractionation method produces two discrete sample extracts for analysis: the aliphatic and aromatic fractions. This cleanup method produces a single extract, which is equivalent to a combination of the aliphatic and aromatic fractions from Method 7.

Where acceptable to the ministry, silica gel treated EPH results are intended for comparison against CSR LEPH/HEPH standards, or against EPH standards where they exist. LEPH and HEPH cannot be calculated from the silica gel treated EPH parameters. The ministry does not plan to issue discrete standards for the silica gel treated EPH results, because the cleanup procedure is not appropriate for indiscriminate use.

Appropriate circumstances for the use of this cleanup method are situations where the end user of the analytical data has good reason to suspect that naturally occurring organics are present at a site, to an extent where EPH results would likely be significantly elevated. For regulatory purposes, the ministry may require written disclosure to indicate when and why silica gel treated EPH results are submitted for comparison with CSR standards. Silica gel treated EPH results must be reported with analyte descriptors that differentiate them from untreated EPH results, using an appended "sg". Consult the Director for further guidance.

Refer to the EPH methods for solids and water for further information about the use and applicability of EPH parameters.

This method contains numerous prescribed (required) elements, but is otherwise a Performance Based Method (PBM). Prescriptive elements are included where necessary to maintain consistency of results among laboratories.

4. Method Summary

Sample extracts obtained from the appropriate EPH method are exchanged to a non-polar solvent and are passed through a column containing 1 gram of 100% activated silica gel. Elution is achieved with a small volume of 1:1 DCM:pentane or 1:1 DCM:hexane. The eluted solvent is then concentrated and analyzed by the appropriate EPH analysis procedure.

5. Matrix

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

If samples are introduced to the silica gel column in a polar solvent, the effectiveness of the cleanup is reduced. Even relatively trace levels of acetone in hexane (as little as 5%) can cause incomplete retention of fatty acids[1].

Sample extracts containing more than approximately 30 mg of petroleum hydrocarbons may overload the retention capacity of a 1g silica gel column, and may require dilution prior to cleanup[1].

Use of silica gel that is less than 100% activated (i.e. containing moisture) may reduce the effectiveness of the cleanup[1].

Do not heat silica gel above 160°C, since it can oxidize at higher temperatures. If Procedure Blanks indicate contamination problems, silica gel can be further cleaned by solvent extraction prior to use.

[1] The Capric Acid Reverse Surrogate provides a positive control for all three of the potential problems listed above.

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 and/or Procedure Blanks.

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. Aparatus and Support Equipment

5-10 cm tall x 10-15 mm i.d. glass chromatography columns
Nitrogen blowdown system
Micro-syringes
Oven (Capable of 130^{o}C)
7-15 mL glass extract vials
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, approximately 60-120 mesh
Dichloromethane (DCM)
Hexane and/or Pentane
Iso-octane (2,2,4-trimethyl-pentane) or Toluene
Sodium sulfate, anhydrous

Glass wool, silanized
Capric acid

10.2 Standard Solutions

10.2.1 EPH Calibration Standard Stock Solution

Prepare an EPH 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. 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.

10.2.2 EPH Cleanup Spike Solution

Dilute the EPH Calibration Standard Stock Solution to make an EPH Cleanup Spike Solution in hexane, containing 50 ug/mL of each component of the EPH Calibration Standard Stock Solution. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated.

10.2.3 Capric Acid Stock Solution

Prepare a Stock Solution of Capric Acid at approximately 10,000 ug/mL in 1:1 DCM:hexane. Ensure that the capric acid is fully dissolved before using the solution. Warm the solution and/or place in an ultrasonic bath if necessary to re-dissolve any precipitated components. Store refrigerated.

10.2.4 Capric Acid Spike Solution

Dilute the Capric Acid Stock Solution to make a Capric Acid Spike Solution at 1,000 ug/mL in hexane. Warm the solution and mix well before use to ensure complete dissolution. Store refrigerated.

11. Quality Control (QC)

11.1 General QC Requirements

Both 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-FID in a set that is referred to as an analysis batch. Refer to the applicable EPH Water or

Soil method for additional Method QC requirements.

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.

11.2 Procedure QC

Procedure QC samples must begin at the start of the cleanup procedure and must be carried through to the end of the analysis component of the appropriate method. Procedure QC samples are intended to measure average procedure performance over time, and to control the performance of the procedure under a statistical process control model.

11.2.1 Procedure Blank

REQUIRED[2] - Recommended frequency of 1 per preparation batch of no more than 50 samples. Procedure Blanks help to identify whether the cleanup 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.

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

11.2.2 EPH Cleanup Spike

REQUIRED - Minimum frequency of 1 per preparation batch of no more than 50 samples. EPH Cleanup Spikes evaluate whether the cleanup is functioning effectively by monitoring the recovery of selected aliphatic and aromatic compounds through the process.

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

It is recommended that the Capric Acid Reverse Surrogate also be added to the EPH Cleanup Spike Sample.

[2] The Method Blank for a sample being cleaned-up by this procedure may be processed in lieu of the Procedure Blank

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).

Long-term averages of component recoveries should be between 70% and 115% for nC10, nC12, and naphthalene, and between 85% and 115% for phenanthrene, pyrene, and for the n-alkanes nC16 through nC32.

The Control Limits applied for individual Cleanup Spikes are at the discretion of the laboratory, but must lie within the ranges of 60-125% for C10, C12, and naphthalene, and within 70-125% for phenanthrene, pyrene, and for the n-alkanes C16 through C32.

11.2.3 Capric Acid Reverse Surrogate

REQUIRED – A Capric Acid Reverse Surrogate must be added to all sample and QC sample extracts immediately prior to silica gel cleanup. Capric acid is a fatty acid that should be 100% retained by the silica gel column (this is the reverse of most surrogates, which should ideally be 100% recovered).

Capric Acid was selected as the reverse surrogate because it does not co-elute with components of the EPH Cleanup Spike or Calibration Standard.

The Capric Acid Reverse Surrogate is added to each sample at an amount equivalent to approximately 500 ug/mL in the final extract. The Capric Acid Reverse Surrogate may be spiked either into the sample extract or directly onto the silica gel column prior to addition of the sample extract.

Capric acid must be added to the EPH Calibration Standard (i.e. the working concentration GC-FID standard) so that identification and quantitation of capric acid in samples may be performed.
If the recovery of capric acid is >1% for any sample, then the cleanup process should be repeated, or the data for that sample must be qualified to indicate that cleanup effectiveness may have been incomplete.

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.

Because this method is not intended for routine application to all samples within a processing batch, Method Blanks or EPH Method Performance Spikes are not required to be carried through the cleanup procedure, provided that the Procedure QC steps described in section 11.2 are followed.

11.3.1 Surrogate Compounds

The use of alkane or aromatic Surrogate compounds are strongly recommended for this procedure (in combination with the EPH water and soil methods). Two surrogates that have been used successfully with these methods are 5-methyl-nonane and nC35 (pentatriacontane), both of which elute outside the EPH10-19 and EPH19-32 ranges. A volatile surrogate (i.e. 5-methyl nonane) is particularly important to monitor evaporative losses. Unlike the Capric Acid Reverse Surrogate, alkane or aromatic surrogates should be quantitatively recovered by this procedure.

12. Sample Preparation Procedure

12.1 Silica Gel Column Preparation

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

Prepare a small glass chromatography column for use. Optimal dimensions of the column are approximately 5-10 cm in height, with a 10-15 mm i.d. The column should have a glass frit base or should use an appropriate filter. Use of a stopcock is optional. The column should be able to contain 1g of silica gel together with about 5mL of solvent.

Weigh (1.0 $\pm$ 0.1) grams of 100% activated silica gel into a prepared chromatography column.

12.2 Preparation of Extracts

For this procedure, the sample extract should be dissolved in an aliphatic solvent. If it is not, then the efficacy of the cleanup must be verified prior to use, as indicated in section 14.1, Initial Validation of EPH Cleanup Method.
The following solvent-exchange procedure is recommended for EPH solid samples which originate from a hexane:acetone extract: Measure an exact portion of the hexane:acetone extract (10-20% is recommended, if detection limit requirements can be met). Add a volume of reagent water approximately equal to the volume of the hexane:acetone portion selected. The extract should partition into two phases. Discard most of the lower aqueous layer (water plus acetone). Then wash the hexane a second time with the same volume of reagent water that was used for the first wash[3]. Separate the upper hexane layer (or a quantitative portion of it) for the silica gel cleanup step. Discard the lower aqueous layer. Concentration by nitrogen blowdown or by the Kuderna-Danish technique may be necessary to bring the total hexane

volume to approximately 2 mL.

Spike each sample extract with 500 uL of the 1,000 ug/mL Capric Acid Spike Solution.

If the portion of sample extract being cleaned up is expected to contain more than approximately 30 mg of petroleum hydrocarbon material, it should be diluted to prevent the possible overloading of the adsorptive capacity of the silica gel. Incomplete retention of the Capric Acid Reverse Surrogate may be an indication that the capacity of the silica gel has been exceeded.

12.3 Silica Gel Cleanup Procedure

Add enough hexane to more than cover the silica gel. If necessary, mix the hexane and silica gel with a Pasteur pipette to eliminate air bubbles.

After the silica gel has settled, add about a 1/4 cm layer of anhydrous sodium sulfate to the top of the column.

Add 5-10 mL of DCM to the column, while eluting to waste. When the solvent reaches the top of the column, add about 10 mL of hexane, and elute this to waste also. If the silica gel dries before the sample is added, repeat the hexane addition step, again eluting to waste.

Quantitatively add the sample extract (or an exact portion of the extract) to the top of the column. Begin collecting the eluant immediately into a suitable glass vial (i.e. 7-15 mL volume).

Rinse the extract vial with two portions of 0.5 mL of 1:1 DCM:pentane or 1:1 DCM:hexane, adding the rinsings each time to the silica gel column.

Add an additional 4-6 mL of DCM:pentane or 1:1 DCM:hexane to complete the elution of the column (pentane is recommended over hexane to reduce losses of volatile EPH components during nitrogen blowdown). The exact volume required to completely elute the column can vary with column dimensions and packing density, and should be verified during method

[3] The second water wash is necessary to reduce residual acetone levels to about 3%. If only one water wash is used, the cleanup effectiveness is reduced, and the silica gel will not fully retain fatty acids, including the Capric Acid Reverse Surrogate.

validation and with daily quality control samples.

Add 1 mL iso-octane or toluene to the vial to act as a non-volatile keeper solvent during the solvent removal step (minimizes the likelihood of over-evaporation of solvent).

Concentrate the extract to an accurate final volume of 1.00 mL using a nitrogen blowdown system. Dilutions or larger final extract volumes may be appropriate for higher level samples.

Avoid concentration of the 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 BC WLAP EPH method. Store remaining extract at 4°C for up to 40 days in case re-analysis is required.

Ensure that EPH Calibration Standards contain capric acid, so that the reverse surrogate may be identified and quantitated.

Report Silica-Gel Treated EPH results as follows:

	EPH 10-19 Fraction	**EPH 19-32 Fraction**
WaterSamples	$EPH_{W10\text{-}19(sg)}$	$EPH_{W19\text{-}32(sg)}$
Sediment/Soil Samples	$EPH_{S10\text{-}19(sg)}$	$EPH_{S19\text{-}32(sg)}$

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 Validation of EPH Cleanup Method

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

The method must be validated using exactly the same solvent or solvent mixture that is used for samples.

Note: If extracts are dissolved in polar solvents (i.e. DCM or toluene), a 1:1 dilution with

hexane or pentane prior to the cleanup step improves the likelihood of meeting the capric acid retention criteria.

A key component of the validation of this method is to verify or optimize the required volume of DCM:hexane elution solvent required to fully elute all the alkane and PAH components of the EPH Cleanup Spike, which may vary depending on the dimensions of the silica gel column used.

For the Initial Validation, the recovery (or average recovery if multiple spikes are performed) of each component must be between 85% and 115% for the n-alkanes nC16 through nC32 and for phenanthrene and pyrene, and between 70% and 115% for nC10, nC12, and naphthalene.

Capric acid in the Cleanup Spike must be > 99% removed by the cleanup procedure. Normally, no capric acid whatsoever should be detected.

14.2 Method Detection Limits

Apply the MDLs determined during method validation of the applicable BC WLAP EPH method as the MDLs for the EPH silica gel treated parameters. If the cleanup process introduces a dilution factor over the standard EPH method, MDLs should be correspondingly increased.

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.

The laboratory's Reporting Detection Limits should be below any regulatory criteria values or regulatory standards specified by BC WLAP or other applicable regulatory body.

14.4 Accuracy and Precision

Refer to the applicable BC WLAP EPH method. No single laboratory or inter-laboratory data was generated for this method from the 1998 BC WLAP inter-laboratory study.

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

15. Use of Alternative Methods

This method contains prescribed (required) elements which may not be modified.

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 listed 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 by BC WLAP:

- Every laboratory that uses this method, whether modified or not, must validate the method (as used) following the protocols described in section 14.1.

- All "REQUIRED" QC elements from section 11 must be completed as specified. Where requirements are not met, data must be qualified.

- Maximum holding time of refrigerated extracts prior to cleanup is 40 days after extraction. Where holding times are exceeded, data must be qualified.

- The cleanup must utilize a column of 100% activated silica gel. "In-situ" cleanup techniques (where silica gel is simply mixed with the sample extract) are not permitted. Preliminary studies have shown that in-situ cleanups can be considerably less effective than column techniques for the removal of medium polarity biogenic material.

- A minimum of one gram of silica gel per 5-20 grams of wet sediment extracted or per 500-1000 mL water sample must be used as the adsorption medium. Commercially prepared silica gel cartridges are acceptable if validation and QC requirements are met, and if they introduce no significant impurities (e.g. phthalates, BHT).

- The elution solvent for this method must be a 1:1 mixture of DCM with an aliphatic solvent (pentane or hexane are recommended due to their volatility).

- The EPH Cleanup Spike must be prepared in the same solvent that is used for samples.

- Use of a low volatility "keeper" solvent is required during solvent concentration steps (iso-octane or toluene is recommended).

- Silica gel treated EPH results must be reported with analyte descriptors that differentiate them from untreated EPH results, using an appended "sg".

- Recovery of the Capric Acid Reverse Surrogate must be <1% for all samples (i.e. capric acid *retention* must be greater than 99%). If not, the data for that sample must be qualified to indicate that cleanup effectiveness may have been incomplete.

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 BC WLAP. This information must be available in the event of audit by BC WLAP or clients.

No additional equivalence testing procedures have been formalized for this procedure. However, it is strongly recommended that any modifications that might be expected to impact the effectiveness of the procedure be evaluated using extracts of samples which are high in naturally occurring organics (e.g. decomposing leaf or plant material, wood waste, peat, etc.). Refer to the analytical methods for EPH for further guidance on equivalence test procedures.

16. References

(1). Extractable Petroleum Hydrocarbons in Solids by GC-FID, Revision Date December 31, 2000, British Columbia Environmental Laboratory Manual For the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples, 2003 Edition. Water & Air Monitoring and Reporting Section, Water, Air and Climate Change Branch, Ministry of Water, Land and Air Protection, Province of British Columbia, July 1, 2003.

(2). Extractable Petroleum Hydrocarbons in Water by GC-FID, Revision Date December 31, 2000, British Columbia Environmental Laboratory Manual For the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples, 2003 Edition. Water & Air Monitoring and Reporting Section, Water, Air and Climate Change Branch, Ministry of Water, Land and Air Protection, Province of British Columbia, July 1, 2003.

(3). Total Petroleum Hydrocarbon Criteria Working Group Series, Volume I, Analysis of Petroleum Hydrocarbons in Environmental Media, page 38, March 1998, Wade Weisman (editor), Amherst Scientific Publishers.

(4). Silica Gel Fractionation of Extractable Petroleum Hydrocarbons (Method 7), Revision

Date September 2001, British Columbia Environmental Laboratory Manual For the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples, 2003 Edition. Water & Air Monitoring and Reporting Section, Water, Air and Climate Change Branch, Ministry of Water, Land and Air Protection, Province of British Columbia, July 1, 2003.

(5). Office of Solid Waste, US Environmental Protection Agency, December 1996, SW846 Method 3630C, Silica Gel Cleanup.

17. Disclaimer

Mention of trade names or commercial products does not constitute endorsement by the British Columbia Ministry of Water, Land and Air Protection.