Section D

ORGANIC CONSTITUENTS AND COMPOUNDS

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SECTION D Organic Constituents and Compounds

Acid Extractable Herbicides in Water by GC/ECD

Parameter

Acid Extractable Herbicide Scan

Analytical Method

Acid Extraction, Methylation, GC/ECD.

Introduction

The acid extractable herbicides are a group of eleven compounds which include chlorinated phenols, phenolic and carboxylic acid herbicides. If the compounds are present as alkyl esters (e.g., 2,4-DB), they will not be determined by this procedure.

Summary

An acidified water sample is extracted with dichloromethane. The raw extract is concentrated and the phenols and acids are reacted with diazomethane, or other suitable derivatizing agent, to produce the corresponding derivatives. If required, the extracts are subjected to Florisil column chromatography and divided into different fractions. The derivatives are analyzed by electron capture gas liquid chromatography.

MDL

Parameter	EMS Code		mg/L
Pentachlorophenol	**P022**	**P008**	0.0001
Tetrachlorophenols (sum)	**T020**	**P008**	-
Trichlorophenols (sum)	**T021**	**P008**	-
2,3,4,5-Tetrachlorophenol	(to be defined on request)		0.0002
2,3,4,6-Tetrachlorophenol	"		0.0002
Dicamba	"		0.0001
2,4,5-T	"		0.0001
Triclopyr	"		0.0001
2,4,5-TP	"		0.0001
2,4-D	"		0.0002
Dichlorprop	"		0.0002
Dinoseb	"		0.0002
Picloram	"		0.0002

Matrix

Fresh water, wastewater, marine water.

Interferences and Precautions

Any organic compound that responds to an electron capture detector may interfere in the gas chromatography step of the analytical procedure. If interfering co-extractives are encountered, a Florisil clean-up step may be incorporated into the procedure. The presence of a compound of interest may be confirmed by analysis on a second chromatography column of different polarity.

Sample Handling and Preservation

Bottle:
amber glass, narrow mouth, 0.5 L, acetone rinsed and heat treated at 350°C.

Preservation:
unfiltered, add 4 mL of 36N H_2S0_4/L in field.

Stability

Holding time:
extract sample within 14 days of sampling, analyze within 40 days.

Storage:
4°C until analyzed.

Procedure

Apparatus

a) Separatory funnels, 500 mL.
b) Graduated cylinders, 12 mL.
c) Round bottom flasks, 250 mL.
d) Glass chromatography columns,
   9 mm ID × 300 mm with a 200 mL reservoir.
e) Diazomethane generator.
f) Glass filtering funnels, 75 mm diameter.

Reagents

a) Solvents, glass distilled, pesticide grade.
    1) Dichloromethane (DCM)
    2) *iso*-octane
    3) Petroleum ether
    4) Ethyl acetate
b) Sulfuric acid, 36 N,
   extracted with a suitable organic solvent prior to use.
c) N-Nitrosomethylurea for diazomethane generation.
d) Sodium hydroxide, 10% weight to volume, aqueous solution.
e) Acidified sodium sulfate, anhydrous, heat treated.
f) Florisil, PR grade,
   heat treated at 650°C and deactivated with 1% deionized water.
g) Acidified glass wool, solvent rinsed and heat treated at 300°C.

Procedure

a) Recovery Control: A 250 mL water sample is spiked with 0.100 mL of
   1 mg/L intermediate herbicide standard to give a 0.0004 mg/L solution.
b) For samples that have not been treated with an acid,
   add 1 mL of 36 N sulfuric acid to a 250 mL sample.
c) Extract a 250 mL sample three times with 60 mL of DCM each time.
d) Filter the DCM extracts through anhydrous sodium sulfate, supported in
   a glass funnel by glass wool, into a 250 mL round bottom flask.
e) Evaporate the combined extracts to about 2 mL
   using a rotary evaporator with the bath set at 40°C.
f) Methylate the extract with diazomethane until a yellow colour persists.
g) Allow the reaction to proceed for one-half hour.
h) Add 2 mL of iso-octane to each flask
   and evaporate the DCM using a rotary evaporator.
i) Transfer to a graduated cylinder and make up to 5.0 mL with iso-octane.
j) Analyze by electron capture gas chromatography.
k) If samples contain interfering material,
   prepare a column containing 10 g of 1% deactivated Florisil
   topped by a 2 cm layer of anhydrous sodium sulfate and elute as follows:
    1) Fraction 1: 150 mL of petroleum ether.
       This fraction contains: PCP and TtCP.
    2) Fraction 2: 100 mL of 2% ethyl acetate in petroleum ether.
       This fraction contains: Dicamba, Dichlorprop, Dinoseb,
       Triclopyr, 2,4-D, 2,4,5-T, and 2,4,5-TP (Silvex).
    3) Fraction 3: 100 mL of 20% ethyl acetate in petroleum ether.
       This fraction contains: Picloram.
l) Add 2–3 mL of iso-octane and concentrate the eluate to 2–3 mL,
   transfer to a graduated cylinder and make up to 5.0 mL.
m) Analyze by electron capture gas liquid chromatography.

Precision	None listed.	
Accuracy	None listed.	
Quality Control	**Method Blank**: One per analytical batch, or 1 in 14.	
	Recovery Control: A 250 mL water sample is spiked with 0.100 mL of 1 mg/L intermediate standard containing all compounds of interest.	
References	None listed.	
Revision History	February 14, 1994: December 31, 2000:	Publication in 1994 Laboratory Manual. EAM codes replaced by EMS codes. Out of print reference deleted.

Adsorbable Organic Halides (AOX) in Water

Parameter

Adsorbable Organic Halides (AOX)

Analytical Method

Carbon adsorption; TOX analyzer.

EMS Code

AOX-X311

Introduction

This procedure measures organically bound halides (chlorides, bromides and iodides) as their chloride equivalent. Fluorides are not included. Since the amounts of organically bound bromides and iodides are small relative to chloride, expression of results as chloride is generally valid.

Summary

An appropriate sample aliquot is passed through two granular activated carbon (GAC) columns in series where the organo-halides are adsorbed. The columns are then rinsed with 0.8M potassium nitrate solution to remove inorganic halides. The columns are combusted individually and the halo-acids thus generated are collected and measured in a microcoulometric cell.

MDL

0.01 mg/L (10 µg/L)

Matrix

Fresh water, wastewater, marine water.

Interferences and Precautions

Test a 10 mL portion of sample for residual chlorine by adding a few crystals of potassium iodide (KI) and five drops of 1% starch solution. If a blue colour is produced, residual chlorine is present. Add sufficient 0.1M $Na_2S_2O_3$ to discharge the blue colour. Add a proportionate amount of sodium sulfite solution to the sample bottle. (This procedure is most properly done in the field, at the time of sampling, to preclude the generation of additional organo-chlorine compounds during shipping and holding.)

Sample Handling and Preservation

Bottle: amber glass, 0.5 L, narrow mouth, Teflon or aluminum foil lined cap, acetone rinsed and heat treated at 350°C.

Preservation: unfiltered, air excluded, add HNO_3 to pH 1.5 to 2.0 and, if required, sufficient 0.1M sodium sulfite to remove residual chlorine.

Stability

Holding time: analyze sample within 14 days of sampling.

Storage: 4°C until analyzed.

Procedure

Apparatus

a) MC-3 TOX Analyzer.

b) AD-3 TOX Adsorption Module.

c) Carbon Plus Industries (CPI) packed GAC column adapters.

d) Volumetric flasks, 100mL.

e) Syringes, Hamilton Model 801, 10µL and 50µL.

Reagents

f) Carbon dioxide (CO_2) gas: 99.99% purity grade.

g) Oxygen (O_2) gas: 99.99% purity grade.

h) Acetic acid, 70% aqueous solution: Dilute 7 parts glacial acetic acid, analytical reagent (A.R.) grade, with 3 parts deionized water.

i) 1,000 µg/mL (ppm) inorganic chloride standard:
Dissolve 0.1648 g NaCl, A.R. grade, in 1.0 L deionized water.

j) Nitrate wash solution (0.08N KNO_3):
Dissolve 8.2 g KNO_3, A.R. grade, in 1.0 L deionized water.

k) Nitric acid: HNO_3 concentrated, A.R. grade.

l) Sodium sulfite ($Na_2S_2O_3$) 0.1M:
Dissolve 12.5 g $Na_2S_2O_3$, A.R. grade, in 1.0 L deionized water.

m) Sample dilution water:
Deionized water, pH adjusted to 1.5–2.0 with concentrated nitric acid.

n) Organohalide standard (1000 µg Cl^-/mL), recovery check solution:
Dissolve 0.186 g 2,4,6-trichlorophenol, A.R. grade,
in 100 mL methanol, A.R. grade.

o) Adsorption columns: Carbon Plus Industries (CPI)
packed granular activated carbon (GAC) columns.

p) Starch indicator solution: 1% aqueous.

q) Potassium Iodide (KI): crystals, A.R. grade.

Procedure

a) Low Level, Receiving Water Samples: Pipet 100 mL of preserved sample directly into the sample reservoir of the absorption unit. Run the sample through two carbon columns in series and rinse with 4 mL of 0.08N KNO_3. Analyze each column separately. The upper column should be analyzed first, followed by the lower column. If the AOX content of the second (lower) column exceeds 10% of that found in the first column, dilute the sample and reanalyze.

b) Wastewaters and Pulp Mill Effluents: Prepare a 100–200 times dilution of the preserved sample, taking at least 5 mL of sample for the first dilution. The dilution water used should be adjusted to pH 1.5–2.0. Total volume of the final dilution should be 100 mL. Transfer the final dilution volume to the sample reservoir of the absorption unit and run the sample through two carbon columns in series and rinse with 4 mL 0.08N KNO_3. Analyze each carbon column separately. The upper column should be analyzed first, followed by the lower column. If the AOX content of the second (lower) column exceeds 10% of that found in the first column, dilute the sample further and reanalyze.

Blanks

a) Nitrate Wash Blank: Analyze, separately, two carbon columns washed, in series, with 4 mL of 0.08N KNO_3. The nitrate wash blank value should be less than 0.700 µg Cl^-/40 mg carbon column. The values of the individual columns should be within 20% of each other. The average result of the two columns is the nitrate wash blank value. Two blanks should be run per week.

b) Dilution Water Blank: Analyze, separately, two carbon columns washed, in series, with 100 mL of dilution water and rinsed with 4 mL of 0.08N KNO_3. The dilution water blank should be prepared in the same manner as the samples to be analyzed, (i.e., if 0.1 mL of 0.1M $Na_2S_2O_3$ has been added to the samples, it should also be added to the blank). The dilution water blank value should be less than 1.00 µg Cl^-/40 mg carbon column. All subsequent dilution water blanks should be within 10% of the original. The average result of the individual carbon columns is the dilution water blank value. Two dilution water blanks should be run per day.

Calculations

The formula for calculating the AOX content of the sample is:

$$C_4 = (C_1 + C_2 - 2C_3) / V$$

where: C_4 = AOX content of the sample in µg Cl^-/L
C_1 = AOX content of 1st carbon column (µg Cl^-)
C_2 = AOX content of 2nd carbon column (µg Cl^-)
C_3 = AOX content of blank column (µg Cl^-)
V = Volume of sample used (L), times dilution

Precision

None listed.

Accuracy

None listed.

Quality Control

a) Granular Activated Carbon (GAC) Quality: Use Carbon Plus Industries (CPI) packed GAC columns. Analyze the carbon from one column twice weekly. The apparent halogen content should be less than 0.700 µg Cl^-/40 mg GAC.

b) Cell Performance Check: Flush titration cell at least twice with 70% acetic acid and fill. Inject 5 µL of inorganic Cl^- standard. The integrated reading at the end of the 5-minute run should be 5.00 µg ±5%. One cell performance check should be performed at the beginning of each day and each time the cell is flushed and refilled. (Recovery criterion: 95–105 %).

c) Direct Injection of Standards: Combust 40 mg GAC in the boat in the furnace. At the end of the run, spike the burnt carbon with 5 µL of 1.00 µg Cl^-/µL 2,4,6-trichloro-phenol standard. Push “START” and switch to “INT”. At the end of the run, (10 minutes), the reading should be 5.00 µg ±5%. (Recovery criterion: 95–105 %).

d) Spike Recovery: Spike a 100 mL aliquot of dilution water or a sample with 10 µL of 1.00 µg Cl^-/µL 2,4,6-trichlorophenol standard and analyze as a regular sample. Run one spike per day. Calculated concentration should be 100 µg Cl^-/L. (Recovery criterion: 90–110 %).

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 5320: Dissolved Organic Halogen.

b) USEPA Method 9020; Total Organic Halides (TOX), Revision O, September 1986.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Out of print references deleted. Manufacturers name deleted.

Alcohols in Soil and Water — PBM

Parameter

Alcohols in soil and water

Analytical Method

Direct injection or Headspace Gas chromatography with Flame Ionization Detection (GC/FID) — PBM.

Introduction

This method is applicable to the quantitative determination of alcohols in soil and water.

Method Summary

Direct injection: A portion of the water or aqueous soil extract is transferred to an autosampler vial and is injected into the GC inlet (on-column or splitless), for direct analysis by GC/FID, using a polar stationary phase (e.g., DB-Wax or DB-624 or equivalent). This method yields detection limits of approximately 1 mg/L and 1 mg/kg. If lower reporting levels are required (e.g., for methanol), GC/FID and headspace is recommended (US EPA method 5021A).

Headspace: a portion of the water sample or aqueous soil extract is transferred to a headspace vial containing salt as matrix modifier. The vial is sealed and heated. When equilibrated, a portion of the headspace above the liquid is introduced into the GC/FID.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. Soil MDL (µg/g)	Approx. Water MDL (µg/L)	EMS Analyte Code
Methanol	67-56-1	0.5–5	500–1,000	M020
Ethanol	64-17-5	0.5–5	500–1,000	N/A
n-Propanol	71-23-8	0.5–5	500–1,000	N/A
2-Propanol (Isopropanol)	67-63-0	0.5–5	500–1,000	N/A
n-Butanol	71-36-3	0.5–5	500–1,000	N/A
2-Butanol	78-92-2	0.5–5	500–1,000	N/A
2-Methyl-1-propanol (Isobutanol)	78-83-1	0.5–5	500–1,000	N/A
2-Methyl-2-propanol (t-Butanol)	75-65-0	0.5–5	500–1,000	N/A

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil: Soil, sediment, sludges, solid wastes.

Water: Freshwater, seawater, groundwater, wastewater

Interferences and Precautions

Alcohols by GC-FID may be subject to interferences by any substance with similar boiling points and chromatographic characteristics that may co-elute under the conditions of the analysis (e.g., by alkanolamines or petroleum hydrocarbons). Matrix spikes and/or GC/MS confirmation is recommended to assist with correct identification of target compounds in samples if co-eluting interferences are suspected.

Hydrocarbon interferences may be removed with a hexane pre-extraction cleanup step, using brief physical agitation.

Isobutane interferes with methanol on a dimethyl polysiloxane column (e.g., DB-1). Use of a polar column phase is recommended to resolve this interference (e.g., DB-624).

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree if carry-over that occurs on their instrument and should take appropriate steps to prevent the occurrence of false positives.

Sample Handling and Preservation

Sample Containers:

Soil: Glass jar with Teflon (or foil) lined lid, 125–250 mL recommended.

Water: 40–60 mL glass vials with Teflon septa and zero headspace (2 vials per sample recommended).

Preservation:

Soil: Chemical preservation is not required. Collect samples with minimized headspace.

Water: Samples may be preserved with $NaHSO_4$ to pH <2 to extend hold times (200 mg solid $NaHSO_4$ per 40 mL sample is recommended).

Storage: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage.

Stability

Holding Time:

Soil: Analyze soil samples within 14 days after collection.

Water: Analyze unpreserved samples within 7 days after collection. Acid preservation extends hold times to 14 days from sampling.

Where holding times are exceeded, test results must be qualified.

Procedure

Soils:

Soil samples are subjected to aqueous extraction prior to direct injection of the aqueous extract. Soils are extracted in water using a 2:1 ratio of water to field-moist soil. Soil samples are physically agitated using a mechanical shaker for a minimum of 30 minutes. Suspended solids may be removed by filtration, or sample extracts may be centrifuged until clear. Moisture content analysis is performed on a separate aliquot. Test results are corrected for moisture content and are reported on a dry-weight basis. Include sample moisture content in the aqueous extract volume for data calculation purposes.

Waters:
Water samples are analyzed by direct aqueous injection by gas chromatography with flame ionization detection (GC/FID). Suspended solids may be removed by filtration, or samples may be centrifuged until clear.

Detailed instrumental analysis procedures are not provided for this method. The procedures described in EPA Method 8015D (see references) are suitable for general guidance.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80–120% for Lab Control Samples or Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for Lab Control Samples at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank (MB) — matrix specific	One per batch (max 20 samples)	Less than reported DL
Calibration Verification Standard (CVS) — 2nd Source	One per initial calibration	85–115%
Continuing Calibration Verification (CCV) — mid-level	At least every 12 hours (max 20 samples), and at end of each batch.	80–120%
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	70–130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	50% RPD (soils) 30% RPD (waters) [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60–140%
Surrogate Compounds	Recommended	Not specified
*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

1. Calibrations must consist of a minimum of 4 calibration standards.
2. For soil extractions, soil moisture content must be accounted for in the extraction solvent volume if using extraction by water or a water-miscible solvent.
3. For FID analysis, at least 80% baseline chromatographic separation must be achieved for all target parameters in calibration standards (valley height of peak overlap must not exceed 20% of maximum peak height).
4. Where sample extracts require filtration or pre-extraction cleanup with hexane, QC samples must be processed in the same manner.
5. All stated performance and quality control requirements must be met.
6. Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

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

b) EPA 5021A. Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis, Revision 2, July 2014.

Revision History

Sept 15, 2017	First version added to BC Lab Manual in support of 2017 CSR updates.

Base-Neutral and Acid Semi-Volatile Extractables in Water

Parameter Base-Neutral and Acid Semi-Volatile Extractables (BNAs)

Analytical Method Extraction, GC/ECD

EMS Code (EMS code will be assigned upon request)

Introduction This analysis is specific for the class of compounds called base-neutral and acid semi-volatile extractables (BNAs). For simplicity this method will target the following compounds:

Acenaphthene	Acenaphthylene
Anthracene	Benz(a)anthracene
Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(g,h,i)perylene	Benzo(k)fluoranthene
2-Chloronaphthalene	Chrysene
Dibenz(a,h)anthracene	Fluoranthene
Fluorene	Indeno(1,2,3-cd)pyrene
Naphthalene	Phenanthrene
Pyrene	

Benzylbutylphthalate	Bis(2-ethylhexyl)phthalate
Di-n-butylphthalate	4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether	Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether	2,4-Dinitrotoluene
Bis(2-chloroethoxy)methane	2,6-Dinitrotoluene
Nitrobenzene	N-Nitrosodi-n-propylamine
N-Nitrosodiphenylamine	

4-Chloro-3-methylphenol	2-Chlorophenol
2,4-Dichlorophenol	2,4-Dimethylphenol
2,4-Dinitrophenol	2-Methyl-4,6-dinitrophenol
2-Nitrophenol	4-Nitrophenol
Pentachlorophenol	Phenol
2,4,6-Trichlorophenol	Tetrachlorophenol(s)

Summary The sample is placed in a separatory funnel, the pH of the sample is adjusted to alkaline and then acidic conditions and extracted each time with DCM to selectively remove compounds (EPA METHOD 3510A). The final extracts (basic and acidic) can be combined or run separately using the following procedures:

- Capillary Column Gas Chromatography with Mass Spectrometry Detection (EPA METHOD 8270B).
- Specific techniques can be used, see "Principle or Procedure".

MDL Actual MDL will vary depending on the instrument sensitivity and matrix effects.

Note: The following detection limits were obtained from the Ontario Regulation 695/88 under the Environmental Protection Act "Effluent Monitoring — General".

PARAMETER GROUP MISA 19	Detection Limits, µg/L (for Standards in Reagent Water)
Acenaphthene	1.3
Acenaphthylene	1.4
Anthracene	1.2
Benz(a)anthracene	0.5
Benzo(a)pyrene	0.6
Benzo(b)fluoranthene	0.7
Benzo(g,h,i)perylene	0.7
Benzo(k)fluoranthene	0.7
2-Chloronaphthalene	1.8
Chrysene	0.3
Dibenz(a,h)anthracene	1.3
Fluoranthene	0.4
Fluorene	1.7
Indeno(1,2,3-cd)pyrene	1.3
Naphthalene	1.6
Phenanthrene	0.4
Pyrene	0.4
Benzylbutylphthalate	0.6
Bis(2-ethylhexyl)phthalate	2.2
Di-n-butylphthalate	3.8
4-Bromophenyl phenyl ether	0.3
4-Chlorophenyl phenyl ether	0.9
Bis(2-chloroisopropyl)ether	2.2
Bis(2-chloroethyl)ether	4.4
2,4-Dinitrotoluene	0.8
2,6-Dinitrotoluene	0.7
Bis(2-chloroethoxy)methane	3.5
Nitrobenzene	*
N-Nitrosodi-n-propylamine	3.1
N-Nitrosodiphenylamine	14
4-Chloro-3-methylphenol	1.5
2-Chlorophenol	3.7
2,4-Dichlorophenol	1.7
2,4-Dimethylphenol	7.3
2,4-Dinitrophenol	4.2
2-Methyl-4,6-dinitrophenol	24.
2-Nitrophenol	*
4-Nitrophenol	1.4
Pentachlorophenol	1.3
Phenol	2.4
2,4,6-Trichlorophenol	1.3
Tetrachlorophenol(s)	1.6

* was not determined in study.

Matrix

Fresh water, wastewater, marine water.

Interferences and Precautions

Analysis of method blanks will identify interferences from glassware, solvent, reagents, etc. Interfering co-extractants will vary depending on the sample matrix, source, and method of detection. The clean-up procedure will eliminate many of these, but unique samples may require additional work, or be subject to higher detection limits. Certain compounds are very light sensitive and samples should be collected in amber glass containers and protected from direct light.

Sample Handling and Preservation

Bottle:
1 litre amber glass, with Teflon or foil lined lid.

Preservation:
80 milligrams of sodium thiosulfate per litre if residual chlorine is present; store cool (4°C) in amber glass or foil-wrapped jars from time of collection to extraction. Collect a representative sample in a wide mouth glass bottle that has been rinsed with solvent and oven-dried. Do not rinse bottle with sample. If duplication is required, a separate one litre sample must be provided.

Stability

Holding Time:
Extract within 7 days of collection. Analyze within 40 days of extraction.

Principle or Procedure

See EPA Methods:

Extraction	-	625	3510A	
Analysis	-	625	8270B	(GC/MS)
	-	604	8040	(GC/ECD)
	-	607	8090	(GC/NPD)
	-	608	8080	(GC/ECD)

Precision

See appropriate method for data.

Accuracy

See appropriate method for data.

Quality Control

Samples: (batch size 1 to 15 samples).
1 method blank per analytical batch.
1 sample duplicate if available;
if not, an instrument duplicate per analytical batch.
1 reagent spike per analytical batch.
Note:
- instrument or solvent blanks should be run after samples that contain high concentrations of analytes.
- surrogate standard recoveries should be reported.

References

a) EPA (1986) Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, U.S. Environmental Protection Agency, SW-846, 3rd Ed. (November 1986).

b) EPA (1984) Federal Register, Part VIII, Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act. U.S. Environmental Protection Agency, 40 CFR Part 136 (October 26, 1984).

c) Ontario Regulation 695/88 under the Environmental Protection Act "Effluent Monitoring — General".

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: Republication. Note neither SEAM nor EMS codes had been assigned.

Biochemical Oxygen Demand (BOD)

Parameter

Biochemical Oxygen Demand (BOD) — Total

Carbonaceous Biochemical Oxygen Demand (C-BOD)

Analytical Method

BOD, 5-day seeded. APHA Standard Methods for the Examination of Water and Wastewater 5210B, 20th Edition.

Introduction

This method is applicable to raw water supplies, treated industrial or municipal effluents, and receiving waters. The oxygen uptake after 5 days of incubation at a test temperature of 20°C is widely recognized as the standard BOD in many countries. BOD values are used for determining the relative oxygen requirements of municipal and industrial wastewaters. The test is widely employed to measure waste loading and to provide an indirect and non-specific measure of the amount of biodegradable organic material (Carbonaceous demand) in a given sample. BOD also includes oxygen used to oxidize inorganic material such as sulfides and ferrous iron.

Method Summary

The BOD is an empirical bioassay type procedure that measures the dissolved oxygen consumed by microbial life while it assimilates and oxidizes the organic matter present during the test period. Test conditions are incubation for five days in the dark at 20°C. A polarographic membrane electrode is typically used to measure dissolved oxygen, although newer luminescence-based sensor technology is coming available. Comparison of the dissolved oxygen content of the sample at the beginning and the end of the incubation period provides a measure of the biochemical demand.

MDL and EMS Codes

The lowest detection limit for the method is 1mg/L times the dilution factor. This is established by the requirement for a minimum DO depletion of 2 mg/L minus the maximum seed correction of 1 mg/L.

Matrix

Waters and wastewaters.

Interferences and Precautions

Oil and Grease interferes with DO measurements if they are present in sufficient quantity to coat the probe's Teflon membrane. Pre-diluting samples and replacing the membrane should improve performance.

Any biodegradable substances in the dilution water may contribute to the measured sample BOD. The DO depletion of a satisfactory dilution water blank should not exceed 0.2mg O_2/L.

Residual chlorine is an example of a toxic substance which must be removed prior to testing for BOD. In most test samples, residual chlorine will dissipate after sitting in light for 1 to 2 hours (typically occurs during transport to the lab). If residual chlorine persists, refer to APHA Method 5210 section 4.b.2 for guidance on dechlorination procedures.

Oxygen supersaturation will cause oxygen loss during incubation. Shake ½ full bottle of sample at 20 ±3°C to achieve oxygen saturation (approximately 9.1mg/L at 20°C and standard pressure).

Sample Handling and Preservation

Samples must be collected and stored such that degradation or alteration of the sample is minimized. Collect sample in a clean polyethylene bottle, taking care to fill completely and cap tightly.

The samples must be unpreserved and stored at 4 ±2°C.

Stability

Samples should be analyzed as soon as possible after sampling.

It is mandatory the holding time does not exceed 72-hours from time of sampling. Results reported from samples past the holding time must be flagged as non-conforming.

Procedure

The APHA 5210 reference method describes in detail recommended protocols for reagent preparation, apparatus, calibration procedures, potential interferences, calculations, and other relationships that can affect BOD and CBOD determinations. The analyst must understand and adhere to the information contained in the reference method. The following procedural information is provided for general guidance.

Reagents:

Refer to APHA Method 5210B for preparation instructions for the following reagents:

- Phosphate buffer solution
- Magnesium Sulfate solution
- Calcium Chloride solution
- Ferric Chloride solution
- 1N H_2SO_4 and 1N NaOH
- Nitrification inhibitor (2-chloro-6-(trichloromethyl)pyridine or commercial preparation)
- glucose-glutamic acid solution (G/GA)
- Seed (natural or commercial formulation — e.g., Polyseed)
- Dilution Water:
  use water of a quality known to produce not more than 0.2mg/L oxygen demand. A water temperature of 20 ±3°C is required. Buffer with nutrients as per the reference method. Saturate with dissolved oxygen.

Apparatus:

- DO Meter
- Incubation bottles — capable of achieving an air free water seal.
- Incubator — thermostatically controlled at 20 ±2°C.
  Exclude all light from incubated samples.
- Glassware as required

Calibration:

Follow manufacturer's instructions for the calibration and maintenance of the DO meter and Probe.

Analytical Method:

The following method requirements are mandatory
(except where stated as recommended):

1. *Residual Chlorine Check*:
All samples must be tested for presence of residual chlorine (e.g., by DPD test kit) unless they are known to be non-chlorinated. Follow APHA 5210B dechlorination instructions if residual chlorine is found.

2. *pH adjustment*:
All samples must be tested for pH. If pH is greater than 8.0 or less than 6.0, adjust temperature to 20 ±3°C and adjust pH to between 6.5 and 7.5 with small quantities of dilute H_2SO_4 or dilute NaOH. All pH-adjusted samples must be seeded.

3. *Dilution Water*:
Temperature 20 ±3°C.
Nutrients: Using reagent concentrations specified in APHA 5210B, add 1mL each phosphate buffer, calcium chloride, magnesium sulfate, and ferric chloride per liter of dilution water (alternate reagent volumes and concentrations may be used if the final concentrations in the dilution water are unchanged). Aerate to saturate with oxygen. Prepare fresh daily.

4. *Seeding*:
Unless sample is known to not require seeding, seeding must be used. All chlorinated/dechlorinated samples, samples that have been pH adjusted, and samples to which nitrification inhibitor has been added must be seeded. Prepare fresh seed daily. Pre-test new seed batches to ensure seed blanks are within 0.6–1.0 mg/L.

5. *Sample Dilution*:
Most wastewater samples will have a dissolved oxygen demand greater than the available dissolved oxygen in an air-saturated sample. Therefore, dilution of the sample is necessary. Where possible, dilutions are determined using prior knowledge of the sampling site. A minimum of three different dilutions are recommended for each sample.

6. *Incubation*:
Samples must contain no trapped air and must have a water seal. The incubator must be dark and must maintain a temperature of 20 ±2°C. Samples must be incubated 5-days ±4 hours.

7. *CBOD*:
Use a suitable nitrification inhibitor.

8. *Final BOD*:
Choose results from dilutions which give a final DO reading of at least 1 mg/L and (for diluted samples only) a DO depletion of at least 2 mg/L. If more than one dilution meets these criteria, report an average result.

9. *Quality Control*:
Each batch of samples must contain a minimum of 1 dilution water blank, 1 seed blank, and 1 G/GA standard

Calculations:

$$BOD_5 \text{ mg/L} = \frac{(D_1 - D_2) - S(V_s)}{P}$$

Where:

D_1 = Initial DO of sample (mg/L)
D_2 = DO of sample after 5 days (mg/L)
P = Decimal volumetric fraction of sample used (P = 1 / Dilution Factor)
S = Oxygen uptake of seed, ΔDO/mL seed
V_s = Volume of seed in test bottle (mL)

If nitrification inhibitor is used, report as CBOD.

If all dilutions result in residual DO of < 1.0 mg/L, calculate BOD as above using the most dilute sample, but report BOD as ">" the calculated value.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Dilution water Blank	1 per batch	Less than 0.2mg/L of BOD
Seeded Method Blank	1 per batch	Between 0.6 and 1.0 mg/L greater than dilution blank
G/GA Spike	1 per batch	Between 167.5 and 228.5 mg/L
Duplicates	1 per batch	30% RPD

* Minimum DQO for duplicates applies only at levels above 10x MDL.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, Method 5210B (2001) 5-day BOD test.

b) Baird, R.B, and R.K. Smith (2002). Third Century of Biochemical Oxygen Demand, Water Environment Federation.

Revision History

July 1, 2003: Pacific Environmental Science Centre PBM method for BOD incorporated into BC Lab Manual to replace 1994 version.

October 13, 2006: Method revised into new format for prescriptive methods. Referenced to APHA 5210B. Mandatory elements of method listed.

Carbamates (N-Methyl) in Water by HPLC — PBM

Parameter

N-Methylcarbamates:
Aldicarb
Aldicarbsulfoxide
Aldicarb-sulfone
Bendiocarb
Carbofuran
Carbaryl
3-Hydroxycarbofuran
Methiocarb
Methomyl
Oxamyl
Propoxur

Analytical Method

HPLC with post column derivatization and fluorescence detection, or by LC/MS, or by LC/MS/MS.

Introduction

N-methylcarbamates are widely used as insecticides for agricultural products. Their residual concentration in such products and in water is determined by HPLC.

Method Summary

An aliquot of the water sample is extracted with dichloromethane (DCM). The raw extract is concentrated and analyzed on an HPLC equipped with a post column derivitization unit and fluorescence detector, or alternatively by LC/MS or LC/MS/MS.

Carbamates are separated on a reverse-phase liquid chromatography column, using a methanol-water gradient mobile phase. Using the post-column fluorescence method, separation is followed by post column hydrolysis to yield methylamine, and formation of a fluorophore with o-phthalaldehyde and 2-mercaptoethanol prior to fluorescence detection.

Mass spectrometric detection can offer enhanced selectivity and sensitivity and permits detection of carbamate pesticides and their derivatives that lack the n-methyl functional group, which must be present for the post-column derivatization technique.

If necessary, the raw extract is cleaned up using Supelclean ENVI-Carb SPE Tubes (0.5g, 6ml).

MDL and EMS Codes

Analyte	Approx. MDL (µg/L)	EMS Code
Aldicarb	0.5	
Aldicarbsulfoxide+Aldicarb-sulfone	0.5	
Bendiocarb	0.5	
Carbofuran	0.5	
Carbaryl	0.5	
3-Hydroxycarbofuran	0.5	
Methiocarb	0.5	
Methomyl	0.5	
Oxamyl	0.5	
Propoxur	0.5	

Matrix

Waters, including wastewaters or leachates.

Interferences and Precautions

Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

When fluorescence detection is used, fluorescent compounds, primarily alkyl amines and compounds which yield primary alkyl amines on base hydrolysis, are potential sources of interferences. Coeluting compounds that are fluorescence quenchers may result in negative interferences.

Application of the recommended cleanup technique reduces matrix interferences from complex samples, regardless of the detection technique employed.

Sample Handling and Preservation

Water samples should be collected in amber glass bottles with Teflon lined lids.

Store samples at 4 ±2°C. Samples should be stored on ice during transport to the lab and must not exceed 10°C during the first 48 hours after collection.

Due to the extreme instability of N-methylcarbamates in alkaline media, water, wastewater and leachates, samples must be preserved immediately after collection by acidifying to pH 4–5 with ChlorAC buffer (as per EPA 8318). The pH adjustment also minimizes analyte biodegradation. ***Preserve samples at time of sampling with Chloroacetic acid buffer (2 mL per litre of sample), and store at 4±2°C.***

Collection of 1L samples is recommended if the stated MDLs (0.5 µg/L) are targeted. According to APHA Method 6610B (2004), water samples are stable for at least 28 days when adjusted to ~pH4 and stored at 4°C.

Stability

Storage and Holding Time:

Preservation at time of sampling is required. Preserved samples must be extracted within 28 days of collection and analyzed within 40 days of extraction.

Procedure

Reagents:

- Solvents: DCM, Acetone, Isooctane, Hexane.
- ChlorAC Buffer: 13% chloroacetic acid / potassium acetate buffer solution. May be purchased commercially (e.g., from Pickering Laboratories, catalogue no. 1700-0132).
- Granular sodium sulfate, anhydrous, reagent grade, heat treated at 300°C.
- Glass wool, heat-treated at 300°C.
- Cellulose, Whatman CF-11.
- Hydrolysis Reagent, 0.05 M Sodium hydroxide, 4 × 950 mL.
- OPA Diluent 0.05 M sodium borate buffer solution, 4 × 950 mL.
- O-Phthalaldehyde, 5 g, chromatographic grade crystals.
- Thiofluor, 2 × 10 g chromatographic grade crystals.
- Phosphoric Acid.

Extraction:

a) Check sample pH and note in the sample extraction sheet of any abnormality.
b) Pour 800 ±10 mL of sample into a 1000 mL separatory funnel. Add preservative to any samples not previously preserved.
c) Adjust the pH of the sample to pH 3–4. Add 80 ±5 mL of DCM. Shake vigorously for one minute.
d) Allow the layers to separate and collect the DCM in a 500 mL round bottom flask after filtering through sodium sulphate supported by glass wool in a glass filter funnel.
e) Repeat the extraction step with two more aliquots of 50 mL DCM.
f) Collect all DCM and concentrate to 2–3 mL in a rotary evaporator.
g) If extract will be analyzed without the SPE cleanup, add 2 mL methanol prior to further concentration.
h) Concentrate the combined extracts to a known final volume (typically 1mL) using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator).
i) The extract is now ready for further cleanup (if necessary), or for analysis by HPLC.

ENVI — Carb SPE Cleanup (Recommended):

a) After assembling the SPE cartridge in the extraction apparatus, wash the cartridge with 30 ml of DCM, using gravity flow. Do not allow the cartridge to go dry.
b) When only a thin layer of solvent remains above the sorbent bed in the cartridge, place a 15 ml test tube under the cartridge and transfer the extracts on to the cartridge.
c) Allow the extract to pass through the cartridge under gravity flow.
d) Wash the cartridge with 5.0 ml DCM.
e) Extract is evaporated to 1mL with a gentle stream of nitrogen. Add 2 mL of Methanol into the extract; mix it well and again blow down to 1 mL.
f) Transfer the final extract to a 2 mL GC vial with Teflon lined aluminum crimp cap. The extract is now ready to be analyzed by HPLC.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance for the standard post column derivatization method:

- EPA SW846 Method 8318 “N-Methylcarbamates by high performance liquid chromatography (HPLC)”. Revision 0, 1994.

Detector conditions for LC/MS or LC/MS/MS are not provided. Numerous publications describing these techniques are available, including application notes by Agilent, Waters, and Varian.

A five-point initial calibration (four-point minimum) over the desired working range is recommended to meet the performance requirements outlined in USEPAMethod 8318. Whenever possible, the use of internal standards is strongly recommended. Internal standards can vastly improve method precision.

Samples must be bracketed by standards.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 method spikes or certified reference materials (CRMs) must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or reference materials at concentrations above ten times the MDL. Average recovery must be between 70–130% for all listed carbamates.

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 <25% for all listed carbamates.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	**Minimum Data Quality Objectives***
Method Blank	One per batch	Less than reported DL
Laboratory Control Sample (Method Spike)	One per batch	50–150%
Lab Duplicates	One per batch	40% RPD
Matrix Spike	One per batch recommended	50–150%
Continuing Calibration Verification (CCV)	Every 12 hours	80–120% for mid level std.
Control standard(ICV) — secondary source	One per batch	80–120% for mid level std

*Minimum DQOs apply to individual QC samples at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met.

Prescribed Elements

The following components of this method are mandatory:

Samples must be preserved at time of sampling by reduction of pH. Preservation must employ either chloroacetic acid buffer (as per EPA 8318) or potassium dihydrogen citrate / sodium thiosulfate (as per APHA 6610B).

All Performance Requirements and Quality Control requirements must be met as outlined in this method.

Analysis must be by HPLC with post-column derivatization and fluorescence detection, or alternatively by LC/MS or LC/MS/MS.

References

Primary Reference:

a) EPA SW846 Method 8318 “N-Methylcarbamates by high performance liquid chromatography (HPLC)”. Revision 0, 1994.

Secondary References:

a) EPA Method 531.2 (revision 1.0) “Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in water by Direct Aqueous Injection HPLC With Post Column Derivatization. (EPA #815-B-01-002, September, 2001).

b) Varian Application Note “The Determination of N-Methylcarbamate Pesticides by HPLC EPA Method 531.1”. No. 25, March 1998.

c) Eaton, A., Clesceri, L.S., Greenberg, A.E., (eds.) 2000. Standard Methods for the Examination of Water and Wastewater. Method 6610B (2004) Carbamate Pesticides, American Public Health Association, Washington DC.

Revision History

February 9, 2007: First drafted as BC PBM.

Chlorinated and Non-Chlorinated Phenols in Soil — PBM

Parameter Chlorinated Phenols, Non-Chlorinated Phenols, Nitrophenols in Soils

Analytical Method Solvent Extraction, GC/MS, LC/MS/MS, or GC-ECD for nitrophenols.

Introduction This method is applicable to the quantitative determination of chlorinated and non-chlorinated phenols in soils.

Method Summary Solvent extraction (with isotope dilution and derivatization if necessary) followed by gas chromatography / mass spectrometry (GC/MS) instrumental analysis, or by gas chromatography with electron capture detection (GC-ECD) for nitrophenols.

Isotope dilution may be used for selected compounds where adequate recovery is otherwise difficult to achieve.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDLs and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/g)	EMS Analyte Code
Non-Chlorinated Phenols			
2,4-Dimethylphenol	105-67-9	0.005–0.02	D048
2,6-Dimethylphenol	576-26-1	0.005–0.02	n/a
3,4-Dimethylphenol	95-65-8	0.005–0.02	n/a
Hydroquinone (4-Hydroxyphenol)	123-31-9	not available	n/a
2-Methylphenol (*ortho*-Cresol)	95-48-7	0.005–0.02	PH33
3-Methylphenol (*meta*-Cresol)	108-39-4	0.005–0.02	PH37
4-Methylphenol (*para*-Cresol)	106-44-5	0.005–0.02	PH37
Phenol	108-95-2	0.02–0.05	0119
Nitrophenols			
2,4-Dinitrophenol	51-28-5	0.05–0.2	D049
2-Methyl-4,6-Dinitrophenol	534-52-1	0.05–0.2	D047
2-Nitrophenol	88-75-5	0.05–0.2	N030
4-Nitrophenol	100-02-7	0.05–0.2	N031
Chlorinated Phenols			
2-Chlorophenol	95-57-8	0.005–0.02	C035
3-Chlorophenol	108-43-0	0.005–0.02	C054
4-Chlorophenol	106-48-9	0.005–0.02	C055
2,3-Dichlorophenol	576-24-9	0.005–0.02	D073
2,4-Dichlorophenol	120-83-2	0.005–0.02	D050
2,5-Dichlorophenol	583-78-8	0.005–0.02	D075
2,6-Dichlorophenol	87-65-0	0.005–0.02	D076
3,4-Dichlorophenol	95-77-2	0.005–0.02	CP07
3,5-Dichlorophenol	591-35-5	0.005–0.02	D077
4-Chloro-3-methyl phenol	59-50-7	0.005–0.02	C036
Pentachlorophenol	87-86-5	0.002–0.01	P022

Analyte	CAS No.	Approx. MDL (µg/g)	EMS Analyte Code
2,3,4,5-Tetrachlorophenol	4901-51-3	0.002–0.01	T036
2,3,4,6-Tetrachlorophenol	58-90-2	0.002–0.01	T037
2,3,5,6-Tetrachlorophenol	935-95-5	0.002–0.01	T038
2,3,4-Trichlorophenol	15950-66-0	0.002–0.01	T033
2,3,5-Trichlorophenol	933-78-8	0.002–0.01	T034
2,3,6-Trichlorophenol	933-75-5	0.002–0.01	T035
2,4,5-Trichlorophenol	95-95-4	0.002–0.01	T043
2,4,6-Trichlorophenol	88-06-2	0.002–0.01	T042
3,4,5-Trichlorophenol	609-19-8	0.002–0.01	T044
Recommended Surrogates			
2,4-Dibromophenol	615-58-7	n/a	n/a
2,4,6-Tribromophenol	118-79-6	n/a	n/a

MDLs may vary substantially depending on analytical technique.

Other phenolic substances not listed above may also be analyzed by this method, subject to validation and achievement of default DQOs for the appropriate phenolic substance category.

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

This method is applicable to the determination of chlorinated and non-chlorinated phenols in extracts prepared from soil samples.

Interferences and Precautions

a) Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

b) Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

c) Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

Sample Handling and Preservation

Container: Glass Jars with Teflon-lined lids.

Preservation: Store at ≤ 6°C.

Stability

Holding Time:

Samples: Extract within 14 days of collection.
Extracts: May be held up to 40 days from time of extraction prior to instrumental analysis if stored at ≤ 6°C.

Storage: Store samples and extracts at ≤ 6°C.

Procedure

Reagents:

a) Organics-free reagent water.
b) Solvents, distilled in glass, pesticide quality, or equivalent.
   - Acetone.
   - Dichloromethane (DCM).
   - Hexane.
   - Isooctane.
c) Sodium Sulfate (Na_2SO_4), anhydrous, purified by heating at 400°C for four hours.

Extraction:

The following instructions apply to Soxhlet extraction with DCM/acetone or hexane/acetone. Microwave and Microscale extraction and other solvents are acceptable alternatives provided the data quality objectives described in the Performance Requirements and Quality Control sections are met.

a) Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Prepare sufficient sample to yield approximately 10 g after homogenization.
b) Blend 10 g of sample with 10 g or a suitable amount of heat-treated sodium sulfate until the moisture is absorbed and the sample is free-flowing.
c) Place the mixture in an extraction thimble or between two layers of glass wool in the Soxhlet extractor.
d) Add surrogate to the samples and spike solution to the sample selected for the matrix spike.
e) If recovery corrections are required to meet Data Quality Objectives (e.g., for hydroxyphenols, phenol, or 2,4-dimethylphenol), spike each sample with deuterated isomers of each compound for purposes of isotope dilution recovery corrections.
f) Add extraction solvent (either DCM/Acetone or Hexane/Acetone) to an extraction flask, attach the flask to the Soxhlet extractor and extract the sample for approximately 16 hours.
g) Allow the extract to cool.
h) Dry the extract by passing through a drying column containing anhydrous sodium sulfate and rinse the column and flask with extract solvent to complete the quantitative transfer.
i) Add 2 mL of iso-octane to the combined extracts and concentrate using an appropriate solvent concentration apparatus (e.g., rotary evaporator or KD).
j) If derivatization is required, a number of derivatization techniques may be used, e.g., acetylation, methylation.
k) Analyze the extracts for target analytes by GC/MS or LC/MS/MS, or GC-ECD for nitrophenols.

Instrumental Analysis:
Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

- USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)”, Revision 5, July 2014.

GC/MS or LC/MS/MS must be used, except that GC-ECD may alternatively be used for nitrophenols. Selective Ion Monitoring (SIM) mode is commonly used with GC/MS to achieve lower detection limits.

A five-point initial calibration over the desired working range is required to meet the performance requirements outlined in US EPA Method 8270D (no more than one point may be excluded).

Some phenolic compounds may co-elute under the selected conditions of analysis (may vary with chromatographic column and phase, GC or LC conditions, and whether derivatization is used). For example, with a DB-5 (or equivalent) GC column, 2,4-dichlorophenol and 2,5-dichlorophenol normally co-elute when acetylated or un-derivatized. Report all co-eluting compound pairs as totals. Compare results for co-eluting pairs to the lowest standard for the two substances.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Lab Control Samples or Reference Materials must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement:
Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Average accuracy must be between 50–130% for nitrophenols (or other phenolic substances not listed in this method) and 70–130% for all chlorinated phenols and all listed non-chlorinated phenols (after isotope dilution corrections where applicable).

Precision Requirement:
Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement:
Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	All CPs and listed NCPs: 50–140% Nitrophenols: 30–130%
Lab Duplicates (DUP)	One per batch (max 20 samples)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	All CPs and listed NCPs: 50–140% Nitrophenols: 30–130%
Isotope Dilution Standards	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%.
Surrogate Compounds	All samples	50–140%
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50–200% of the initial calibration (average or mid-point) or initial CVS.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80–120%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	80–120%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Blank: *Required*.
Prepare a Method Blank using clean oven-baked sand.

Lab Duplicates: *Required*.

Laboratory Control Sample (Method Spike): Required. Prepare a Laboratory Control Sample by fortifying clean sand (+20% moisture) with known concentrations of the analytes.

Matrix Spike or Reference Material: *Required*.
Spike a duplicate sample with known concentrations of the test analytes.

Surrogate Compounds: *Required*.
Recommended compounds are 2,4-Dibromophenol and 2,4,6-Tribromophenol.

Calibration Verification Standard (CVS): *Required*.
A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): *Required*.
A mid-point calibration standard must be analyzed throughout the instrument run at least every 12 hours and at the end of the run to monitor calibration drift. A CVS may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by GC/MS, LC/MS/MS, or by GC-ECD for nitrophenols. For GC/MS at least one qualifier ion per analyte must be monitored (two recommended where possible). Initial calibrations must include at least 5 points (no more than 1 point may be excluded).

All Performance Requirements and Quality Control requirements must be met.

Isotope dilution recovery correction must be used for any listed parameters where the stated DQOs cannot routinely be met, or where the stated Accuracy Requirements cannot be met (Accuracy Requirements reflect the long-term average performance of the method). For typical solvent-extraction methods, isotope dilution is recommended for hydroxyphenols, phenol, and 2,4-dimethylphenol.

If an alternative to the Soxhlet extraction technique with DCM/acetone or hexane/acetone is utilized for extractions, laboratories must conduct and document a validation of phenolic compound extraction efficiency for the alternate method, either by a minimum of triplicate evaluations of at least one Certified Reference Material (certified for at least a representative sub-set of the test analytes), or by evaluation of at least 5 natural soil Matrix Spike samples that have been mixed and equilibrated with all test analytes (spiked in acetone) for at least 1 hour prior to extraction. All test samples (CRMs or Matrix Spikes) must contain at least 20% moisture content to be representative of typical soil samples. Accuracy DQOs from the Performance Requirements section must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are used.

References

1) US EPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)”, Revision 5, July 2014.
2) US EPA Method 3540C, “Soxhlet Extraction”, SW-846 Revision 3, December 1996.
3) US EPA Method 3541, “Automated Soxhlet Extraction”, SW-846 Update II, September 1994.
4) US EPA Method 3546, “Microwave Extraction”, SW-846 Revision 0, February 2007.
5) US EPA Method 3550C, “Ultrasonic Extraction”, SW-846 Revision 3, February 2007.
6) US EPA Method 3570, “Microscale Solvent Extraction (MSE)”, SW-846 Revision 0, November 2002.
7) US EPA Chapter 4, “Organic Analytes”, SW-846 Update V Revision 5, July 2014.

Revision History

15-Sep-2017	Consolidates and replaces several existing methods in PBM format. Updated to include additional phenolic substances listed in the 2017 CSR. GC-ECD option added for nitrophenols for improved sensitivity and detection limits. LC/MS/MS option added.

Chlorinated and Non-Chlorinated Phenols in Water — PBM

Parameter

Chlorinated (CPs), Non-Chlorinated Phenols (NCPs) and Nitrophenols in Water

Analytical Method

Methyl-tert-butyl ether (MTBE) Liquid-Liquid Extraction, with analysis by GC/MS, LC/MS/MS, or GC-ECD for Nitrophenols.

Introduction

This method is applicable to the quantitative determination of chlorinated and non-chlorinated phenols in water.

Method Summary

Method Summary:

Liquid-liquid extraction with methyl-*tert*-butyl-ether (MTBE) and dichloromethane (DCM) solvent (with isotope dilution and derivatization, if necessary) followed by gas chromatography mass spectrometry (GC/MS) or liquid chromatography with tandem mass spectrometry (LC/MS/MS). GC with electron capture detection (GC-ECD) may alternatively be used for nitrophenols.

Isotope dilution is used for selected compounds where adequate recovery is otherwise difficult to achieve.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/L)	EMS Analyte Code
Non-Chlorinated Phenols			
Catechol (2-Hydroxyphenol)	120-80-9	1–5	n/a
2,4-Dimethylphenol	105-67-9	0.1–0.5	D048
2,6-Dimethylphenol	576-26-1	0.1–0.5	n/a
3,4-Dimethylphenol	95-65-8	0.1–0.5	n/a
Hydroquinone (4-Hydroxyphenol)	123-31-9	1- 5	n/a
2-Methylphenol (*ortho*-Cresol)	95-48-7	0.1–0.5	D084
3-Methylphenol (*meta*-Cresol)	108-39-4	0.1–0.5	D085
4-Methylphenol (*para*-Cresol)	106-44-5	0.1–0.5	D086
Phenol	108-95-2	0.1–0.5	0119
Resorcinol (3-Hydroxyphenol)	108-46-3	1-5	n/a
Nitrophenols			
2,4-Dinitrophenol	51-28-5	1–10	D049
2-Methyl-4,6-Dinitrophenol	534-52-1	1–10	D047
2-Nitrophenol	88-75-5	1–10	N030
4-Nitrophenol	100-02-7	1–10	N031

Analyte	CAS No.	Approx. MDL (µg/L)	EMS Analyte Code
Chlorinated Phenols			
2-Chlorophenol	95-57-8	0.1–0.5	C035
3-Chlorophenol	108-43-0	0.1–0.5	C054
4-Chlorophenol	106-48-9	0.1–0.5	C055
4-Chloro-3-Methylphenol	59-50-7	0.1–0.5	C036
2,3-Dichlorophenol	576-24-9	0.05–0.1	D073
2,4-Dichlorophenol	120-83-2	0.05–0.1	D050
2,5-Dichlorophenol	583-78-8	0.05–0.1	D075
2,6-Dichlorophenol	87-65-0	0.05–0.1	D076
3,4-Dichlorophenol	95-77-2	0.05–0.1	CP07
3,5-Dichlorophenol	591-35-5	0.05–0.1	D077
Pentachlorophenol	87-86-5	0.05–0.1	P022
2,3,4,5-Tetrachlorophenol	4901-51-3	0.05–0.1	T036
2,3,4,6-Tetrachlorophenol	58-90-2	0.05–0.1	T037
2,3,5,6-Tetrachlorophenol	935-95-5	0.05–0.1	T038
2,3,4-Trichlorophenol	15950-66-0	0.05–0.1	T033
2,3,5-Trichlorophenol	933-78-8	0.05–0.1	T034
2,3,6-Trichlorophenol	933-75-5	0.05–0.1	T035
2,4,5-Trichlorophenol	95-95-4	0.05–0.1	T043
2,4,6-Trichlorophenol	88-06-2	0.05–0.1	T042
3,4,5-Trichlorophenol	609-19-8	0.05–0.1	T044
Recommended Surrogates			
2,4-Dibromophenol	615-58-7	n/a	n/a
2,4,6-Tribromophenol	118-79-6	n/a	n/a

MDLs may vary substantially depending on analytical technique.

Other phenolic substances not listed above may also be analyzed by this method, subject to validation and achievement of default DQOs for the appropriate phenolic substance category.

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

This method is applicable to the determination of chlorinated and non-chlorinated phenols in extracts prepared from freshwater, marine water and wastewater samples.

Interferences and Precautions

Interferences may result from contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

The decomposition of some analytes has been demonstrated under basic extraction conditions. Phenols may react to form tannates. These reactions increase with increasing pH.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

Sample Handling and Preservation

Container: 1 L amber glass bottles with Teflon® or foil-lined lid. Smaller bottles may be used (consult with laboratory).

Preservation: Preserve with sodium bisulfate or H_2SO_4 to pH < 2 to extend hold times to 14 days. In addition, 0.5 g ascorbic acid per litre of sample may be added as antioxidant, which can further stabilize some phenolics, such as chlorocatechols (Alberta Environment).

Stability

Holding Time:

Preserved Samples: Extract within 14 days of sample collection.
Unpreserved Samples: Extract within 7 days of sample collection.
Extracts: May be held up to 40 days from time of extraction prior to instrumental analysis.

Storage: Store samples and extracts at ≤ 6°C.

Procedure

Reagents:

a) Organics-free reagent water
b) Solvents, distilled in glass, pesticide grade, or equivalent:
   - Methyl-tert-butyl ether (MTBE),
   - Dichloromethane (DCM),
   - Iso-Octane.
c) Ascorbic acid.
d) Sodium bisulfate or H_2SO_4.
e) Sodium sulfate, anhydrous, reagent grade.
f) Hydrochloric acid, reagent grade.
g) Sodium chloride (NaCl), reagent grade.

Extraction:

a) Measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials and any surface film.
b) Ensure sample pH is less than 2. If necessary, adjust pH using hydrochloric acid.
c) Add a small amount of NaCl into the sample (e.g., 10 g per 1000 mL of sample) to improve extraction efficiency of water-soluble phenolics. Use of larger quantities of NaCl may further improve extraction efficiency.
d) Spike the sample with deuterated phenolic surrogates. Refer to the Quality Control section.
e) If recovery corrections are required to meet Data Quality Objectives (e.g., for hydroxyphenols, phenol, or 2,4-dimethylphenol), spike each sample with deuterated isomers of each compound for purposes of isotope dilution.
f) Add 100 mL of MTBE to the sample bottle and rinse contents into the separatory funnel. Shake vigorously for a minimum of one minute with frequent venting. Allow layers to separate and drain the MTBE (top layer) through sodium sulfate into a round bottom flask.
g) Repeat extraction two more times with 100 mL of MTBE each time.
h) Repeat extraction one more time using 50 mL of DCM. Note, however, that the DCM solvent layer will be the bottom layer.
i) Add 2 mL of iso-octane to the combined extracts and concentrate using an appropriate solvent concentration apparatus (e.g., rotary evaporator or KD).
j) Transfer the concentrated extract to a test tube and evaporate under nitrogen to 1 mL.

Optional:
Derivatization techniques, including *in-situ* derivatization (e.g., acetylation or methylation) may be used to improve chromatographic performance provided method validation and minimum Data Quality Objectives (DQO) can be demonstrated.

Instrumental Analysis:
Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

USEPA Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", Revision 4, February 2007.

GC/MS or LC/MS/MS must be used, except that GC-ECD is a permitted option for nitrophenols (recommended where low detection limits are required). Selective Ion Monitoring (SIM) mode is commonly used with GC/MS to achieve lower detection limits.

A five-point initial calibration over the desired working range (four-point minimum if an outlying calibration point must be rejected) is required to meet the performance requirements outlined in US EPA Method 8270D.

Some phenolic compounds may co-elute under the selected conditions of analysis (may vary with chromatographic column and phase, GC or LC conditions, and whether derivatization is used). For example, with a DB-5 (or equivalent) GC column, 2,4-dichlorophenol and 2,5-dichlorophenol normally co-elute when acetylated or un-derivatized. Report all co-eluting compound pairs as totals. Compare results for co-eluting pairs to the lowest standard for the two substances.

Whenever possible, the use of internal standards is recommended. Internal standards can improve method precision.

Due to their high water solubility and other issues, the isomers of hydroxyphenol, phenol, and 2,4-dimethylphenol have shown low and erratic recoveries from waters. For typical solvent extraction methods, recovery correction by the isotope dilution technique will be required in order to meet the DQO of this method for some or all of these parameters. For the isotope dilution technique, labeled deuterium isotopes of each compound are added to samples prior to sample preparation procedures, and are then used as internal standards to correct for recovery.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Specific Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Laboratory Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement:
Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Average accuracy must be between 50–130% for nitrophenols (or other phenolic substances not listed in this method) and 70–130% for all chlorinated phenols and all listed non-chlorinated phenols (after isotope dilution corrections where applicable).

Precision Requirement:
Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement:
Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max. 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max. 20 samples)	All CPs and listed NCPs: 60–130% (isotope dilution correction may be required for some compounds, e.g., hydroxyphenols, phenol, and 2,4-DMP). Nitrophenols: 30–130% recovery
Field Duplicates	Recommended, One per batch (max 20 samples) Requires 2nd bottle	50% RPD [or within 2x reported DL for low level results]
Matrix Spike	Recommended, One per batch (max. 20 samples) Requires 2nd bottle	All CPs and listed NCPs: 50–140% Nitrophenols: 30–130%
Surrogate Compounds	All samples	See LCS recovery limits

Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50–200% of the initial calibration (average or mid-point) or initial CVS
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Isotope Dilution Standards	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80–120%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	80–120%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. No corrective actions are required for field duplicate DQO exceedances.		

Method Blank: *Required*.
Minimum one per batch.

Laboratory Control Sample: *Required*.
A clean matrix spike with known amounts of all chlorinated and non-chlorinated phenols being tested must be used.

Field Duplicates: *Recommended*.

Matrix Spike: *Recommended*.
Spike a duplicate sample with known concentrations of test analytes.

Surrogate Compounds: *Required*.
At minimum, two phenolic surrogate compounds are required for each sample and quality control sample. Surrogates must be deuterium-labeled or other non-naturally occurring phenols (e.g., fluorinated or brominated phenols).

Calibration Verification Standard (CVS): *Required*.
A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): *Required*.
A mid-point calibration standard must be analyzed throughout the instrument run at least every 12 hours and at the end of the run to monitor calibration drift. A CVS may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by GC/MS or LC/MS/MS, or by GC-ECD for nitrophenols.
   For GC/MS, at least one qualifier ion per analyte must be monitored (two recommended where possible). Initial calibrations must include at least 4 points and meet the requirements of SW 846 8270D.
2. The entire contents of the sample container must be analyzed, including any accompanying suspended or settled material and any surface film that may be present. If this is not possible, the client must be contacted for direction and any method deviations must be clearly identified on the final report.
3. All Performance Requirements and Quality Control requirements must be met.
4. Isotope dilution recovery correction must be used for any listed parameters where the stated DQOs cannot routinely be met or where the stated Accuracy Requirements cannot be met (Accuracy Requirements reflect the long-term average performance of the method). For typical solvent-extraction methods, isotope dilution is recommended for hydroxyphenols, phenol, and 2,4-dimethylphenol.

Apart from these limitations and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are used.

References

a) US EPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 4, February 2007.
b) US EPA Method 3510C, “Separatory Funnel Liquid-Liquid Extraction”, Revision 3, December 1996.
c) US EPA Chapter 4, “Organic Analytes”, SW-846 Update V Revision 5, July 2014.
d) Alberta Environment, Method No. AE130.0 Chlorinated Phenolic Compounds in Bleached Kraft Mill Effluents and Receiving Waters.

Revision History

10-Jul-2017	Method revised to include additional phenolic substances from 2017 CSR Omnibus updates. GC-ECD option added for nitrophenols to improve sensitivity where required. LC/MS/MS option added. QC requirements and DQOs updated for better consistency with CCME methodology guidelines. Preservation protocols modified to make the use of ascorbic acid optional (as per CCME).
01-Oct-2013	New method added to BC Lab Manual.

Didecyldimethylammonium Chloride (DDAC) in Aqueous Samples

Parameter Didecyldimethylammonium chloride

Analytical Method Extraction, GC/NPD.

EMS Code DDAC X364

Introduction Didecyldimethylammonium chloride is a quaternary alkylammonium compound (QAC) that has gained acceptance as an anti-sapstain chemical in preference to compounds with greater toxicity to aquatic biota such as chlorophenols (or chlorophenates), copper-8-quinolinolate and 2-(thiocyano-methylthio)-benzothiazole (TCMTB). The analysis of QACs by gas chromatography involves pyrolytic conversion (in the heated injection port) to tertiary amines which are readily chromatographed and detected. Use of a nitrogen-phosphorus detector enhances analytical specificity.

Summary Samples are treated in the field with hydrochloric acid. Both sacrificial and surrogate quaternary ammonium compounds are added and the acidified sample is extracted with dichloro-methane. The extract is concentrated, a performance standard is added and the extract is made to final volume for analysis by gas chromatography using a nitrogen-phosphorus specific detector (NPD).

MDL Typical: 0.025 mg/L

Matrix Fresh water, wastewater, marine water.

Interferences and Precautions Any compound that co-extracts, co-elutes under the analytical conditions and causes a response on the nitrogen-phosphorus detector may interfere. The use of a sacrificial quaternary alkylammonium compound is advised due to the tendency for DDAC to adsorb onto glass surfaces (especially rough or scratched surfaces) during the analysis.

Sample Handling and Preservation

Sample container: Amber glass bottle, 0.5L or larger with a Teflon-lined cap.

Preservation: 2mL 6N HCl per L sample.

Stability

Holding time: Acidified samples stored in amber glass bottles for up to three weeks showed negligible degradation.

Storage: Store acidified at 4°C until analyzed.

Principle or Procedure DDAC is isolated from the sample matrix by liquid/liquid extraction using dichloromethane under acidic conditions. The concentrated extract is analyzed by capillary column gas chromatography with a nitrogen-phosphorus detector, utilizing the fact that DDAC quantitatively degrades to didecyldimethylamine in the heated injection port.

Precision Synthetic samples spiked at 0.100 mg/L had a COV of 1.1%.

Authentic samples spiked at 0.100 mg/L had a COV of 3.8%.

Accuracy Synthetic samples spiked at 0.100 mg/L;

average recovery = 99%.

Authentic samples spiked at 0.100 mg/l;

average recovery = 110%.

Quality Control	Blanks: 1 per batch (10%).
	Spikes: 1 per batch (10%).
	Surrogate: 25 µg Didodecyldimethylammonium chloride added to each sample.
	Performance standard: Cetyltrimethylammonium chloride added at a concentration of 5.0 µg/mL in the final extract.
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual.
	December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

Diisopropanolamine (DIPA) in Water and Soil Samples by HPLC — PBM

Parameter

Diisopropanolamine (DIPA) in Water and Soil

Analytical Method

High Performance Liquid Chromatography with UV or Fluorescence Detection.

Introduction

DIPA is a secondary alkanolamine which is a hygroscopic polar solvent that is completely miscible in water. DIPA has a wide variety of applications such as a solvent used in the Sulfinol process by the petroleum industry to remove acid gases from natural gas streams through chemical absorption. The neutralizing capacity of DIPA salts, their high foaming properties and low level of skin irritation allow them to be commonly used as components of cosmetics, personal care products and detergents (CCME 2006).

Method Summary

This method uses a derivatization step which transforms mono and diethanolamines into products with strong UV absorbance and fluorescence properties by reaction with 9-fluorenylmethyloxycarbonyl (FMOC-CL). The derivatized products are injected directly into an HPLC system with separation on an octadecylsilyl (C18) column and using UV or fluorescence detection.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS Number	Approx. MDL	EMS Analyte Code
Diisopropanolamine (DIPA)	110-97-4	100 µg/L (waters) 0.10 mg/kg (soils)	defined on request

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil: Soil, sediment, sludge, solid waste.

Water: Freshwater, seawater, groundwater, wastewater.

Interferences and Precautions

Solvents, reagents, glassware and other sample processing materials must be demonstrated to be free from interferences by analysis of a method blank.

Any UV absorptive or fluorescent compound with similar retention time to FMOC-CL derivatized DIPA (including unknown FMOC-CL derivatives within a sample) can be a potential interference by this method. Retention time alone does not constitute definitive proof of chemical identity by this method. If interference is suspected, analysis by an alternate HPLC column or using mass spectrometric detection is recommended for confirmation.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system, and should take appropriate steps to prevent the occurrence of false positives.

Sample Handling and Preservation

Sample Containers:

Water Samples: Collect water samples in Polypropylene (PP), Polyethylene Terephthalate (PET), High-Density Polyethylene (HDPE), or amber glass bottles with Teflon-lined lid. Consult the laboratory for sample volume requirements.

Soil Samples: Collect soil samples in glass jars with a Teflon-lined lids. 125 mL or 250 mL soil jars containing at least 50 g of soil are recommended.

Preservation:

Water Samples: No chemical preservation is required. Samples may be preserved with $NaHSO_4$ or HCl to pH <2 to extend hold times (200 mg solid $NaHSO_4$ per 40 mL sample is recommended).

Soil Samples: No chemical preservation is used.

Stability

Holding Time: DIPA is known to biodegrade under aerobic conditions when sufficient concentrations of nutrients are present. Rates of biodegradation are expected to slow at reduced temperature.

Water Samples: Extract unpreserved samples within 7 days from date of sampling. Acid preservation extends hold times to 14 days from sampling. Sample extracts may be analyzed up to 40 days after date of extraction if extracts are acidified or exchanged to an organic solvent to halt biodegradation.

Soil Samples: Extract soil samples within 14 days from date of sampling. Sample extracts may be analyzed up to 40 days after date of extraction if extracts are acidified or exchanged to an organic solvent to halt biodegradation.

Storage: Sample temperature should be chilled to ≤ 10°C immediately after sampling and during transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C. Avoid freezing to prevent sample breakage.

Procedure

Borate Buffer Preparation:

Prepare a solution of 19.108 g $Na_2B_4O_7 \cdot 10H_2O$ in 1 L of water, and a second solution of 12.404 g H_3BO_3 and 9.925 g NaCl in 1 L of water. Mix equal volumes of the two solutions and adjust to pH 9.5 using 20% NaOH.

Derivatization Reagent Preparation:

Prepare 2.5 mmol FMOC-Cl solution in acetonitrile. Store FMOC-CL solution in a freezer at ≤ -10°C. Shelf life is one year.

Water Samples:

Filter a small portion of as-received water sample into a 10 mL test tube using a syringe and 0.45 um syringe filter. To facilitate derivatization, check or adjust sample pH such that it is >6 (add a minimum volume NaOH if necessary to avoid dilution of sample). Using a pipette, transfer 0.50 mL of the filtered sample into a 1–2 mL vial for derivatization and analysis (e.g., PTFE filter vial).

Solids Extraction:

Accurately weigh approximately 10 g of well-mixed soil (avoiding large stones or non-representative material) into a cellulose thimble, and transfer to clean Soxhlet or Dean Stark extraction glassware. Add 100 mL of 0.01 N HCl, and reflux for a minimum 1-hour period, beginning when the solvent begins to boil. Cool and filter a portion of the extract into a 10 mL test tube using a syringe and 0.45 um syringe filter. To facilitate derivatization, adjust extract pH such that it is >6 (add a minimum volume of NaOH to avoid dilution of extract). Using a pipette, transfer 0.50 mL of the

filtered sample extract into a 1–2 mL vial for derivatization and analysis (e.g., PTFE filter vial).

Derivatization and Analysis:

Add 25 µL of borate buffer for every 0.5 mL of sample, add 100 µL of FMOC-CL derivatization agent of every 0.5 mL of sample. Incubate the vials under low heat for about 30 minutes.

After incubation, remove the filter vial caps and add 10 µL of 30% HCl for every 0.5 mL of sample, vortex and analyze the samples by HPLC-UV using an octadecylsilyl (C18) reverse phase column.

Calibration standards must be derivatized using the same procedure.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirements: Laboratories must demonstrate method accuracy (measured as average recovery) of 80–120% or better for Lab Control Samples or Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Initial Validation Requirement for Alternative Extraction Methods (Soils): For soils using alternative extraction methods to the technique described here, prepare and analyze DIPA Matrix Spike samples on a minimum of three different predominantly clay-matrix soil samples (each conducted in triplicate) to validate effectiveness of the extraction technique on samples with high cation exchange potential. Matrix Spikes must be equilibrated with soil sub-samples for at least 12 hours prior to initiating the extraction process. Average DIPA recoveries for the three or more samples evaluated must be 70–130% for this performance verification.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Surrogate Compounds	Recommended	Not specified
Calibration Verification Standard (CVS) — 2nd source	1 per initial calibration	80–120%

Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	70–130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60–140%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80–120% for mid-level standards
*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

All stated Performance Requirements and Quality Control requirements must be met.

Where samples or extracts require filtration or any pre-extraction cleanup, QC samples must be processed in the same manner.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

CCME 2006. Canadian Environmental Quality Guidelines for Diisopropanolamine (DIPA): Water and Soil, Scientific Supporting Document, PN 1367, Canadian Council of Ministers of the Environment, 2006.

AE 2010. Soil and Groundwater Remediation Guidelines for Monoethanolamine and Diethanolamine, Alberta Environment, Dec 2010.

CCME 2016. Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 4 Analytical Methods, PN 1557, Canadian Council of Ministers of the Environment, 2016.

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.

Diquat and Paraquat in Water by HPLC — PBM

Parameter

Diquat
Paraquat

Analytical Method

Extraction and HPLC/UV.

Introduction

This method is for the determination of Diquat (1,1-ethylene-2,2-bipyridilium dibromide salt) and Paraquat (1,1-dimethyl-4,4-bipyridilium dichloride salt) in water and drinking water.

Method Summary

An aliquot of the water sample is pH adjusted to between 7.0 and 9.0. The target organic compounds in the water sample are extracted using a prepared C_8 or C_{18} solid sorbent cartridge by reversed-phase / ion-pair Solid Phase Extraction (SPE). The target compounds are then extracted from the C_8 or C_{18} cartridge by elution with an acidic aqueous solvent. The eluate is then injected into a HPLC system where the diquat and paraquat are separated. Quantification is achieved by measuring absorbance at 308 nm and 257 nm, respectively. A photodiode detector is utilized to provide simultaneous detection and confirmation of the analytes.

MDL and EMS Codes

Analyte	Approx. MDL (mg/L)	EMS Code
Diquat	0.005	
Paraquat	0.005	

Matrix

Fresh water, wastewater, drinking water.

Interferences and Precautions

1. Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis. All glassware must be silanized and scrupulously cleaned.
2. Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

Sample Handling and Preservation

Water samples should be collected in 1L amber plastic bottles with Teflon lined lids. If amber bottles are not available, protect the samples from light. Samples are preserved by adding 100 mg/L sodium thiosulfate in the field to remove residual chlorine.

Samples must also be iced or refrigerated at 4 ±2°C from the time of collection until storage.

Stability

Holding and Storage Time and Particulars:

The US-EPA stipulates water samples are stable for at least 7 days when kept at 4 ±2°C.

The water samples must be extracted within 7 days of collection and analyzed within 21 days of extraction.

Procedure

Reagents

1. Methanol, CH3OH: HPLC grade
2. **I**sopropanol (Isopropyl alcohol (IPA)), $(CH_3)_2CHOH$
3. Orthophosphoric acid, 85% (w/v) — reagent grade
4. Sodium Hydroxide — reagent grade
5. Cetyl Trimethyl Ammonium Bromide, 95%
6. 1-Hexanesulfonic Acid, sodium salt, 98%
7. Ammonium Hydroxide, Conc.

Conditioning Solution A. Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5ml of concentrated ammonium hydroxide in 500 ml of deionized water and dilute to 1000 ml in volumetric flask.

Conditioning Solution B. Dissolve 20 g of 1-hexanesulfonic acid, sodium salt and 20 ml of concentrated ammonium hydroxide in 500 ml of deionized water and dilute to 1000 ml in a volumetric flask.

Cartridge eluting solution. Add 13.5 ml of orthophosphoric acid and 10.3 ml of diethylamine to 500 ml if deionized water and dilute to 1000ml in a volumetric flask.

Ion-pair concentrate. Dissolve 3.75 g of 1-hexanesulfonic acid in 15ml of the cartridge eluting solution and dilute to 25 ml in a volumetric flask with cartridge eluting solution.

Silanize solution — Sigmacote.

Extraction

Let samples warm-up to room temperature.

Adjust pH to between 7.0 and 9.0 using 10% NaOH or 10%HCl. For samples with very low pH (e.g., leachate sample) use 30% NaOH.

Pour off sample into a 250 ml HDPE (High Density Polyethylene) plastic bottle and centrifuge for 5 minutes to settle any flocculated material.

Transfer approximately 200 mls of sample into 250 ml graduated cylinder or into a 250 ml HDPE (High Density Polyethylene) plastic bottle.

Run sample through conditioned SPE column never letting sample level get below the top of the C_8 or C_{18} cartridge.

Place C_8 or C_{18} cartridge into 10 ml graduated flat-bottomed Mailing Tube.

Add 4ml eluting solution to cartridge and 100 µL ion-pair solution to the Mailing Tube and wait for about 10 minutes.

If C_8 or C_{18} cartridge does not drip apply a vacuum. Eluting speed is about 2 ml per minutes.

When solution has finished dripping make up final volume of graduated 10ml flat-bottomed plastic tube to 5 ml final volume.

Using a 0.45u or 0.20u syringe filter, filter the sample and place in a polypropylene snap ring vial and cap.

SPE Column Conditioning: Run the following solvents into the SPE apparatus in the sequence indicated.

Apply low vacuum (1–2" Hg) immediately after adding the first solvent (IPA) and maintain the vacuum throughout the conditioning sequence.

When the level of one solution is just above the top surface of the C_8 or C_{18} cartridge add the next solution. ***Do not allow any air to pass through the disk or to reach the top surface of the C_8 or C_{18} cartridge.*** Vacuum should be sufficient to draw a 2–3 ml per minute's continuous flow.

Instrumental Analysis

Instrument: High Performance Liquid Chromatography

Detector: Diode Array

Guard Column: C_8 or C_{18} — 4mm L × 3.0 mm ID

Primary Column: C_8 or C_{18} — 25cm L × 4.6 mm ID

Column Temperature: 40°C

Flow Rate: 1 mL/min

Mobile Phase A: 13.5 ml of orthophosphoric acid, 10.3 ml of diethyamine

, 3.0 g of 1-hexanesulfonic acid, sodium salt to 500 ml of RODI water.
Mix and dilute with RODI water to a final volume of 1 litre,
filter through 0.2 um 47 mm Nylon Membrane filter.

Mobile Phase B: Methanol

Injection Volume: 100 μL

Wavelength Range: 257/308 nm

Sample Rate: 1 scan / sec

Wavelength Step: 1 nm

Integration Time: 1 sec

Whenever possible, the use of internal standards is strongly recommended. Internal standards can vastly improve method precision.

In the absence of internal standards, samples must be bracketed by standards and pass performance criteria.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement:
Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or reference materials at concentrations above ten times the MDL. Average recovery must be between 70–130% for Diquat and Paraquat.

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 <20% for Diquat and Paraquat.

Sensitivity Requirement:
Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Method Spike	One per batch	40–120%
Lab Duplicates	One per batch	40% RPD
Continuing Calibration Verification (CCV)	Every 12 hours	80–120% for mid level std.
Control standard(ICV) — secondary source	One per batch	80–120% for mid level std

Prescribed Elements

The following components of this method are mandatory:

a) Analysis by HPLC using Diode Array or MS detection is required.

b) All Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

Primary Reference:

a) EPA Method 549.2 (Revision 1.0 June 1997), Determination Of Diquat and Paraquat In Drinking Water By Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection.

Revision History

31-Jul-2008: First drafted as BC PBM.

Ethinylestradiol, 17α-(EE2) in Water by LC/MS/MS — PBM

Parameter

17α-ethinylestradiol (EE2) in water, dissolved or total

Analytical Method

Analysis by Liquid Chromatography tandem-mass spectrometry (LC-MS/MS)

Introduction

17α-ethinylestradiol (EE2) is a synthetic hormone and a derivative of estradiol, the major endogenous estrogen in humans. Used in almost all formulations of birth control pills, it has become ubiquitous in the environment due to its resistance to degradation and tendency to accumulate in organic matter. EE2 is an endocrine disrupting compound (EDC).

This method is applicable to the quantitative determination of EE2 and other endocrine disruptors such as 17β-estradiol and bisphenol A in water.

BC CSR standards for EE2 are applicable to the dissolved fraction of EE2 in water; however, the BC Water Quality Guidelines for EE2 are applicable to total EE2 in water. Different analytical procedures are required for dissolved or total EE2, as outlined in the procedure.

Method Summary

For Dissolved EE2, Centrifugation is used to remove suspended particulate (filtration is not permitted due to the potential for extraction of EE2 by the filtration process). Samples are acidified with sulfuric acid, passed through a C18-based solid phase extraction (SPE) column, and eluted with a polar solvent such as acetonitrile.

For Total EE2, SPE may be utilized to extract and elute both the dissolved and particulate fraction of a sample (for up to approximately 1% solids), or the particulate fraction may be separated by filtration or centrifugation and extracted separately, with extracts or final test results combined to determine the total EE2 concentration in the sample.

An internal standard is added to the extract, which is analyzed by LC-MS/MS.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/L)	EMS Analyte Code
17α-ethinylestradiol	57-63-3	0.0005	defined on request

EMS Method Code(s)

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Freshwater, groundwater, seawater, wastewater.

Method Limitations

EE2 has a relatively high octanol/water partition coefficient (Kow ≈ 4). Therefore, it binds rapidly to organic matter. Samples to be analyzed for dissolved EE2 must not be filtered prior to analysis as this may result in a low bias.

EE2 has a solubility of approximately 9 mg/L in water at room temperature. Solubility decreases as ionic strength increases. Therefore, this method is not suitable for EE2 concentrations above the solubility limit.

Interferences and Precautions

Contamination from personal care products and medications used by laboratory staff is possible, therefore it is important to take precautions to avoid contamination of the samples, e.g., wear protective gloves and clothing.

All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by DI water. Glassware can be heated in a muffle furnace at 400ºC for two hours or solvent rinsed.

Solid phase extraction media may be a source of interferences. The analysis of method blanks can provide important information regarding the presence or absence of such interferences. Each brand and lot of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system and should take appropriate steps to prevent the occurrence of false positives.

Sample Handling and Preservation

Sample Containers: Collect samples in clean amber glass containers with PTFE-lined caps (consult laboratory for volume requirements; 1L is typical).

Preservation: Chlorinated samples must be preserved with sodium thiosulfate (~80 mg/L is recommended, to neutralize up to ~15 mg/L of free chlorine), or with ascorbic acid (~50 mg/L). No preservation is required for non-chlorinated samples, however addition of 2-mercaptopyridine-1-oxide, sodium salt (~65 mg/L) is recommended as an antimicrobial preservative to extend hold times. Protect from light (Ref: EPA 539 & EPA-820-R-10-008).

Stability

Holding Time: Samples should be extracted as soon as possible, but must be extracted within 7 days, or within 28 days if preserved with 2-mercaptopyridine-1-oxide. Extracts must be analyzed within 30 days after extraction (Ref: EPA 539 & EPA-820-R-10-008).

Storage: Sample temperature should be chilled to ≤ 10°C immediately after sampling and during transit to the laboratory. In the laboratory, samples and extracts must be refrigerated at ≤ 6°C. Avoid freezing of samples to prevent sample breakage. Storage of extracts at ≤ -10°C is recommended. Samples and extracts must be protected from light until analysis (EE2 is subject to photodegradation).

Procedure

Sample Preparation for Dissolved EE2 Analysis:

If Dissolved EE2 analysis is required, centrifuge any samples with visibly evident turbidity (~ 10 NTU) to physically separate suspended particulate matter prior to analysis of the clarified supernate (do not filter). All samples may optionally be centrifuged, which may be necessary for direct injection methods.

Sample Preparation for Total EE2 Analysis:

If Total EE2 analysis is required, shake samples well prior to sub-sampling. If the amount of particulate matter is low enough to prevent clogging of the SPE cartridge, (labs may establish a suitable limit, which may not exceed 1% by estimation), then a representative portion of the sample is extracted in total by SPE, using the elution solvent to extract the particulate fraction. For samples with higher levels of particulate matter, separate the particulate matter from the aqueous phase by filtration (with a glass fiber filter) or centrifugation, with particulate matter extracted separately by Soxhlet or an alternative solvent extraction technique. The dissolved and particulate fractions may be combined prior to analysis, or may be analyzed separately with the results combined to determine total EE2 concentration in the sample. Refer to EPA Methods 1694 or 1698 for further guidance.

Sample Extraction by SPE:

Fortify samples with a surrogate and pass them through solid phase extraction (SPE) disks containing octadecyl (C18) functional groups to extract EE2 and surrogate. Test analytes are eluted from the solid phase with a small amount of methanol. The extract is concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1 mL volume with 50:50 methanol:water after addition of internal standards.

Instrumental Analysis:

Transfer a portion of the reconstituted extract to an auto-sampler vial. Analysis by direct injection LC/MS/MS (GC-MS/MS is also acceptable, but derivatization is necessary to improve stability).

Initial calibrations must be five points or more (no more than one outlying point may be excluded). Stored calibrations may be used until the Calibration Verification Standard fails to meet acceptance criteria.

Refer to EPA 539 for detailed operating conditions suitable for this test. General guidance is provided as follows:

HPLC Parameters:

Mobile Phase A: methanol

Mobile Phase B: ammonium hydroxide (0.2%)

Flow Rate: 0.2 mL/min

Injection Volume: 50 µL

Column Temperature: 35°C

Column: C18, 2.1 × 150 mm, 3.5 µm

MS/MS Parameters:

Sample Introduction: Electrospray ionization (ESI)

Polarity: Negative

Capillary Voltage: 3 kV

Source Temperature: 120°C

Desolvation Gas Temperature: 350°C

Desolvation Gas Flow: 15 L/min

Cone gas Flow: 0.8 L/min

Extractor Lens: 2 V

RF Lens: 0.1 V

MRM Transitions:

17α-ethinylestradiol: 295.1 → 144.7

17α-ethinylestradiol-d4 (surrogate): 299 → 144.7

^{13}C2-Ethynylestradiol (internal standard): 297 → 144.7

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80–120% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The

method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Internal Standard Area Checks	All samples and QC	Peak area counts for all internal standards in all injections must be 50–150% of the initial calibration (average or mid-point) or initial CVS (Ref: EPA 539)
Surrogate Compounds	All samples and QC	70–130%
Calibration Verification Standard (CVS) — 2nd source	1 per initial calibration	85–115% recovery
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	70–130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60–140%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80–120% recovery for mid-level standards
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements The following components of this method are mandatory:

Tandem mass spectrometry is required to achieve sensitivity and selectivity objectives (LC/MS/MS or GC/MS/MS). At least two MRM transitions are required to be monitored. Labs must define appropriate criteria for confirmation of analyte identity by secondary transitions.

A suitable surrogate (Ethynylestradiol-d4 is recommended) is required to be added to all samples and QC prior to analysis. If solid phase extraction (or alternate extraction technique) is utilized, the surrogate must be added prior to extraction.

An internal standard, e.g., ^{13}C2-Ethynylestradiol, is required to be added to all samples prior to analysis.

Test results for EE2 must clearly indicate whether they are applicable to Total or Dissolved EE2 concentrations. Sample preparation procedures prior to Dissolved and Total EE2 analysis must be followed as described.

Stated calibration requirements must be met. Calibration standards must be solvent-matched with samples unless equivalency is demonstrated.

If this method is utilized for seawaters or brine samples, method validation for that matrix must be conducted prior to use using Matrix Spikes and/or Reference Materials.

All stated Performance Requirements and Quality Control requirements must be met.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

EPA Method 539, Determination of Hormones in Drinking Water by Solid Phase Extraction (SPE) and Liquid Chromatography Electrospray Ionization Tandem Mass Spectrometry (LC-ESI-MS/MS), United States Environmental Protection Agency Office of Water, November 2010.

EPA Method 1694, Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS, United States Environmental Protection Agency Office of Water, December 2007.

EPA Method 1698, Steroids and Hormones in Water, Soil, Sediment, and Biosolids by HRGC/HRMS, United States Environmental Protection Agency Office of Water, December 2007.

BC MOE Water Quality Guidelines for Pharmaceutically Active Compounds (PhACs), 17α-ethinylestradiol (EE2), Technical Appendix, British Columbia Ministry of Environment, September 2009.

EPA-820-R-10-008, Stability of Pharmaceuticals, Personal Care Products, Steroids, and Hormones in Aqueous Samples, POTW Effluents, and Biosolids, United States Environmental Protection Agency Office of Water, September 2010.

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.

Extractable Hydrocarbons, Total (C_{10}–C_{30}) in Water by GC/FID

Parameters

Total Extractable Hydrocarbons (nC_{10}–nC_{30}) (TEH_{10-30}) in water

Analyte Symbols and EMS Codes*

Analyte Symbol Code*	Approx MDL	EMS Analyte Code*	EMS Method
TEH_{10-30}	250 µg/L	H109	EPH3

* Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Analytical Method

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

Method Summary

Total Extractable Hydrocarbons (nC_{10}–nC_{30}) in water is analyzed and calculated using the BC ENV method for Extractable Petroleum Hydrocarbons in water but using a hydrocarbon range of nC_{10}–nC_{30} instead of nC_{10}–nC_{32}. The hydrocarbon range of nC_{10}–nC_{30} for this method has been selected to maintain consistency with legacy definitions of TEH, which were in use prior to the adoption of the BC EPH method. Silica gel cleanup is not conducted with this method.

This method for TEH_{10-30} is Director-authorized and intended for use in support of the BC Petroleum Storage and Distribution Facilities Storm Water Regulation. This method is deemed equivalent to US EPA SW-846 method 3510/8000A (utilizing extraction with methylene chloride) but has been updated to utilize current BC industry standard methods for analysis of extractable hydrocarbons in water using hexane micro-extraction techniques, to reduce the use of chlorinated solvents in environmental testing laboratories, improving health, safety, and environmental impacts of testing.

Matrix

Fresh water, wastewater, seawater.

Procedure

Calculate TEH_{10-30} as follows:

$TEH_{10-30} = EPH_{w10-19} + EPH_{w19-30}$

Where:

EPH_{w10-19} is analyzed by the EPHw test method.

EPH_{w19-30} is analyzed by the EPHw test method as per EPH_{w19-32} but using peak area integrations beginning at the apex of the nC_{19} peak and ending at the apex of nC_{30}.

Refer to the BC ENV Lab Manual method for Extractable Petroleum Hydrocarbons (EPH) in Water by GC/FID for all specific details and requirements of the test method.

Revision History

Dec 20, 2019	Method revised to use current BC ENV industry standard EPHw hexane micro-extraction method (as per EPH_{w10-19} and EPH_{w19-32}), for standardization, and to reduce health, safety, and environmental impacts of testing. Legacy DCM extraction method is no longer in effect.
Dec 31, 2000	SEAM codes replaced by EMS codes. Note that Freon extraction methods now deleted.
Feb 14, 1994	Publication in 1994 Laboratory Manual (DCM extraction).

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

Parameters

Extractable Petroleum Hydrocarbons (nC_{10}–nC_{19}) in water

Extractable Petroleum Hydrocarbons (nC_{19}–nC_{32}) in water

Analyte Symbols and EMS Codes

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

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Analytical Method

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

Introduction

This method measures the aggregate concentration of Extractable Petroleum Hydrocarbons (EPH) in water, divided into two boiling point ranges, each quantitated against eicosane (nC_{20}). EPH_{w10-19} measures hydrocarbons that elute between nC_{10} and nC_{19} (b.pt. range of ~ 174–330˚C). EPH_{w19-32} measures hydrocarbons that elute between nC_{19} and nC_{32} (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 ~ nC_{10}–nC_{32} (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 nC_{32} are not captured by EPH.

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

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

Method Summary

Water samples are extracted using hexane directly from within the original sample container. A single extraction using a small volume of hexane is conducted using vigorous mechanical agitation. Modified procedures are provided for circumstances where the standard extraction procedure may be ineffective (samples with high solids, or with observed presence of Non-Aqueous Phase Liquids (NAPL), either light (LNAPL) or dense (DNAPL). A quantitative portion of the hexane extract is concentrated by evaporation if necessary to

achieve detection limit requirements and is analyzed by capillary column gas chromatography with flame ionization detection.

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

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

Matrix

Fresh water, wastewater, seawater.

Interferences and Precautions

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

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

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

Sample Handling and Preservation

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

Preservation with ~ 1 gram / 250 mL sample with Sodium Bisulfate ($NaHSO_4$) or with HCl or H_2SO_4 (to pH ≤ 2) is recommended.

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

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

Stability

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

Storage Conditions: Store samples at ≤ 10˚C during shipment to lab, and at ≤ 6˚C at the laboratory. Store extracts refrigerated or in a freezer at ≤ 6˚C.

Sample Inspection and Selection of Appropriate Procedure

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

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

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

Standard Micro-Extraction Procedure

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

If sample was preserved, add NaOH or KOH solution to neutralize the acidity of the preservative (e.g., add ~1.5 mL of 6N NaOH or equivalent per 1 gram of sodium bisulfate). If PAHs will be concurrently extracted, it is recommended that pH is verified to be ≥ 7 to ensure that ionizable nitrogen-containing PAHs like acridine and quinoline are in their neutral (solvent extractable) forms, to prevent the necessity for re-extractions in case N-PAH surrogate recoveries do meet meet acceptance criteria. Do not routinely add excess base if not necessary, because high hydroxide ion concentrations can cause emulsions in some samples. Adjustment of pH is optional if PAHs will not be concurrently extracted and analyzed.

Add at least one surrogate compound to all samples and QC samples by addition of a 100% acetone surrogate solution. Surrogates highlight possible problems with analyses or with the extraction process (e.g., due to emulsions or excessive sediment loads). Use of a volatile surrogate that elutes slightly earlier than nC_{10} (e.g., 2-methylnonane or 2-bromobenzotrifluoride) is required as a check for evaporative losses if extract concentration steps are applied.

Add an exact amount of hexane extraction solvent into the original sample container (mixtures of hexane isomers or n-hexane are allowed). The amount of hexane extraction solvent used must be within a ratio of 20:1 to 30:1 for sample volume to hexane volume. Cap the vessel tightly to ensure no leakage occurs during extraction.

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

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

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

Modified Extraction Procedure for Samples Containing NAPL

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

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

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

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

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

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

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

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

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

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

Modified Extraction Procedure for Samples With High Solids

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

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

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

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

Determine the volume of hexane to be used for extraction of the solids, which should be approximately equal to the estimated volume of the solids (more hexane may be used if necessary). Accurately add the determined volume of hexane extraction solvent to the solids portion of the sample, in its original

sample container. Cap the vessel tightly to ensure no leakage during extraction. Record the volume of hexane used for extraction of the solids portion.

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

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

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

High Solids Method Example:

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

Water Portion: ~ 234 mL of water was extracted with 10.0 mL hexane.

Solids Portion: ~ 26 mL of wet solids was extracted with 30.0 mL of hexane.

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

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

Sample Volume (Vol): 260 mL

Final Volume of extract (FV): 40.0 mL

Extract Concentration Factor, post-extraction (ECF): 10.0 (unitless)

GC-FID Analysis

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

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

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

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

Example GC-FID Conditions

The following GC-FID conditions are provided as an example only. Any conditions that can baseline resolve the solvent peak from nC_{10} and that meet

specified QC and relative response requirements are acceptable. GC phase type must be 100% dimethylpolysiloxane.

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

Standards

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

Calibration Standard Stock Solution

Prepare or purchase a Calibration Standard Stock Solution containing decane (nC_{10}), nonadecane (nC_{19}), eicosane (nC_{20}), and dotriacontane (nC_{32}). 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 (nC_{10}), nonadecane (nC_{19}), eicosane (nC_{20}), dotriacontane (nC_{32}), 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 (nC_{20}) in hexane at 50 µg/mL or near the mid-point of the calibration. The CVS must be prepared from a source independent from the Calibration Standard.

Diesel / Motor Oil (DMO) Stock Solution

Prepare a stock solution of 1:1 diesel #2 : motor oil (non-synthetic SAE30 or 10W30) in hexane by weight (e.g., weigh 1.25 g of diesel #2 and 1.25 g motor oil into a 25 mL volumetric flask to make a 100,000 mg/L solution). Record the source of the diesel and motor oil used. Retain additional quantities of these spiking materials for future use, because new target concentrations must be determined whenever new sources are used.

Note that the nominal concentration of diesel + motor oil (i.e., the weight/volume of diesel + motor oil) is not exactly equal to the concentration of EPH_{w10-19} + EPH_{w19-32} (the nominal concentration may be higher).

Diesel / Motor Oil (DMO) Spiking Solution

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

Detection Limit Check Standard

Dilute the DMO Stock Solution to prepare a Detection Limit (DL) Check Standard in hexane. Prepare the standard at a concentration that is approximately equal to the extract concentration that corresponds to the Reported Detection Limits for EPH_{w10-19} and EPH_{w19-32}. This standard is required for Initial Calibration QC.

Quality Control

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

Summary of EPHw QC and Calibration Requirements		
QC Component	**Minimum Frequency**	**Data Quality Objectives***
Instrument Performance QC		
Instrument Performance Check	Daily at beginning of each analysis batch, repeated at least every 24 hours.	Relative response ratios must be 0.7–1.3 for nC_{10}/nC_{20} and nC_{32}/nC_{20}. nC_{10}, nC_{19}, nC_{32} retention times ±0.2 mins of initial calibration
Calibration QC and Verification		
RSD of nC_{20} 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	nC_{20} within 15% of initial calibration. nC_{10}, nC_{19}, nC_{32} retention times ±0.2 mins of initial calibration.
Method QC		
Method Blank	1 per 20 samples (1 per batch minimum)	< Reported Detection Limit.
Laboratory Control Sample (Diesel/Motor Oil Method Spike)	1 per 20 samples (1 per batch minimum)	70–130% recovery.
Laboratory Duplicates	Not applicable due to whole sample analysis	Not applicable.
Surrogates	add to every sample	60–140%.**

Field QC		
Field Duplicates	Recommended	Not specified.

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

** Surrogate DQOs do not apply when samples contain high levels of hydrocarbons that interfere with the measurement of the surrogate. Non-measureable surrogate recoveries due to interference does not indicate a data quality issue.

Instrument Performance QC

Instrument Performance Check

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

Measure and control relative response ratios of EPH components,

Determine retention time windows for EPH integration ranges, and

Confirm resolution of decane (nC_{10}) 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 nC_{10}/nC_{20} and for nC_{32}/nC_{20}, 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 nC_{10}, nC_{19}, and nC_{32} retention time markers. After each initial calibration, update retention times used for EPH_{w10-19} and EPH_{w19-32} integrations if new retention times differ significantly from last update (e.g., by more than 0.05 minutes for the example GC program).

Within a run, confirm that nC_{10}, nC_{19}, and nC_{32} retention times are stable. Establish lab-specific acceptance criteria for allowable retention time drift, up to a maximum deviation of ±0.2 minutes from retention times of the initial calibration. Substantial retention time drifting normally indicates a GC inlet leak, which requires correction and re-analysis of affected samples.

Calibration QC

Instrument Blank (IB)

REQUIRED. Minimum 1 per initial calibration and every 24 hours. Inject a solvent blank to the GC system using the injection solvent (e.g., hexane) to establish the chromatographic baseline and to ensure its suitability. Compute an effective Instrument Blank concentration from its absolute EPH fraction areas using typical sample calculation factors. The resulting EPH concentrations for the IB must be below 2x the Reporting Detection Limit. Instrument Blank EPH fraction areas may then be subtracted from corresponding sample EPH fraction areas as described in the Calibration & Analysis Procedure.

Calibration Verification Standard (CVS)

REQUIRED. Minimum 1 per initial calibration. CVS must contain nC_{20}, prepared independently from calibration standards (at least from alternate stock solutions). Acceptance criteria is ±15% of target, for a mid-concentration standard.

Detection Limit Check

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

Continuing Calibration Verification (CCV)

REQUIRED. Minimum every 12 hours and at end of analysis batch if > 6 hrs from previous check. Use a mid-level nC_{20} calibration standard as CCV. Verify that retention times of nC_{10}, nC_{19}, and nC_{32} fall within the lab-specified acceptance range, as defined under the Instrument Performance Check (to a maximum of ±0.2 min from initial calibration retention times).

Method QC

Method Blank (MB)

REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Prepare a Method Blank using organic-free reagent water. Method Blanks must be subjected to all sample preparation steps experienced by samples, including optional elements such as centrifugation.

Laboratory Control Sample (LCS)

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

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

Laboratory Duplicates

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

Surrogate Compounds

REQUIRED. At least one Surrogate Compound is required. If extract concentration steps are applied within the method, a volatile Surrogate Compound (eluting earlier than nC_{10}) must be used (e.g., methyl-nonane or 2-bromobenzotrifluoride). Surrogate(s) must be added to each sample in acetone solution prior to extraction. Surrogates that elute outside the EPH retention time range are recommended so that there is no need to subtract them from integrated EPH peak areas.

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

Field Duplicates

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

Calibration & Analysis Procedure

Initial Calibration

A minimum 3-point linear average response factor (not linear regression) calibration against eicosane (nC_{20}) 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 nC_{20} calibration, calculate a Response Factor (RF) for eicosane (nC_{20}):

RF_{nC20} (mL/µg) = nC_{20} area / [nC_{20}] (µg/mL).

Average the Response Factors for all calibration levels to obtain an Averaged Response Factor for nC_{20}, $RF_{nC20,\,Avg}$.

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 nC_{20} 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 nC_{20} Response Factor remains within 15% of the average Response Factor from the initial calibration (for a mid-level CVS).

Integration of Total Areas for EPH_{w10-19} and EPH_{w19-32}

EPH_{w10-19} and EPH_{w19-32} are defined to include all GC-FID peaks eluting between decane (nC_{10}) and dotriacontane (nC_{32}). Determine the total integrated peak area of each EPH range, where:

a) EPH_{w10-19} begins at the apex of the nC_{10} peak and ends at the apex of the nC_{19} peak.

b) EPH_{w19-32} begins at the apex of the nC_{19} peak and ends at the apex of the nC_{32} peak.

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

Peak integration must include all peaks, whether resolved or not, that are above the chromatographic baseline, as established by Instrument Blanks within the analysis batch (correction for instrument blank background may done using column compensation or by peak area subtraction, or both).

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

Both EPH_{w10-19} and EPH_{w19-32} are quantitated against eicosane (nC_{20}) using a linear averaged response factor calibration.

If any surrogate compound(s) utilized elute within the EPH range of nC_{10}–nC_{32}, then the contribution to EPH of those surrogates must be excluded or subtracted from EPH results.

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

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

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

where:

$A_{(10-19)}$ = Total area between nC_{10} and nC_{19} for the sample chromatogram (after subtraction of Instrument Blank C_{10-19} area, if applicable).

$A_{(19-32)}$ = Total area between nC_{19} and nC_{32} for the sample chromatogram (after subtraction of Instrument Blank C_{19-32} area, if applicable).

RF_{nC20} = Average Response Factor for nC_{20} standard (mL/µg).

FV = Final Volume of extract (mL).

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

Dil = Dilution factor of sample extract (unitless).

Vol = Volume of sample extracted (mL).

Dilution Requirement for High Level Sample Extracts

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

Method Validation Requirements

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

Initial Verification of Relative Response Requirements

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

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

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

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

Determination of GC/FID linear range for EPH_{w10-19} and EPH_{w19-32} (calibration range).

Determination of EPH_{w10-19} and EPH_{w19-32} Instrument Detection Limits (IDLs).

Preparation of DL Check Standards and LCS Solutions.

Calculation of EPH_{w10-19} and EPH_{w19-32} targets for DL Check Standards and LCS Solutions.

Use the following procedure to calculate the *Actual EPH_{w10-19} and EPH_{w19-32}*

Concentrations of a DMO Stock Solution:

Prepare a reference solution of 1:1 Diesel: Motor Oil from the DMO Stock Solution at a concentration at least 10x greater than the estimated Instrument Detection Limits for EPH_{w10-19} and EPH_{w19-32}. A nominal DMO concentration of at least 2,000 µg/mL is recommended for this purpose (for the example GC conditions provided). This concentration is referred to in the example below as [DMO].

Perform a minimum of 3 replicate analyses of the DMO solution from above using the selected GC-FID method conditions.

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

% EPH_{w10-19} in DMO solution = 100% × [$EPH_{w10-19,\ measured}$] / [DMO]

% EPH_{w19-32} in DMO solution = 100% × [$EPH_{w19-32,\ measured}$] / [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 nC_{10}–nC_{32} boiling point range.

To calculate the *Actual EPH_{w10-19} and EPH_{w19-32} Concentrations* of other dilutions of the same DMO source, multiply the nominal DMO concentration of the solution by the percentages determined above.

Establish Instrument Calibration Working Range and Estimated IDLs

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

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

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

Establishing Method Detection Limits

Determine the Method Detection Limits (MDLs) at the 99% confidence level for EPH_{w10-19} and EPH_{w19-32}, using the procedure outlined in the British Columbia Environmental Laboratory Manual.

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

Calculate the Method Detection Limit (MDL) at the 99% confidence level for EPH_{w10-19} and EPH_{w19-32}.

Average recoveries of the MDL Method Spikes for EPH_{w10-19} and EPH_{w19-32} must

be between 60–140%. If this condition is not met, repeat the MDL determination at a higher spike level.

It is not required to formally validate an MDL for the modified extraction procedures for samples with NAPL or high solids, since these procedures are required for samples that are generally high in EPH. For the modified procedures, use the Reported Detection Limits for the standard micro-extraction procedure, but increased for any higher dilution factors used.

Determination of DL Check Standard Concentration and EPH Targets

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

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

For Example, if:

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

Vol = 250 mL = Volume of sample extracted

FV = 10 mL = Final Volume of extract

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

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

Then DMO DL Std Concentration = 0.50 mg/L* 250mL / 10mL * 4 / 0.8 = 62.5 mg/L

Accuracy and Precision

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

6 LCS samples (3 mid level & 3 high level) using Deionized Water.

6 LCS samples (3 mid level & 3 high level) using Lake Water or Groundwater.

6 LCS samples (3 mid level & 3 high level) using Seawater.

Determine LCS targets using Actual EPH_{w10-19} and EPH_{w19-32}. Concentrations of the DMO solution as described above. The minimum accuracy requirement for Initial Validation is an average recovery of 85–115%. The minimum precision requirement for Initial Validation is a Relative Standard Deviation of ≤ 15%.

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

Use of Alternative Methods

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

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

Prescribed Elements

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

Specified Method Validation requirements must be met.

All elements from Quality Control sections must be completed as specified, and must meet specified acceptance criteria, or sample data must be qualified.

Sample Handling and Preservation guidelines must not be modified.

Extraction with hexane is required (mixtures of hexane isomers are recommended, which are typically composed of ~60–65% n-hexane). The ratio of sample volume to hexane must be between 20:1 and 30:1 for the standard micro-extraction procedure.

Except when validated as described below in the Performance Based Method Changes section, a minimum agitation time of 30 minutes is required using vigorous mechanical shaking (e.g., by wrist shaker, rapid tumbler at ≥ 60 rpm, paint shaker, orbital or reciprocal platform shaker, or automated separatory funnel shaker, but not by on-axis rolling extraction).

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

If required, removal of sample to make room for hexane extraction solvent and air space must be conducted by pipette or other device from the sub-surface, without pouring, and immediately following inversion and mixing of the sample. No more than 20% of the total volume of the sample may be removed.

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

For BC MOE compliance purposes, the entire sample as submitted must be extracted and analyzed (except as described above). If test results are not for compliance purposes and if test results are clearly qualified on reports, samples with high solids or that are multi-phasic may be physically separated into aqueous or solids or NAPL phases with the phase(s) of interest tested as dictated by the client of the laboratory.

Gas Chromatography with Flame Ionization Detection is required.

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

Eicosane (nC_{20}) must be used as the calibration standard for EPH_{w10-19} and

EPH_{w19-32}. A minimum 3-point averaged response factor (linear) calibration is required.

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.

EPH_{w10-19} and EPH_{w19-32} method detection limits and Reporting Detection Limits must be based on diesel / motor oil spikes (see the Establishing Method Detection Limits section).

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

Performance Based Method Changes

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

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

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

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

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

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

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

A shorter extraction time (to a minimum of 15 minutes) may be used if the average of the 3 samples extracted for the shorter time demonstrates EPH C_{10-19} results that are at least 75% of the average of the results for the 3 samples extracted for 60 minutes.

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

References

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

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

Revision History

Sept 15, 2017	Corrected formula error with ECF in Calibration and Analysis section. EMS method and analyte codes added.
Nov 30, 2015	Revised to change method from DCM extraction to hexane micro-extraction to more selectively target petroleum hydrocarbon contaminants and to ensure inter-laboratory consistency. Usage of a surrogate was made mandatory, and a volatile surrogate must be used if extract concentration steps are applied (including silica gel cleanup steps). Method Performance Spikes were replaced with Laboratory Control Samples (diesel / motor oil) as QC requirement. Maximum batch size changed from 50 to 20 samples as per industry standard practice. Calibration changed to minimum 3 point linear by average response factor with narrower 15% CCV requirement. DQOs and minimum frequency were added for Instrument Blanks and for retention time monitoring. Preservatives and hold times were updated to reflect recent BC updates. Effective date: Jan 4, 2016.
April 2007	Revision of hold times and preservation requirements.
Dec 31, 2000	SEAM codes replaced by EMS codes. Out of print reference deleted. Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; Mandatory tests made bold.
July 1999	Finalization of method (revised by ALS under contract to BC MOE) based on results of round robin vetted by BCLQAAC (now BCELTAC).
March 1997	Initial publication of v1.0 of Volatile Petroleum Hydrocarbons in Solids.

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

Parameters

Extractable Petroleum Hydrocarbons (nC_{10}–nC_{19}) in solids

Extractable Petroleum Hydrocarbons (nC_{19}–nC_{32}) 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 of Environment and Climate Change Strategy website for all 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 (nC_{20}). EPH_{s10-19} measures hydrocarbons that elute between nC_{10} and nC_{19} (b.pt. range of ~ 174–330˚C). EPH_{s19-32} measures hydrocarbons that elute between nC_{19} and nC_{32} (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 ~ nC_{10}–nC_{32} (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., kerosene, jet fuels, and weathered gasolines). Heavy hydrocarbons with boiling points greater than nC_{32} 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_{s10-19} 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 µL 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 nC_{10}–nC_{12} 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 nC_{10}) 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 nC_{10} 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 (nC_{10}), nonadecane (nC_{19}), eicosane (nC_{20}), and dotriacontane (nC_{32}). 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 (nC_{10}), nonadecane (nC_{19}), eicosane (nC_{20}), dotriacontane (nC_{32}), 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 (nC_{20}) in hexane at 50 µg/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 nC_{10}/nC_{20} and nC_{32}/nC_{20}. nC_{10}, nC_{19}, nC_{32} retention times ±0.2 mins of initial calibration.
Calibration QC and Verification		
RSD of nC_{20} 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	nC_{20} within 15% of initial calibration. nC_{10}, nC_{19}, nC_{32} 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:

Measure and control relative response ratios of EPH components,

Determine retention time windows for EPH integration ranges, and

Confirm resolution of decane (nC_{10}) 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 nC_{10}/nC_{20} and for nC_{32}/nC_{20}, 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 nC_{10}, nC_{19}, and nC_{32} retention time markers. After each initial calibration, update retention times used for EPH_{s10-19} and EPH_{s19-32} 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 nC_{10}, nC_{19}, and nC_{32} 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 nC_{20}, 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 nC_{20} calibration standard as CCV. Verify that retention times of nC_{10}, nC_{19}, and nC_{32} 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 nC_{10}) 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 (nC_{20}) 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 nC_{20} calibration, calculate a Response Factor (RF)

for eicosane (nC_{20}):

RF_{nC20} (mL/µg) = nC_{20} area / [nC_{20}] (µg/mL).

Average the Response Factors for all calibration levels to obtain an Averaged Response Factor for nC_{20}, $RF_{nC20, Avg.}$

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 nC_{20} 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 nC_{20} 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 (nC_{10}) and dotriacontane (nC_{32}). Determine the total integrated peak area of each EPH range, where:

a) EPH_{s10-19} begins at the apex of the nC_{10} peak and ends at the apex of the nC_{19} peak.

b) EPH_{s19-32} begins at the apex of the nC_{19} peak and ends at the apex of the nC_{32} 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 (nC_{20}) using a linear averaged response factor calibration.

If any surrogate compound(s) utilized elute within the EPH range of nC_{10}–nC_{32}, 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} (µg/g) = [$A_{(10-19)}$ ÷ RF_{nC20}] * [FV * Dil / DryWt]

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

where:

$A_{(10-19)}$ = Total area between nC_{10} and nC_{19} for the sample chromatogram (after subtraction of Instrument Blank C_{10-19} area, if applicable).

$A_{(19-32)}$ = Total area between nC_{19} and nC_{32} for the sample chromatogram (after subtraction of Instrument Blank C_{19-32} area, if applicable).

RF_{nC20} = Average Response Factor for nC_{20} standard (mL/µg).

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:

Determination of GC/FID linear range for EPH_{s10-19} and EPH_{s19-32} (calibration range).

Determination of EPH_{s10-19} and EPH_{s19-32} Instrument Detection Limits (IDLs).

Preparation of DL Check Standards and LCS Solutions.

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:

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.

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

% EPH_{s10-19} in DMO solution = 100% × [$EPH_{s10-19,\ measured}$] / [DMO]

% EPH_{s19-32} in DMO solution = 100% × [$EPH_{s19-32,\ measured}$] / [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 nC_{10}–nC_{32} boiling point range.

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) µg/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 µg/g* 10g / 10mL * 1 / 0.8 = 160 µg/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 (nC_{10})	6	0.98	6.3%	8	1.01	1.8%
Naphthalene	6	1.03	6.9%	8	1.07	1.3%
Dodecane (nC_{12})	4	0.98	3.1%	8	1.00	1.4%
Hexadecane (nC_{16})	7	0.99	2.8%	8	1.00	1.5%
Phenanthrene	7	1.05	4.6%	8	1.06	0.8%
Nonadecane (nC_{19})	7	1.00	0.8%	8	0.99	0.4%
Eicosane (nC_{20})	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 (nC_{30})	5	0.90	17.2%	8	1.02	1.5%
Dotriacontane (nC_{32})	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 Rec.	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%
$LEPH_s$	6	3302	9.9%	8	3417	2.6%
$HEPH_s$	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:

Specified Method Validation requirements must be met.

All elements from Quality Control sections must be completed as specified, and must meet specified acceptance criteria, or sample data must be qualified.

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.

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

If anhydrous salts are used to dry sediment samples prior to extraction, a volatile surrogate (eluting earlier than nC_{10}) must be used and must be added prior to the drying process.

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).

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).

Gas Chromatography with Flame Ionization Detection is required.

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

Eicosane (nC_{20}) 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.

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.

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:

Apparatus.

Reagents and Standards.

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:

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

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

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

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

Revision History

Dec 22, 2016	Revised to new format, eliminated Method Performance Check Spikes, added LCS and surrogate requirement, added requirement for minimum 3-level calibration, 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: January 1, 2017.
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.

Extractable Petroleum Hydrocarbons, Light and Heavy, in Solids or Water — Calculation

Parameters

$LEPH_W$ — Light Extractable Petroleum Hydrocarbons in water

$HEPH_W$ — Heavy Extractable Petroleum Hydrocarbons in water

$LEPH_S$ — Light Extractable Petroleum Hydrocarbons in solids

$HEPH_S$ — Heavy Extractable Petroleum Hydrocarbons in solids

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Code
$LEPH_W$	250 µg/L	LEPH F064
$LEPH_{W\text{-}SG}$	250 µg/L	code pending
$HEPH_W$	250 µg/L	HEPH F064
$HEPH_{W\text{-}SG}$	250 µg/L	code pending
$LEPH_S$	200 µg/g	LEPH F085
$LEPH_{S\text{-}SG}$	200 µg/g	code pending
$HEPH_S$	200 µg/g	HEPH F085
$HEPH_{S\text{-}SG}$	200 µg/g	code pending

(Note that the above EMS codes are for results corrected for PAHs).

Analytical Method

Refer to the following LEPH/HEPH precursor methods:

Extractable Petroleum Hydrocarbons in Water by GC-FID.

Polycyclic Aromatic Hydrocarbons in Water by GC/MS/SIM.

Extractable Petroleum Hydrocarbons in Solids by GC-FID.

Polycyclic Aromatic Hydrocarbons in Solids by GC/MS/SIM.

Units

Waters: µg/L

Soils: µg/g (dry weight)

Introduction

Light and Heavy Extractable Petroleum Hydrocarbons are calculated using the results from selected methods as listed above. The calculation procedure for LEPH and HEPH requires that both Extractable Petroleum Hydrocarbons (EPH) and Polycyclic Aromatic Hydrocarbons (PAHs) are analyzed using methodologies which have been approved by the Director.

Selected PAHs are subtracted from EPH results to produce LEPH and HEPH values. These PAHs are excluded from LEPH and HEPH because they are regulated directly under the British Columbia (BC) Contaminated Sites Regulation (CSR). PAHs subtracted from HEPH/LEPH for waters are listed in Schedule 6 of the CSR. PAHs subtracted from HEPH/LEPH for soils are listed in Schedules 4 and 5 of the CSR. The Procedure section lists which of the excluded PAHs are to be subtracted from LEPH, and which are to be subtracted from HEPH, for both waters and soils.

Silica Gel treated LEPH and HEPH results may be used for comparison to the BC CSR LEPH/HEPH standards, but only where clearly indicated through the use of uniquely identified parameter names (containing "SG"), and only where there is justification for the use of silica gel cleanup at the site based on the anticipated or observed presence of interferences to EPH due to a prevalence of naturally occurring organics.

Approval to subtract additional target compounds that are not listed below is at the discretion of the Director of Waste Management.

Procedure

Subtract the total applicable PAHs from the appropriate EPH fraction:

LEPH = $EPH_{10\text{-}19}$ -Σ PAHs from CSR schedule(s) within $EPH_{10\text{-}19}$ range

HEPH = $EPH_{19\text{-}32}$ -Σ PAHs from CSR schedule(s) within $EPH_{19\text{-}32}$ range

Treat PAH results reported as less than detection limit as zero (no subtraction).

To calculate $LEPH_W$ (or $LEPH_{W\text{-}SG}$), subtract the individual results for acenaphthene, acridine, anthracene, fluorene, naphthalene, and phenanthrene from the $EPH_{W10\text{-}19}$ (or $EPH_{W10\text{-}19\text{-}SG}$) concentration obtained by the approved EPH GC/FID method.

To calculate $LEPH_S$ (or $LEPH_{S\text{-}SG}$), subtract the individual results for naphthalene and phenanthrene from the $EPH_{S10\text{-}19}$ (or $EPH_{S10\text{-}19\text{-}SG}$) concentration obtained by the approved EPH GC/FID method.

To calculate $HEPH_W$ (or $HEPH_{W\text{-}SG}$), subtract the individual results for benz(a)anthracene, benzo(a)pyrene, fluoranthene, and pyrene from the $EPH_{W19\text{-}32}$ (or $EPH_{W19\text{-}32\text{-}SG}$) concentration obtained by the approved EPH GC/FID method.

To calculate $HEPH_S$ (or $HEPH_{S\text{-}SG}$), subtract the individual results for benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, and pyrene from the $EPH_{S19\text{-}32}$ (or $EPH_{S19\text{-}32\text{-}SG}$) concentration obtained by the approved EPH GC/FID method.

PAH results used for the calculation of LEPH and HEPH must be by GC/MS or by HPLC.

Report results in units of mg/kg (dry weight) for solids, and in units of µg/L or mg/L for waters.

Co-Reporting Requirements

Designated regulated PAH substances are allowed (and required) to be subtracted from EPH concentrations because they are regulated independently. Consequently, it is required that the subtracted PAHs must be co-reported whenever LEPH and HEPH results are reported. Laboratories are not permitted to remove test results for co-reported parameters after initial reporting.

LEPH/HEPH Co-Reporting Requirements are as follows:

$LEPH_S$	naphthalene	phenanthrene
$HEPH_S$	benz[a]anthracene, benzo[a]pyrene benzo[b]fluoranthene benzo[k]fluoranthene	dibenz[a,h]anthracene indeno[1,2,3-cd]pyrene pyrene
$LEPH_W$	acenaphthene acridine anthracene	fluorene naphthalene phenanthrene
$HEPH_W$	benz(a)anthracene benzo(a)pyrene	fluoranthene pyrene

Revision History

Nov 6, 2015: Revised to include allowance for LEPH/HEPH with silica gel cleanup. Added and defined new co-reporting requirement for PAHs. Removed maximum reporting limit guidance. Aligned preferred units to CSR standards. Effective Date: Jan 4, 2016.

Dec 31, 2000: Incorporated into main BC Laboratory Manual, EMS codes added, former methods superseded.

1998–1999: Revision of historical hydrocarbon methods by ASL (now ALS) under contract to BC MOE with guidance from BCLQAAC (now BCELTAC).

Extractable Petroleum Hydrocarbons, Silica Gel Cleanup

Parameter

EPH $_{(nC_{10}-nC_{19})}$ in water (Silica-gel treated) — $EPH_{W10-19(sg)}$
EPH $_{(nC_{19}-nC_{32})}$ in water (Silica-gel treated) — $EPH_{W19-32(sg)}$
EPH $_{(nC_{10}-nC_{19})}$ in solids (Silica-gel treated) — $EPH_{s10-19(sg)}$
EPH $_{(nC_{19}-nC_{32})}$ in solids (Silica-gel treated) — $EPH_{s19-32(sg)}$

Analyte Symbols MDLs, and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL	Analyte EMS Code
$EPH_{W10-19(sg)}$		250 µg/L	LEPHsg
$EPH_{W19-32(sg)}$		250 µg/L	HEPHsg
$EPH_{s10-19(sg)}$		100 mg/kg	LEPHsg
$EPH_{s19-32(sg)}$		100 mg/kg	HEPHsg

EMS Method Code(s)

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Analytical Method

Silica Gel adsorptive cleanup for EPH in Solids or Waters.

Refer to specific EPH methods for extraction and instrumental analysis procedures:

- Extractable Petroleum Hydrocarbons (EPH) in Solids by GC-FID
- Extractable Petroleum Hydrocarbons (EPH) in Water by GC-FID

Introduction

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

Silica gel cleanup can exclude biogenic 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

Silica gel cleanup may not be entirely selective to the removal of only biogenic organics and can remove non-biogenic organics if they are sufficiently polar. Most common refined petroleum hydrocarbon environmental contaminants such as diesel or motor oil are fully recovered by this procedure. Polar components of complex PHC materials such as crude oils, bunker fuel, or highly weathered or biologically degraded PHC materials may not be recovered. For this reason, silica gel cleanup should not be used indiscriminately except where biogenic interferences are suspected. Non-polar or slightly polar biogenic components (e.g., some plant waxes) will not be removed by silica gel.

This cleanup method and elution solvent are designed to include and quantify non-polar saturated and unsaturated aliphatic hydrocarbons (such as alkanes and alkenes), as well as medium polarity hydrocarbons up to and including PAHs. The DCM/hexane elution solvent is intended to include PAHs (alkylated and non-alkylated), which are included within the EPH parameter definitions.

After cleanup, sample 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.

Silica gel cleanup is appropriate for use 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 (or associated LEPH/HEPH results) are submitted for comparison with CSR standards. Silica gel treated EPH results (and associated LEPH/HEPH results) must be reported with analyte descriptors that differentiate them from untreated results, using an appended "sg". Consult the Director and/or the lab manual procedures for calculation of LEPH/HEPH for further guidance.

Method Summary

Sample extracts obtained from the appropriate EPH method are exchanged to hexane (if required) and are passed through a micro-column containing 0.5 grams of 100% activated silica gel. Elution is achieved with a small volume of 1:1 DCM:hexane. The eluted solvent is then concentrated (if required) and analyzed by the appropriate EPH analysis procedure.

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

Matrix

Freshwater, Marine water, Groundwater, Wastewater, Soil, Sediment

Interferences and Precautions

The effectiveness of the silica gel cleanup can be reduced if hexane sample extracts contain significant amounts of a polar solvent such as acetone. For hexane/acetone soil extracts, this method uses two water partition steps to reduce acetone content to trace levels (< 0.1% versus ~ 2% acetone after a single water partition step).

Sample extracts containing more than approximately 15 mg of petroleum hydrocarbons could potentially overload the retention capacity of a 0.5 g silica gel column and may require dilution prior to cleanup*.

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

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 method through the regular analysis of Method Blanks and/or Procedure Blanks.

*Note: The Capric Acid Reverse Surrogate provides a sample-specific control to identify potential problems with silica gel capacity or activation.

Sample Handling and Preservation

Container and preservation requirements

Sampling Containers:	
Preservation:	
Holding Time:	Maximum holding time for refrigerated extracts is 40 days from extraction. Where holding times are exceeded, data must be qualified.
Storage:	Store extracts in a refrigerator or freezer at ≤ 6°C

Reagents

Use analytical grade or better for all reagents:

- Silica Gel. Pore size 60 Angstroms, particle size ~60–200 µm, mesh size 70–230.
- Organic Free Water
- Dichloromethane (DCM)
- Hexane
- Sodium sulfate, anhydrous, granular
- Glass wool
- Capric acid

Standards

EPH Cleanup Spike Solution for Initial Method Validation

Prepare or purchase an EPH Cleanup Spike Solution containing at least decane (nC_{10}), nonadecane (nC_{19}), dotriacontane (nC_{32}), naphthalene, phenanthrene, and pyrene, prepared in hexane (recommended concentration 50 µg/mL for each component). Warm the solution and mix well before use to ensure complete dissolution of all components. Minimize trace levels of polar solvents such as DCM or acetone in this solution to prevent recovery problems that may not be indicative of the cleanup procedure for typical samples.

Capric Acid Stock Solution

Prepare a Stock Solution of Capric Acid at approximately 10,000 µg/mL in 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.

Capric Acid Spike Solution

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

Procedure Spike Solution

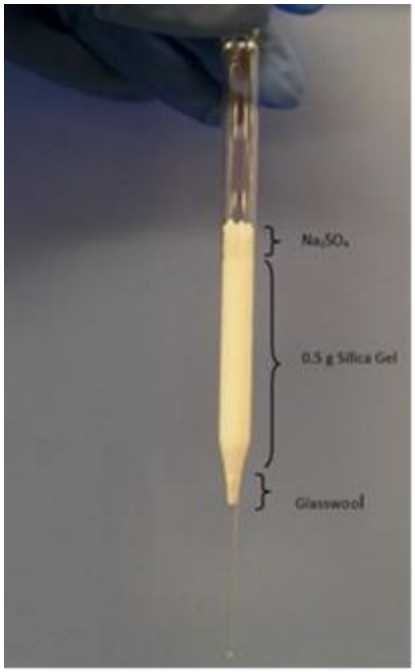
Dilute the DMO Stock Solution (refer to EPH solids or water method for details) into hexane to prepare a DMO Spiking Solution.

Procedure

Silica Gel Column Preparation

Activate silica gel by baking at 130–250°C for a minimum of 16 hours, e.g., using a beaker or shallow glass dish covered with aluminum foil. Remove from the oven and allow to cool before use. Cooling and storage of silica gel in a desiccator or sealed vessel is recommended. [For activation temperature, EPA 3630C specifies 130–160°C; EPA 1664B specifies 200–250°C].

1. Place a small amount of rolled glass wool at the bottom of a disposable 5¾" Pasteur pipette (i.d. ~ 0.6 mm). Pack the glass wool sufficiently so that the silica gel cannot pass through. The glass wool should be approximately 0.5 cm in height.
2. Weigh or measure 500 ±25 mg of 100% activated silica gel into the pipette. The silica gel sorbent bed will be approximately 4 cm in height.
3. Add approximately 0.5 cm sodium sulfate onto the top of the silica gel column.
4. When correctly packed, a gravity-fed flow rate of roughly 1 drop per second (±~ 50%) should be achieved (measurement of flow rate is not required, and marginally slower or faster flows should not significantly affect performance).
5. Place a solvent waste vial under the column.
6. Fill the column with DCM and elute to waste. Repeat the DCM rinse one or more times, as needed to pre-clean the silica gel.
7. Fill the column with hexane and elute this to waste also. Repeat this step one more time. Do not allow the silica gel columns to dry before adding sample extracts (re-wet with hexane if necessary).



Pasteur Pipette Silica Gel Micro-Column

Preparation of Soil Sample Extracts

1. Transfer an appropriate volume of hexane:acetone EPH soil sample extract to a suitable container for the water partition step. Either the entire extract or a portion of the extract may be processed for the water partition step.
2. If required, spike each sample with a volatile EPH surrogate compound (only required if an extract concentration step will be conducted, and the method doesn't already include a volatile EPH surrogate).
3. Add a volume of reagent water equal to at least three times the volume of the hexane:acetone portion selected for partitioning.
4. The extract will partition into two phases. Discard the entire lower aqueous layer (water plus acetone), or transfer all or a portion of the hexane phase for a second partition.
5. Wash the hexane phase a second time with reagent water (use at least three times the volume of hexane). Separate the upper hexane layer (or a quantitative portion of it) for the silica gel cleanup step. Select the amount of hexane extract to be cleaned up based on detection limit and analytical method requirements.
6. Discard the lower aqueous layer.
7. Extract concentration by nitrogen blowdown or other evaporative concentration technique may be necessary to bring the total hexane volume desired for cleanup to 2.00 mL. For mineral soils with typical moisture contents, no concentration may be necessary (depending on analytical method sensitivity). For organic / peat soils with high moisture contents (typically > 80%), or other high moisture soils, cleanup of additional extract with further extract concentration of 3–4x prior to cleanup is highly recommended (unless required detection limits can easily be met without concentration).

Preparation of Water Sample Extracts

Water sample extracts may not require any processing prior to silica gel cleanup.

1. If required, spike each sample with a volatile EPH surrogate compound (only required if an extract concentration step will be conducted, and the method doesn't already include a volatile EPH surrogate).
2. Extract concentration by nitrogen blowdown or other evaporative concentration technique is not normally required for waters but may be conducted if required to meet detection limit requirements.

Silica Gel Cleanup Procedure

If the portion of sample extract being cleaned up is expected to contain more than approximately 15 mg of petroleum hydrocarbon material, dilution is recommended to prevent 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.

1. Spike each sample extract with 500 µL of the 1,000 µg/mL Capric Acid Spike Solution (in hexane).
2. Add enough hexane to more than cover the silica gel. If the silica gel dries before the sample is added, repeat the hexane addition step, again eluting to waste.
3. Quantitatively add 2.0 mL of the hexane sample extract to the top of the column. Begin collecting the eluant immediately into a suitable glass vial (i.e., 7–8 mL capacity). Allow the extract to elute to the top of the silica gel before adding rinses.
4. Rinse the extract vial with two portions of 0.5 mL of 1:1 DCM:hexane, adding the rinsings each time to the silica gel column. Allow the extract to elute to the top of the silica gel before adding each rinse.
5. Add an additional 2.0 mL of 1:1 DCM:hexane to complete the elution of the column.
6. Concentrate or dilute to the desired final extract volume with or without a solvent keeper such as iso-octane or toluene. Avoid concentration of the extract to below 0.5 mL to minimize losses of volatile components.

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

Quality Control

General QC Requirements

Refer to the EPH methods for solids and water for additional details about Instrument Performance QC, Calibration QC, and Method QC pre-requisites for analysis of EPH prior to cleanup.

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB) or Procedure Blank	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS) / Procedure Spike (DMO Spike)	One per batch (max 20 samples)	70–130% recovery
Lab Duplicate (DUP)	Soils: One per batch * (max 20 samples) Waters: n/a	40% RPD [or within 2x reported DL for low level results]
Surrogate Compounds EPH Surrogate Capric Acid Reverse Surrogate	All samples	50–140% < 2% breakthrough
* Lab Dup frequency requirement refers to sample extraction batches, not silica gel prep batches.		

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

Method Blank

Either a Method Blank (processed through the entire EPH method) or a Procedure Blank (processed only through the silica gel cleanup step) must be processed to monitor for contaminants introduced by the cleanup step.

Prepare a Procedure Blank by processing hexane for water samples or 1:1 hexane:acetone for soil samples through the cleanup process, and analyze together with samples processed in the same preparation batch. Using a Procedure Blank instead of a Method Blank isolates contaminant monitoring to the silica gel procedure step alone.

Lab Control Sample or Procedure Spike

Either a Lab Control Sample; Diesel/Motor Oil (DMO) spike, processed through the entire EPH method, or a Procedure Spike (processed only through the silica gel cleanup step) must be processed to monitor for EPH_{10-19} and EPH_{19-32} recovery.

Prepare a Procedure Spike by processing a suitable volume of DMO spiking solution (prepared in hexane for waters or hexane/acetone for soils) through the cleanup process. Using a Procedure Spike isolates recovery monitoring to the silica gel procedure step alone.

Surrogate Compound(s):

EPH Surrogate

At least one surrogate compound must be monitored through the silica gel cleanup procedure for all samples and QC. If sample extracts will be concentrated as an element of the silica gel cleanup step, then a volatile surrogate that elutes slightly earlier than nC_{10} (e.g., 2-methylnonane or 2-bromobenzotrifluoride) is required as a check for evaporative losses. It is acceptable to measure two independent surrogates, one for the extraction process, and one for the cleanup process.

Capric Acid Reverse Surrogate

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 (e.g., 0% breakthrough is the target).

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 µg/mL in the final extract. The Capric Acid Reverse Surrogate should be spiked into the sample extract or onto the silica gel column prior to addition of the sample extract.

Capric acid must also be added to the EPH Calibration Standard so that identification and quantitation of capric acid in samples may be performed.

If the breakthrough of capric acid is >2% 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.

Method Validation Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Initial Validation of EPH Silica Gel Cleanup Method

Before proceeding with further validation steps, verify that the method as used meets the requirements outlined below by performing at least three EPH Cleanup Spikes of discrete hydrocarbon and PAH components, which includes at minimum nC_{10}, nC_{19}, nC_{32}, naphthalene, phenanthrene, and pyrene, plus EPH surrogate(s) and capric acid.

Discrete compound recovery for the method must be validated using the same solvent or solvent mixture that is used for samples. Calculate the recovery of each component of the mixture by quantitation against a calibration standard prepared from the EPH Cleanup Spike Solution (i.e., calculate naphthalene against naphthalene).

For the Initial Validation, average component recoveries must be between 70% and 115% for nC_{10} and naphthalene, and between 85% and 115% for phenanthrene, pyrene, nC_{19} and nC_{32}. Surrogate recoveries must meet the requirements specified in the QC requirements table.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 DMO Lab Control Samples or Procedure Spikes must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement:

Laboratories must demonstrate method accuracy (measured as average recovery of EPH_{10-19} and EPH_{19-32}) of 80–120% for DMO Lab Control Samples at concentrations above ten times the MDL.

Precision Requirement:

Laboratories must demonstrate method precision less than 15% relative standard deviation for DMO Lab Control Samples at concentrations above ten times the MDL, for EPH_{10-19} and EPH_{19-32}.

Sensitivity Requirement:

Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

References

1. Extractable Petroleum Hydrocarbons in Solids by GC-FID, Dec 22, 2016, British Columbia Environmental Laboratory Manual.
2. Extractable Petroleum Hydrocarbons in Water by GC-FID, Sept 15, 2017, British Columbia Environmental Laboratory Manual.
3. Silica Gel Cleanup, SW-846 Method 3630C, December 1996, US EPA
4. n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, Method 1664B, February 2010, US EPA.

Revision History

31-May-2004	First version of EPH silica gel method
20-Dec-2019	Revised to a prescriptive method to improve cleanup performance for peat soils, and to improve inter-laboratory comparability. Updated to newer method format and harmonized with most recent versions of EPH solids and waters methods. Replaced method performance check spike for daily QC (using discrete PHC components) with diesel/motor oil mixture. Draft version for public comment.
19-Jun-2022	Updated to new Prescriptive Method Template Format

Extractable Petroleum Hydrocarbons, Silica Gel Fractionation

Parameters and Analyte Symbols			**Analyte Code**
	Aliphatic EPHs$_{(nC_{10}-nC_{19})}$ in water	=	Aliphatic-EPH$_{W_{10-19}}$
	Aromatic EPHs$_{(nC_{10}-nC_{19})}$ in water	=	Aromatic-EPH$_{W_{10-19}}$
	Aliphatic EPHs $_{(nC_{10}-nC_{19})}$ in solids	=	Aliphatic-EPH$_{s10-19}$
	Aromatic EPHs $_{(nC_{10}-nC_{19})}$ in solids	=	Aromatic-EPH$_{s10-19}$
	Aliphatic EPHs $_{(nC_{19}-nC_{32})}$ in water	=	Aliphatic-EPH$_{W_{19-32}}$
	Aromatic EPHs $_{(nC_{19}-nC_{32})}$ in water	=	Aromatic-EPH$_{W_{19-32}}$
	Aliphatic EPHs $_{(nC_{19}-nC_{32})}$ in solids	=	Aliphatic-EPH$_{s19-32}$
	Aromatic EPHs $_{(nC_{19}-nC_{32})}$ in solids	=	Aromatic-EPH$_{s19-32}$

Analytical Method

Aliphatic/Aromatic fractionation by Silica Gel adsorption column chromatography.

Refer to specific EPH methods for instrumental analysis procedures:

a) Extractable Petroleum Hydrocarbons in Solids by GC-FID, July 1999, version 2.1 [a].

b) Extractable Petroleum Hydrocarbons in Water by GC-FID, July 1999, version 2.1 [b].

Introduction

This method is used in conjunction with the BCMELP 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 EPH$_{10-19}$ and EPH$_{19-32}$ 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. British Columbia Ministry of Environment, Lands and Parks 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.

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.

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, wastewater, marine water.

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.

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.

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.

Apparatus

a) Glassware and Support Equipment

25–30 cm × 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)

Reagents and Standards

a) 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

b) Calibration Standard Stock Solution

Prepare a Calibration Standard Stock Solution in DCM containing 1,000 µg/mL of each of decane (nC_{10}), dodecane (nC_{12}), hexadecane (nC_{16}), nonadecane (nC_{19}), eicosane (nC_{20}), dotriacontane (nC_{32}), 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 $(4 \pm 4)^{\circ}C$.

EPH Fractionation Performance Check Solution

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

Quality Control (QC)

a) 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 [c]. 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 EPH_{10-19} and EPH_{19-32} 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.

b) 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.

Procedure Blank

OPTIONAL*. 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).

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.

* 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.

EPH Fractionation Performance Check Spike

OPTIONAL*. 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 nC_{13} through nC_{32}, and between 70% and 115% for nC_{10}, nC_{12}, 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).

* 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.

c) 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.

Sample Preparation Procedure

a) 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 × 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 $\pm$ 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.

b) 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 ±□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 napthalene 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 ±□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.

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 BCMELP 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}

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.

a) 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 nC_{16} through nC_{32}, including phenanthrene and pyrene, and between 70% and 115% for nC_{10}, nC_{12}, 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).

b) Method Detection Limits

Apply the MDL's determined during method validation of the applicable BCMELP EPH method as the MDLs 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	Alipathic-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

c) 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 BCMELP or other applicable regulatory body.

d) Accuracy and Precision

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

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.

a) Prescribed Elements

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

- 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).

b) 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 BCWLAP. This information must be available in the event of audit by BCWLAP.

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.

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.

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 BCWLAP on request.

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:

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 EPH$_{10-19}$ and EPH$_{19-32}$ 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

At least one soil / sediment Reference Material extract*. While available, either of the two RMs analyzed within the 1998 BCMELP 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 EPH$_{10-19}$ and EPH$_{19-32}$ at ≥ 3 times the laboratory's routinely reported detection limits may be substituted.

***** 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:

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:

$$\mathbf{RPD = \left| (X_1 - X_2) / mean_{(x_1, x_2)} \right| * 100\%}$$

OR,

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 [h]. 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 [g].

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 [g].

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

References

a) British Columbia Ministry of Environment, Lands and Parks, July 1999, Extractable Petroleum Hydrocarbons in Solids by GC/FID, version 2.1.

b) British Columbia Ministry of Environment, Lands and Parks, July 1999, Extractable Petroleum Hydrocarbons in Water by GC/FID, version 2.1.

c) Canadian Standards Association, January 1995, Requirements for the Competence of Environmental Laboratories, CAN/CSA-Z753.

d) Massachusetts Department of Environmental Protection, January 1998, Method for the Determination of Extractable Petroleum Hydrocarbons (EPH).

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

f) 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 and D.

g) 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.

h) John Keenan Taylor, 1990, Statistical Techniques for Data Analysis, Lewis Publishers, pages 75–78 and 98.

Disclaimer

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

Acknowledgments

Mark Hugdahl and Scott Hannam, of ALS Environmental and members of the BCLQAAC Technical Sub-Committee, 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)” [d].

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

Glycols in Soil and Water by GC/FID — PBM

Parameter

Glycols in soil and water.

Analytical Method

Direct injection - Gas chromatography with Flame Ionization Detection (GC/FID) — PBM.

Introduction

This method is applicable to the quantitative determination of glycols in soil and water.

Method Summary

A portion of the water or aqueous soil extract is transferred to an autosampler vial and is injected into the GC inlet (on-column or splitless), for direct analysis by GC/FID using a polar stationary phase (e.g., DB-Wax or DB-624 or equivalent). This method yields reporting limits that are suitable to meet BC CSR standards. If lower reporting limits are required, samples may be analyzed by GC/MS or by HPLC/MS (US EPA Method 8321B) with a large volume injection.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. Soil MDL (µg/g)	Approx. Water MDL (µg/L)	Analyte EMS Code
Ethylene glycol	107-21-1	5	2,000	E020
Propylene glycol,1,2-	57-55-6	5	2,000	P020
Diethylene glycol	111-46-6	5	2,000	E220
Triethylene glycol	112-27-6	5	2,000	E320

Note: This method may also be applicable to the analysis of other BC CSR substances such as glycol monoalkyl ethers.

EMS Method Code

GLYC (Glycols in Soil and Water by GC/FID)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil: Soil, sediment, sludge, solid waste.

Water: Freshwater, seawater, groundwater, wastewater.

Interferences and Precautions

Glycols by GC-FID may be subject to interferences by any substance with similar boiling points and chromatographic characteristics that may co-elute under the conditions of the analysis (e.g., by alkanolamines or petroleum hydrocarbons). Matrix spikes and/or GC/MS confirmation is recommended to assist with correct identification of target compounds in samples if co-eluting interferences are suspected.

Hydrocarbon interferences may be removed with a hexane pre-extraction cleanup step, using brief physical agitation.

Propylene glycol and ethylene glycol can be difficult to separate when one analyte is found at significantly higher concentration than the other.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carry-over that occurs on their instrument and should take appropriate steps to prevent the occurrence of false positives.

Samples with high salt or total dissolved solids content can cause contamination of the GC inlet and column, resulting in degradation of chromatographic performance.

Sample Handling and Preservation

Sample Containers:

Soil: Glass jar with Teflon (or foil) lined lid, 125–250 mL recommended.

Water: 40–60 mL glass vial with Teflon lined lid.

Preservation:

Soil: Soil samples are not chemically preserved.

Water: Water samples may be preserved with $NaHSO_4$, HCl, or H_2SO_4 to pH <2 to extend hold times.

Storage: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage.

Stability

Holding Time:

Soil: Analyze soil samples within 14 days after collection. If organic solvent extraction is conducted, samples must be extracted within 14 days, and extract hold time is 40 days.

Water: Analyze unpreserved water samples within 7 days after collection. Acid preservation extends hold times to 14 days from sampling.

Where holding times are exceeded, test results must be qualified.

Procedure

Soils: Soil samples are subjected to aqueous extraction prior to direct injection of the aqueous extract. Soils are extracted using deionized water using a 2:1 ratio of water to field-moist soil. Soil samples are physically agitated using a mechanical shaker for a minimum of 30 minutes. Suspended solids may be removed by filtration, or sample extracts may be centrifuged until clear. Moisture content analysis is performed on a separate aliquot. Test results are corrected for moisture content and are reported on a dry weight basis. Include sample moisture content in the aqueous extract volume for data calculation purposes.

Waters: Water samples are analyzed by direct aqueous injection by gas chromatography with flame ionization detection (GC/FID). Suspended solids may be removed by filtration, or samples may be centrifuged until clear.

Detailed instrumental analysis procedures are not provided for this method. The procedures described in EPA Method 8015D (see references) are suitable for general guidance.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes

(e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80–120% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank (MB) — matrix specific	One per batch (max 20 samples)	Less than reported DL
Calibration Verification Standard (CVS) — 2nd Source	One per initial calibration	85–115%
Continuing Calibration Verification (CCV) — mid-level	At least every 12 hours (max 20 samples), and at end of each batch.	80–120%
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	60–140% (soils) 70–130% (water)
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	50% RPD (soils) 30% RPD (water) [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60–140%
Surrogate Compounds	Recommended	Not specified

*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

Recommended surrogate compounds include tetramethylene glycol or 1,3-propylene glycol.

Prescribed Elements

The following components of this method are mandatory:

Calibrations must consist of a minimum of 4 calibration standards.

For soil extractions, soil moisture content must be accounted for in the extraction solvent volume if using extraction by water or a water-miscible solvent.

For FID analysis, at least 80% baseline chromatographic separation must be achieved for all target parameters in calibration standards (valley height of peak overlap must not exceed 20% of maximum peak height).

Where sample extracts require filtration or pre-extraction hexane cleanup, QC samples must be processed in the same manner.

All stated performance requirements and quality control requirements must be met.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

US EPA method 8015D, Nonhalogenated organics using GC/FID (Revision 4, June 2003).

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.

Glyphosate and AMPA in Water by HPLC — PBM

Parameter

Glyphosate

AMPA

Analytical Method

Derivatization, extraction, HPLC/UV-VIS.

Introduction

This method is for the determination of the herbicide glyphosate and its metabolite, aminomethylphosphonic acid (AMPA).

Method Summary

An aliquot of the water sample is reacted with dinitrofluorobenzene (DNFB) to form derivatives of glyphosate and AMPA. Analysis is by high performance liquid chromatography. If required, interferences may be removed from the reaction mixture by extraction with dichloromethane. A subsequent extraction with iso-butanol removes the derivatives, which are then back-extracted into a borax solution prior to HPLC analysis.

MDL and EMS Codes

Analyte	Approx. MDL (mg/L)	EMS Code
Glyphosate	0.05	**G001 X365**
AMPA	0.05	**A001 X365**

Matrix

Fresh water, wastewater.

Interferences and Precautions

Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

Glyphosate rapidly decomposes in chlorinated waters.

Sample Handling and Preservation

Water samples should be collected in amber glass bottles with Teflon lined lids. Samples are preserved by adding 100 mg/L sodium thiosulfate in the field to remove residual chlorine and reduce the potential for degradation of glyphosate. Store samples at 4 ±2°C. Samples should be stored on ice during transport to the lab and must not exceed 10°C during the first 48 hours after collection.

Stability

Holding Time and Storage:

Standard Method 6651B (2000) stipulates water samples are stable for at least 14 days when preserved and kept under 4 ±2°C.

The preserved water samples must be extracted within 14 days of collection.

Procedure

Reagents

Buffer Solution: 0.005 M Potassium Dihydrogen Phosphate.

Derivatization Reagents: 2,4-Dinitro-fluorobenzene (DNFB) 2% (v/v).

Note: DNFB is a suspected cancer-causing agent.
Handle in a fume hood and wear gloves.

Dichloromethane (DCM), glass distilled pesticide grade.

Acetone, glass distilled pesticide grade.

Disodium tetraborate.

Hydrochloric Acid (6 N).

Cleanup Extraction

Measure about 0.1 g of di-sodium tetraborate (Borax: $Na_2B_4O_7 \cdot 10H_2O$) and transfer into a 15mL test tube.

Pipette 5mL of the sample into the tube. Prepare a set of working standards to be processed through the procedure at the same time as the samples.

Heat the sample and $Na_2B_4O_7 \cdot 10H_2O$ for approximately 30 seconds at 60°C in a water bath, then vortex to dissolve and mix $Na_2B_4O_7$. Check to see that it has completely dissolved.

Add 1.0mL of 2% DNFB solution.

Vortex to mix and heat at 60°C for 30 minutes in a water bath.

Remove from the water bath and allow to cool to room temperature.

Clean up the sample by adding 0.15 mL of 6 N HCl drop wise until an intense yellow colour changes to light yellow and vortex for 30 sec.

Add 5mL of DCM and vortex for about 30 seconds.

Wait about 10 min, allowing phases to separate.

Remove 1 mL of aqueous (top) layer and place in a GC vial for HPLC analysis.

Additional Cleanup (if required):

This is not recommended unless necessary, due to reductions in analyte recovery and increased variability.

Where this cleanup is employed, calibration standards should be taken through the same process to correct for processing losses.

Add 2 × 5 mL iso-butanol (saturated with water), collecting, with a Pasteur pipette, each extract (top layer) into a clean 15 mL graduate centrifuge tube. Be careful not to collect any of the aqueous layer.

Add 1.2 mL of 0.1 M $Na_2B_4O_7$, and vortex 20 sec. Centrifuge for 2 min. at approximately 2000 rpm.

Pipette off the iso-butanol layer (top) and discard.

Acidify the aqueous layer with 2 drops of 12 N HCl, checking that the pH is acid with litmus paper.

Add 5 mL DCM and vortex 20 sec.

Allow to separate and analyze the aqueous (top) layer.

Instrumental Analysis

Detector: UV

Guard Column: C18 (4mm L × 3.0 mm ID)

Column Temperature: 40°C

Flow Rate: 1 mL/min

Mobile Phase A: 0.005 M Potassium Dihydrogen Phosphate (0.688 g/L), adjust pH to 3.0 with phosphoric acid and filter through 0.2 µm or 0.45 µm nylon membrane filter (Gelman 66602 nylon 47 mm or equivalent).

Mobile Phase B: Methanol

Gradient Program:

Time	Phase A	Phase B
3 min.	95 %	5 %
6 min.	50 %	50 %
8 min.	25 %	75 %
10 min	5 %	95 %
12 min	95 %	5 %

Injection Volume: 100 µL

Wavelength: 370 nm

Bandwidth: 4 nm

Reference Wavelength: 500 nm

Bandwidth: 100 nm

Whenever possible, the use of internal standards is strongly recommended. Internal standards can vastly improve method precision.

Sample concentrations must be bracketed by standards.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or reference materials at concentrations above ten times the MDL. Average recovery must be between 70–130% for glyphosate and AMPA.

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 <20% for glyphosate and AMPA.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The

method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Laboratory Control Sample (Method Spike)	One per batch	60–140%
Lab Duplicates	One per batch	40% RPD
Continuing Calibration Verification (CCV)	Every 12 hours	80–120% for mid level std.
Control standard(ICV) — secondary source	One per batch	80–120% for mid level std

*Minimum DQOs apply to individual QC samples at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by HPLC with derivatization. Detection by either UV or post column fluorescence detection may be employed.

All Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

Primary Reference:

British Columbia Environmental Laboratory Manual 1974 Edition, “Glyphosate and AMPA”.

Secondary References:

Standard Methods for the Examination of Water and Wastewater. Method 6651B. Glyphosate Herbicides (2000). American Public Health Association, Washington DC.

EPA Method 547 (EPA-500 Series, Supplement I, July 1990), Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection.

Revision History

October 13, 2006: First drafted as BC PBM.

IPBC (3-Iodo-2-propenyl-n-butylcarbamate) in Aqueous Samples

Parameter	3-Iodo-2-propenyl-n-butylcarbamate (IPBC)
Analytical Method	Extraction, GC/NPD
EMS Code	IPBC X364
Introduction	The anti-sapstain formulation, NP-1™, contains two active ingredients: 3-iodo-2-propenyl-n-butylcarbamate (IPBC) and didecyldimethylammonium chloride (DDAC). This formulation has gained acceptance as an alternative to traditional anti-sapstain compounds such as chlorophenols (or chlorophenates), 2-(thiocyanomethylthio)benzo-thiazole (TCMTB) and copper-8-quinolinolate (Cu-8). This methodology provides a means of analyzing for the IPBC ingredient of NP-1™, independently of DDAC.
Summary	Samples are treated in the field with hydrochloric acid. The acidified samples are extracted with dichloromethane and the extracts concentrated. Quinaldine is added as a performance standard and, after being made to final volume in n-hexane, the extracts are analyzed by capillary column gas chromatography with a nitrogen-phosphorus detector.
MDL	0.025 mg/L
Matrix	Fresh water, wastewater, marine water.
Interferences and Precautions	Any compound that co-extracts, co-elutes under the analytical conditions, and produces a response on the nitrogen- phosphorus detector may interfere.
Sample Handling and Preservation	**Sample container:** Polyethylene bottle, 0.5 L or larger. **Preservation:** 2 mL 6N HCl per litre of sample (added in the field).
Stability	**Holding time:** maximum storage time is 2 weeks. **Storage:** store samples at 4° C until analyzed.
Principle or Procedure	IPBC is isolated from the sample matrix by liquid/liquid extraction using dichloromethane under acidic conditions. The concentrated extract is analyzed by capillary column gas chromatography with a nitrogen-phosphorus detector that responds to the carbamate nitrogen. Alternately, an electron capture detector can be used to monitor the iodine present in the compound of interest.
Precision	Synthetic samples spiked at 0.050 mg/L; COV = 2.8%. Authentic samples spiked at 0.050 mg/L; COV = 5.1%.
Accuracy	Synthetic samples spiked at 0.050 mg/L; average recovery = 97%. Authentic samples spiked at 0.050 mg/L; average recovery = 84%.
Quality Control	**Blanks:** 1 per batch (1 in 14). **Replicates:** 1 duplicate per batch (1in 14).

Recovery control: 1 spike per batch (1 in 14).

Performance standard: Quinaldine added at a concentration of 2.5 µg/mL in the final extract.

References None listed.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Out of print reference deleted.

Leachability of Metals, Inorganics, and SVOCs in Soil as a Function of pH

Parameters

Liquid-Solid Partitioning (Leachability) potential of metals, inorganics, and semi-volatile organic compounds (SVOCs) from soils as a function of leachate pH.

Analytical Method

Parallel extractions of as-received solid material in dilute acid or base and de-ionized water.

Introduction

This method is intended to be used as part of an environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness, and site remediation options.

This method is a leaching characterization method that is used to provide values for intrinsic material parameters that control leaching of selected inorganic and organic substances under equilibrium conditions. This test method is intended as a means for obtaining a series of extracts of a solid material (i.e., the eluates or leachates), which may be used to estimate the liquid-solid partitioning (e.g., solubility and release) of constituents as a function of pH under the laboratory conditions described.

This method is not applicable for characterizing the leachability of volatile organic substances or semi-volatile organic substances with very low water solubility.

This method is not for use under the Hazardous Waste Regulation for the classification of hazardous wastes (see TCLP) or for determining suitability for disposal in a secure landfill (see MLEP).

Method Summary

This method consists of a minimum of three extractions of a soil in dilute acid or base and deionized water at a 20:1 fluid to soil (dry weight) ratio. A schedule of acid and base additions is formulated from a pre-test titration curve or from prior knowledge to estimate the required equivalents of acid or base per gram of sample to be added to the series of extraction vessels so as to yield three eluates having final pH values of 5.0 ±0.5, 7.0 ±0.5, and 9.0 ±0.5, plus a fourth at the natural soil eluate pH if it is outside 4.5 to 9.5. Achieving the target pH values may be difficult and may require several iterations. More than three samples may be run initially in order to increase the likelihood of meeting the target pH values. In addition to the three (or four) required test extractions, two method blanks (low and high pH) without solid samples are carried through the procedure in order to verify that analyte interferences are not introduced as a consequence of reagent impurities or equipment contamination. A Lab Control Sample (lowest pH only) is also required to verify analyte recovery. Extraction bottles are tumbled in an end-over-end fashion for 48 hours. At the end of the contact interval, the liquid and solid phases are roughly separated via settling or centrifugation. Extract pH, conductivity (i.e., specific conductance), and oxidation-reduction potential (ORP) measurements are then made on an aliquot of the liquid phase and the remaining bulk of the eluate is clarified by pressure filtration or vacuum filtration. Analytical samples of the filtered eluate are collected and preserved as appropriate for the desired chemical analyses. The eluate concentrations of constituents of potential concern (COPCs) are determined and reported. In addition, COPC concentrations may be plotted as a function of eluate pH and compared to QC and assessment limits for the interpretation of method results.

This method is prescriptive. It must be followed exactly as described. Where options or minor deviations are permitted, these are indicated in the text.

Instrumental analysis for parameters of interest may be conducted using any BC ENV approved instrumental technique. MDLs vary substantially by technique employed. For lowest detection limits, ICPMS is recommended for analysis of most metals, and CVAAS or CVAFS is recommended for analysis of mercury.

Parameter List and MDL(s)

Standard Metallic Analytes	CAS Number
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Chromium, Hexavalent	18540-29-9
Cobalt	7440-48-4
Copper	7440-50-8
Lead	7439-92-1
Manganese	7439-96-5
Molybdenum	7439-98-7
Nickel	7440-02-0
Selenium	7782-49-2
Uranium	7440-61-1
Vanadium	7440-62-2
Zinc	7440-66-6

SVOC Analytes	CAS Number
Diisopropanolamine (DIPA)	110-97-4
Ethylene Glycol	107-21-1
Nonylphenol & Nonylphenol Ethoxylates (see BC Lab Manual method for definition)	n/a
Pentachlorophenol (PCP)	7440-23-5
Perfluorooctanesulfonic acid (PFOS)	126-33-0
Phenol	108-95-2
Sulfolane	126-33-0

Important Note: Of the above parameters, only metals and PCP require leaching at all three pH levels (or four where natural pH leaching is required). The others require only one leach at the natural soil pH.

Leachability of other prescribed substances from CSR Schedule 3.1 Parts 2 and 3 may also be assessed by this procedure if permitted under Protocols 2 or 13 or if acceptable to the Director.

EMS Method Code

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil

Interferences and Precautions

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each analytical method to be used for specific guidance on instrumental QC procedures.

Sample Handling and Preservation

Containers: As per table below. 2 × 500 mL soil jars recommended. A minimum of 500 grams dry weight equivalent sample is required for the test.

Sample Collection: Samples should be collected in such a way as to exclude particle sizes >9.5 mm, where possible. Sampling should be representative and reproducible.

Preservation:

Soil Samples: None.

Leachates: For metals, preserve with HNO_3 (pH < 2). Preserve leachates for organics with sodium bisulfate (pH < 2) to extend hold time to 14 days. Preserve only after filtration has been completed.

Analytes	Leaching Container	Filter*	Comments
Metals	Glass or Plastic	0.45 µm	-
SVOC Analytes	Glass	Glass Fibre	-
PFOS	Glass or Polypropylene	Glass Fibre	No Teflon™ materials or coatings of any kind may be used.

*Filters should be tested for compatibility (no adsorption or leaching of analytes of interest).

Stability

Holding Times:

Analytes	Soil Hold Time	Extract Hold Time	Preservative
Metals	180 days	180 days	HNO_3 to pH <2
Electrical Conductivity (EC)	unlimited	28 days	none
SVOC Analytes (including PFOS)	14 days	14 days	$NaHSO_4$ to pH <2
		7 days	none
pH, ORP	180 days	1 hour	none

Storage:

Soil Samples: Store soils refrigerated at ≤6°C. For metals and inorganics only, soils may be stored at ambient temperature.

Leachates: Store leachates refrigerated at ≤6°C. For metals and inorganics only, leachates may be stored at ambient temperature.

Procedure

1. Reagents

Deionized Water (interference-free)

2.0 N Nitric Acid (HNO_3): Trace Metals grade, or as required to sufficiently control background metal concentrations. Alternative solution normalities may be used as necessary. In such cases, the amounts of HNO_3 solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions.

1.0 N Potassium Hydroxide (KOH): ACS Grade or better. Alternative solution normalities may be used as necessary. In such cases, the amounts of KOH solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions.

2. Homogenization

Analysts are advised to take reasonable measures to ensure that the sample as received is homogenized to the extent practical, prior to employment of this method. If the heterogeneity of the sample is suspected as the cause of unacceptable precision in replicate test results or is considered significant based on professional judgment, the sample mass used in the test procedure may be increased to a greater minimum dry mass than 50 g with the amount of extractant increased proportionately to maintain the designated liquid/solid ratio (L/S).

3. Moisture Content

Dry approximately 10 g of homogenized sample to a constant weight at 105 ±5°C as per the BC Environmental Laboratory Manual moisture content method.

3.1 Calculate the solids content as follows:

SC = Mdry / Mtest

Where:

SC = solids content of "as-tested" material (g-dry/g)

Mdry = mass of dry material specified in the method (g-dry)

Mtest = mass of "as-tested" solid equivalent to the dry-material mass (g)

3.2 Calculate the moisture content (wet basis) as follows:

MCwet = (Mtest - Mdry) / Mtest

Where:

MCwet = moisture content on a wet basis (gH_2O/g) (Multiply x100 to convert units to percent moisture.)

Mdry = mass of dry material specified in the method (g-dry)

Mtest = mass of "as-tested" solid equivalent to the dry-material mass (g)

4. Particle Size Reduction

This method is intended for the characterization of soils (as opposed to wastes). Particle size reduction is not required or recommended. As-received samples are mixed well and subsamples are taken, avoiding particles > 9.5 mm.

5. Pre-test Titration (Optional)

In order to conduct the parallel batch test in Section 7, a schedule of acid and base additions may be formulated from a pre-test titration. This section describes the procedure for obtaining a titration curve of the test material (note: this step is not necessary for semi-volatile organic analytes except for PCP, since leaching of

these analytes is only required at the natural soil pH). Note that test results are required for pH, ORP, and conductivity for a soil eluate with no added acid or base, taken from either a pre-test sample or from a full-scale natural pH sample extraction.

Conduct a 5-point parallel extraction test using 10 g dry weight equivalent samples. Prepare 5 bottles each containing as-received soil (10 g dry weight) plus 20 meq base, 10 meq base, 20 meq acid, 10 meq acid, and zero acid or base. Add sufficient water to achieve a 20:1 liquid:soil ratio, taking into account the moisture content of the sample.

For example:

If sample has 20% moisture = 80% solids content (SC = 0.80), prepare the test sample containing 20 meq base as follows:

Weigh 10/0.8 = 12.5 g sample as received. Add 50 mL DI water.

Add 20 mL 1.0 N KOH

(1.0 N KOH = 1000 meq/L. 20 meq = 20/1000 = 0.020 L = 20 mL 1.0 N KOH.)

Add 200 - 50 - 20 - 2.5 = 127.5 mL DI water to achieve a 20:1 ratio.

200 ml = required final volume

50 mL = water added initially

20 mL = volume of base added

2.5 mL = volume of water in the 12.5 g sample

Tumble the samples as per Section 7. Measure the pH, ORP, and conductivity within 1 hour from completion of tumbling. The pH from the test sample with no acid or base added may be used to report the natural soil eluate pH (for section 7.1).

5.1 Plot pH vs. meq of acid and base added and interpolate to estimate the meq of acid and base required to achieve the target pH values of 5, 7, and 9.

5.2 Additional pH tests using smaller additions of acid and base may be helpful if the initial curve does not provide sufficient definition to accurately estimate the required additions.

6. Formulation of Acid and Base Additions Schedule

A schedule of acid and base additions is used in the main extraction procedure (Section 7) to set up three or more extractions of the test material plus two method blanks and an LCS. Based on either prior knowledge of the acid/base titration curve of the sample or the results of the pre-test titration procedure in Section 5, formulate a schedule of test extractions using the following steps.

6.1 Calculate and record the amount of "as-tested" material equivalent to the dry-material mass of 50 g as follows:

Mtest = Mdry / SC

Where:

Mtest = mass of "as-tested" solid equivalent to the dry-material mass (g) Mdry = mass of dry material specified in the method (g-dry)

SC = solids content of "as-tested" material (g-dry/g)

6.2 Determine the acid volumes and base volumes required to achieve the target final pH of 5.0 ±0.5, 7.0 ±0.5, and 9.0 ±0.5. The required volumes may be

estimated as follows. Prior knowledge, experience, or other estimation techniques may also be used:

Va/b = (Eqa/b × F) / Na/b

Where:

Va/b = volume of acid or base to be used (mL)

Eqa/b = equivalents of acid or base selected for the target pH as determined from the pre-test titration curve or other techniques (meq/g sample) remembering that 10 g is used (by default) for the pre-test and routinely 50 g is used for the test:

F = scale-up factor, mass used in test (g) / mass used in pre-test (g), default = 5

Na/b = normality of the acid or base solution (meq/mL)

6.3 Calculate the volume of moisture contained in the "as tested" sample as follows:

VW, sample = Mtest × (1 - SC)

Where:

VW, sample = volume of water in the "as tested" sample (mL)

Mtest = mass of "as-tested" solid equivalent to the dry-material mass (g)

SC = solids content of "as-tested" material (g-dry/g)

6.4 Calculate the volume of deionized water required to bring each extraction to a L/S of 20 mL/g-dry solid as follows:

VRW = Mdry × L/S − VW,sample − Va/b

Where:

VRW = volume of deionized water required to complete L/S (mL)

Mdry = mass of dry material specified in the method (g-dry)

L/S = liquid-to-dry-solid ratio (20 mL/g)

VW, sample = volume of water in "as tested" sample (mL) Va/b = volume of acid or base for the extraction recipe (mL)

6.5 Method Blanks and LCS

In the schedule table, include two additional extractions for processing Method Blanks.

Method Blank extractions are performed using the same equipment, reagents, and extraction process as the test samples, but without solid sample.

The Method Blanks and LCS should include:

a) MBacid: deionized water + maximum volume of acid used

b) MBbase: deionized water + maximum volume of base in the schedule

c) LCS: deionized water + maximum volume of acid used + a spike of all the analytes of interest.

7. Extraction Procedure:

Use the schedule of acid and base additions (Section 6) as a guide to set up the tests as follows:

7.1 Place the dry equivalent mass (50 ±0.5 g) of the "as tested" sample, calculated above, into each of the required extraction test vessels (minimum three). If the natural pH of the sample eluate is unknown or is outside the range of pH 4.5–9.5

(as determined in Section 5 or otherwise), or if EC and ORP have not already been measured at the natural soil pH, then include a natural pH extraction test where no acid or base is added.

NOTE: Do NOT put any solid material (e.g., synthetic or clean soil matrix) in the method blank or LCS extraction vessels.

7.2 Add 200 ±5 mL of deionized water to both the test sample and Method Blank and LCS vessels.

7.3 Add and record the appropriate volume of acid or base (±2% of target value) to each vessel to achieve the target pH.

7.4 Taking into account the moisture content contributed by the sample, the 200 mL already added and the volume of acid or base, add the appropriate volume of deionized water (±5% of target value) to the test samples and Method Blank and LCS samples to achieve the required 20:1 liquid:solid ratio.

7.5 Tighten the leak-proof lid on each bottle and tumble all extraction vessels (i.e., test samples, Method Blanks and LCS's) in an end-over-end fashion at a speed of 30 ±2 rpm at 23 ±2°C for 48 ±4 hours. Remove the extraction vessels from the rotary tumbler.

7.6 For each extraction vessel, decant a small portion of unpreserved, unfiltered eluate into a secondary container for pH and ORP measurement. Measure and record the pH and ORP of the extracts within 1 hour of the completion of tumbling to avoid neutralization of the solution due to exposure to carbon dioxide, especially when alkaline materials are tested.

NOTE: ORP measurement is required for potential evaluation of whether oxidation is likely to change the liquid-solid portioning (LSP) of COPCs.

NOTE: If the final pH is > ±0.5 units from the target, the test must be repeated with adjusted conditions until all 3 target pH levels have been achieved within ±0.5 pH units. In rare cases, it may not be possible to achieve all 3 target pH levels (depending on the pH and buffering characteristics of the test sample). If one or more pH target(s) cannot be achieved after multiple trials, test results must be qualified on the report.

7.7 Clarify the eluates (prior to filtration) by allowing the bottles to stand or centrifuge the extraction vessels if required to achieve a clear extract that can be filtered (e.g., 3000–4000 rpm for 10–30 minutes using a standard benchtop centrifuge).

7.8 Separate the solid from the remaining liquid in each extraction vessel by pressure or vacuum filtration through a clean 0.45 µm pore-size membrane (metals, inorganics) or glass fibre filter (organics). The filtration apparatus may be exchanged for a clean apparatus as often as necessary until sufficient liquid has been recovered to conduct the required tests. If multiple filters are required for any samples in the batch, the same treatment should be applied to the Method Blank.

7.9 Immediately preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed. Since samples for metals are filtered and preserved, and because dissolved phase metal concentrations in the leachates are intended for measurement, digestion is not necessary prior to analysis unless turbidity is observed in the filtrate (i.e., due to precipitation after filtration and/or preservation). Filtration and preservation must be completed within no more than 4 hours of the completion of tumbling time.

Quality Control

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	Two per batch (max 20 samples) at high and low pH levels	Less than reported DL
Lab Control Sample (LCS); spiked post-extraction	One per batch (max 20 samples) at low pH level	80%–120% (metals & inorganics) 60–140% (organics)
Lab Duplicates (DUP)	One per batch (max 20 samples)	<50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS); spiked post-extraction	Optional	None

If DQOs are not met, repeat testing or report qualified test results.

Method Performance Characteristics

Typical precision is tabulated below (taken from US EPA Method 1313). Actual precision achieved will vary with sample matrix and instrumental analysis method used.

Analyte	Symbol	Repeatability		Reproducibility	
		Median $\%RSD_r$	IQR $\%RSD_r$	Median $\%RSD_R$	IQR $\%\ RSD_R$
Antimony	Sb	16%	12–25%	33%	24–45%
Arsenic	As	19%	13–24%	47%	37–61%
Barium	Ba	10%	7–15%	22%	18–36%
Boron	B	7%	5–9%	12%	8–21%
Calcium	Ca	5%	4–11%	9%	6–28%
Molybdenum	Mo	15%	6–23%	30%	18–46%
Selenium	Se	9%	6–13%	21%	18–31%
Vanadium	V	10%	6–12%	27%	23–41%

References

US EPA Method 1313, Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure, Revision 0, October 2012.

Revision History	Dec 20, 2019	Method revised such that final pH targets must be met within ±0.5 pH units (or qualified in rare cases where all targets cannot be achieved). Clarified that pre-test procedure is optional; other procedures or prior knowledge may be used to estimate volumes of acid and based required to achieve final pH objectives.
	Sept 15, 2017	First version. Method was designed by the CSAP Leachate Testing Procedure Working Group, with translation into a working method by BCELTAC.

Leachability of Volatile Organic Compounds (VOCs) in Soil

Parameter

Liquid-Solid Partitioning (Leachability) potential of volatile organic compounds (VOCs) in soil samples

Analytical Method

Extraction of as-received solid material with a dilute buffered aqueous solution of glacial acetic acid and sodium hydroxide (pH 4.93 ±0.05) using the Zero Headspace Extraction technique from the EPA Method 1311 Toxicity Characteristic Leaching Procedure.

Introduction

This method is intended to be used as part of an environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness, and site remediation options.

This method is a leaching characterization method that is used to provide values for intrinsic material parameters that control leaching of selected volatile organic species under equilibrium conditions. This test method is intended as a means for obtaining an extract of a solid material (i.e., the eluate), which may be used to estimate the liquid-solid partitioning (e.g., solubility and release) of constituents under the laboratory conditions described.

The Zero Headspace Extraction (ZHE) portion of EPA Method 1311 must be used as written, except for modifications as noted herein.

This method is not applicable for characterizing the leachability of metals, inorganics, or semi-volatile organic substances.

This method is not for use under the Hazardous Waste Regulation for the classification of hazardous wastes (see EPA 1311) or for determining suitability for disposal in a secure landfill (see MLEP).

Method Summary

This method follows the EPA Method 1311 TCLP procedure for Zero Headspace Extraction (ZHE) of volatile organic compounds from soil samples. The EPA 1311 Method is followed exactly, except that no particle size reduction is done, and alternative hold times, sample storage requirements, and QC requirements are used as described herein.

The EPA 1311 ZHE procedure extracts 25 gram samples of soils in a zero headspace extraction device for 18 ±2 hours, tumbled in a rotary extraction box at 30 ±2 rpm at 23 ±2 ºC, using a 20:1 fluid to soil (dry weight) ratio with extraction fluid #1 from the TCLP method. Extraction fluid #1 is a dilute solution of glacial acetic acid and sodium hydroxide with pH of 4.93 ±0.05. Following the leaching procedure, extracts are pressure filtered prior to preservation and analysis for VOCs. Instrumental analysis for parameters of interest may be conducted using any appropriate BC MOE approved instrumental analysis technique (normally Headspace or Purge and Trap with GCMS detection, which provides low detection limits with few interferences).

The leachate concentrations of constituents of potential concern (COPCs) are determined and reported.

MDL(s) and EMS Analyte Code(s)

Analytes	CAS Number	Approx MDL (µg/L)	EMS Analyte Code
benzene	71-43-2	1.0	n/a
ethylbenzene	100-41-4	1.0	n/a
methanol	67-56-1	10–50	n/a
naphthalene	91-20-3	1.0	n/a
tetrachloroethylene	127-18-4	1.0	n/a
toluene	108-88-3	1.0	n/a
trichloroethylene	79-01-06	1.0	n/a
xylenes, total	1330-20-7	2.0	n/a

Leachability of other prescribed substances from CSR Schedule 3.1 Parts 2 and 3 may also be assessed by this procedure if permitted under Protocols 2 or 13 or if acceptable to the Director.

EMS Method Code

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil

Interferences and Precautions

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each analytical method to be used for specific guidance on instrumental QC procedures.

Sample Handling and Preservation

Containers: Glass soil jars, packed tightly to minimize headspace. 125–250 mL recommended.

Sample Collection: Samples should be collected in such a way as to exclude particle sizes >9.5 mm, where possible. Sampling should be representative and reproducible. Pack soil jars as fully as possible to minimize headspace / pore space. Pack samples on ice as quickly as possible (to at least ≤ 10ºC, ideally to ≤ 6ºC if possible). Transport as soon as possible to the laboratory for commencement of testing or freeze to ≤ -10ºC. If samples will be frozen, leave an air gap prior to freezing of ~5–10% of the container volume to allow for expansion, to minimize the chance of breakage.

Preservation:

Soil Samples: No chemical preservation is used. Zero headspace (or minimized headspace) and cold storage minimizes loss of volatiles prior to analysis.

Leachates: Preserve leachates with solid sodium bisulfate ($NaHSO_4$) to pH < 2. Preserve only after filtration has been completed.

Stability

Holding Times:
Soil samples must be leached within 48 hours from time of sampling, or within 14 days if frozen within 48 hours of sampling (to ≤ -10ºC). Field methanol preservation is not possible for this test, so hold times must be minimized. The EPA 1311 hold times for VOCs are not used for this method, to maximize consistency with standard BC MOE protocols for VOCs in soils. Leachates preserved with $NaHSO_4$ must be analyzed within 14 days of preservation.

Storage:

Soil Samples:
Store soils refrigerated at ≤6°C (or frozen at ≤ -10ºC) at the laboratory, and at ≤ 10ºC during transport to the laboratory. If samples have been frozen for preservation purposes, thaw in a refrigerator at ≤ 6°C as close as possible to the time the test will be initiated (no more than 24 hours). If samples will be frozen, leave an air gap prior to freezing of ~5–10% of the container volume to allow for expansion, to minimize the chance of breakage. After initial sub-sampling it is recommended to freeze remaining soil immediately (if within hold time) to permit re-analysis.

Leachates: Store leachates refrigerated at ≤6°C.

Procedure

Follow the Zero Headspace Extraction procedure from the US EPA 1311 TCLP Method without modification, except for differences noted and prescribed in this document.

Particle size reduction as described in EPA 1311 is not required or recommended. Particle size reduction within the 1311 method may cause significant losses of COPCs and is intended for heterogeneous waste samples, whereas this method is intended only for use with soils.

Quality Control

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS); spiked post-extraction	One per batch (max 20 samples)	60–140%
Lab Duplicates (DUP); includes leaching procedure	One per batch (max 20 samples)	<50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS); spiked post-extraction	Optional	None

*If DQOs are not met, repeat testing or report qualified test results.

References

US EPA SW 846 Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, US EPA Office of Solid Waste.

Revision History

Sept 15, 2017 First version. Method was designed by the CSAP Leachate Testing Procedure Working Group, with translation into a working method by BCELTAC.

Lipid Content in Animal Tissue

Parameter	Lipid (fat) content
Analytical Method	Extraction, gravimetric
EMS Code	a) units = µg/g **LIPI X232** b) units = % **LIPI X269**
Introduction	Many pesticides are lipophilic; therefore, it is often of interest to express results on a 'concentration in lipid' basis. This requires determination of the lipid content.
Summary	Lipid material is extracted from the tissue with a suitable solvent, the solvent is removed by heating and the residue is determined gravimetrically.
MDL	0.1%
Matrix	Animal Tissue.
Interferences and Precautions	None listed
Sample Handling and Preservation	Plastic or glass wide-mouth bottles, Whirl-Pak® bags. No preservation required; samples may be stored frozen.
Stability	M. H. T. = indefinite if hard frozen.
Principle or Procedure	Lipid material is soluble in organic solvents.
Precision	None listed
Accuracy	None listed
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Nonylphenols and Ethoxylates in Water by LC/MS/MS

Parameter Nonylphenol and Nonylphenol Ethoxylates (TEQ)

MDLs and EMS Analyte Codes	Analytes	CAS#	Approx. MDL µg/L	EMS Analyte codes
	NP (Nonylphenol)	84852-15-3	0.4	N032
	NP1EO (Nonylphenol Monoethoxylate)	104-35-8	0.4	
	NP2EO (Nonylphenol Diethoxylate)	20427-84-3	0.4	
	NP3EO (Nonylphenol Triethoxylate)		0.5	
	NP4EO (Nonylphenol Tetraethoxylate)		0.5	
	NP5EO (Nonylphenol Pentaethoxylate)		0.5	
	NP6EO (Nonylphenol Hexaethoxylate)		0.5	
	NP7EO (Nonylphenol Heptaethoxylate)		0.5	
	NP8EO (Nonylphenol Octaethoxylate)		0.5	
	OP (Octylphenol)	140-66-9	0.4	
	OP1EO (Octylphenol Monoethoxylate)	2315-67-5	0.4	
	OP2EO (Octylphenol Diethoxylate)	2315-61-9	0.4	
	OP3EO (Octylphenol Triethoxylate)		0.5	
	OP4EO (Octylphenol Tetraethoxylate)		0.5	
	OP5EO (Octylphenol Pentaethoxylate)		0.5	
	OP6EO (Octylphenol Hexaethoxylate)		0.5	
	OP7EO (Octylphenol Heptaethoxylate)		0.5	
	OP8EO (Octylphenol Octaethoxylate)		0.5	
	Nonylphenol and Nonylphenol Ethoxylates (TEQ)		2.5	

Analytical method SPE extraction - LC/MS/MS

Introduction

This method is for the quantitative determination of nonylphenol, octylphenol, and their ethoxylates in water samples by LC/MS/MS.

Endocrine disruptors (EDs), such as nonylphenol, affect reproduction in humans, as well as wildlife. Thus, the need to monitor EDs in wastewater is of importance for public safety. For more than forty years alkylphenols such as NP, NPE, OP, and OPE have been used as detergents, emulsifiers, wetting agents and more. Their presence in the environment is solely due to human activities, and mainly from WWTPs (wastewater treatment plant) and direct discharge. Over 80% of alkylphenol produced are nonylphenol based compounds. The rest are mostly octylphenol based compounds.

NPEs are degraded to shorter chain nonylphenol ethoxylates as well as shorter nonylphenol ethoxycarboxylates under aerobic condition, before being biodegraded to nonylphenol. Shorter ethoxylate chain alkylphenols have greater toxicity than longer ones. CCME describes Toxic Equivalent Factors from Environment Canada for NPnEO ($1 \leq n \leq 8$) and OPnEO($1 \leq n \leq 8$) as half the relative toxicity of NP and OP.

Certified nonylethoxylate and octylethoxylate standards greater than NP3EO and OP2EO are almost nonexistent and therefore characterization of ethoxylate distribution in technical grade standards such as nonoxynol and triton-X are suitable alternatives.

Method summary

Water samples are extracted using polymeric sorbent SPE. Cartridges are cleaned with dichloromethane (DCM) to eliminate all alkylated phenols leftover from manufacturing, packaging or handling. Then, SPE sorbents are conditioned with methanol and acidified water. Samples are spiked with a labelled surrogate solution and loaded onto the SPE. After washing the sorbent beds with a methanol solution in water, they are vacuum dried. Elution is done by percolating a methanol/DCM solution through the SPE cartridges. A labelled internal standard is added before LC/MS/MS analysis.

Matrix

Freshwater, groundwater, seawater, wastewater.

Interferences and Precautions

Contaminants present in solvents, reagents, sample containers, or sample processing equipment may cause interferences or yield artefacts. Plastic containers should be avoided. High purity grade solvents should be used.

Matrix dependant interferences can cause signal suppression or signal enhancement in the Electrospray Ionisation source (ESI). Extract dilution may help to damper these effects.

A method blank helps to demonstrate a contamination free procedure. Background subtraction of method blank is not allowed.

Solvent blanks should be run before and after LC/MS/MS analysis to clean the system of alkylphenol contaminants.

Solvent blanks should also be run after highly contaminated samples to eliminate carryover.

Sample Handling and Preservation

Container: Amber glass bottles (consult laboratory for volume requirements).

Preservation: Acidify to pH <2 with HCl or sodium bisulfate ($NaHSO_4$) to extend hold times to 14 days.

Stability

Holding time:

Sample: Extract unpreserved samples within 7 days of sampling. Hold time is extended to 14 days if preserved.

Extract: Analyze extract up to 40 days after extraction.

Storage: Refrigerate samples at ≤6°C. Keep extracts below ≤6°C.

Procedure

Calibration stock:

Individual standards can be purchased as neat material or in solution but are only available for Nonylphenol, Octylphenol and mono- and di- ethoxylates. A technical grade mix must be used to calibrate for the remainder of the ethoxylates. This requires the technical grade mix to be characterized initially by HPLC to determine the ethoxylate concentration distribution. All identifiable isomers (branched and linear) of each substance class must be included with this analysis. Individual mono- and di-ethoxylate standards should be used to provide a more accurate quantification than technical grade mix for the primary components.

Extraction:

Shake samples prior to sub-sampling. If the amount of particulate matter in a sample is low enough to prevent clogging of the SPE cartridge (labs may establish a suitable limit, which may not exceed 1% by estimation), then a representative portion of the sample is extracted in total by SPE, using the elution solvent to extract the particulate fraction. Samples with higher levels of particulate are filtered on glass fibre filters. Filters with particulate should be extracted using the soil

extraction protocol, with extracts combined before SPE extraction (or analyzed separately, with results combined to reflect the total concentration). Where extracts from the aqueous and particulate fractions will be combined for analysis, the surrogate(s) from the aqueous fraction should not be added to the particulate fraction (use of a secondary surrogate to independently monitor the particulate fraction is recommended).

Samples are acidified and representative sub-samples are measured for extraction. Sub-samples are spiked with labelled surrogate solution.

SPE cartridges are mounted on a vacuum manifold and cleaned by percolating DCM through the cartridge. DCM is flushed away under full vacuum. SPE are conditioned with methanol and acidified water. Cartridges should not go dry during or after conditioning. Samples are loaded on to the cartridges at a rate of 2–5mL per minute.

Once all the samples have completely passed through the SPE beds, flasks are washed with a methanol/water solution and the solutions are added to the cartridges and eluted. SPE cartridges are dried under full vacuum for 15–30 minutes, until sorbent is visibly dry and free flowing.

Elution is done by percolating a methanol/DCM solution. Elution solution is drawn in the sorbent and left to soak for 1 minute before percolation. Extracts are diluted to volume with elution solution. A labelled internal standard solution is added to extracts before LC/MS/MS analysis.

UPLC Parameters

Column: ODS UPLC column
Mobile Phase A: Ammonium acetate in water
Mobile Phase B: Acetonitrile
Mode: Gradient elution

MS/MS Parameters

MS/MS transitions:

Analytes	**Transitions (m/z)**	**ESI Polarity**
NP	219->133;147	Neg.
NP1EO	282->127;265	Pos.
NP2EO	326->183;121	Pos.
NP3EO	370->227;353	Pos.
NP4EO	414->271;397	Pos.
NP5EO	458->315;440	Pos.
NP6EO	502->89;485	Pos.
NP7EO	546->89;529	Pos.
NP8EO	591->89;573	Pos.
OP	205->133;106	Neg.
OP1EO	268->113;250	Pos.
OP2EO	312->295;183	Pos.
OP3EO	356->339;295	Pos.
OP4EO	400->383;271	Pos.
OP5EO	444->427;315	Pos.
OP6EO	488->471;359	Pos.
OP7EO	532->515;403	Pos.
OP8EO	576->559;447	Pos.

Calculations

Nonylphenol and Nonylphenol Ethoxylates (TEQ) = ([NP] × 1) + ([NP 1EO] × 0.5) + ([NP2EO] × 0.5) + ([NP3EO] × 0.5) + ([NP3EO] × 0.5) + ([NP4EO] × 0.5) + ([NP5EO] × 0.5) + ([NP6EO] × 0.5) + ([NP7EO] × 0.5) + ([NP8EO] × 0.5) + ([OP] × 1) + ([OP1EO] × 0.5) + ([OP2EO] × 0.5) + ([OP3EO] × 0.5) + ([OP4EO] × 0.5) + ([OP5EO] × 0.5) + ([OP6EO] × 0.5) + ([OP7EO] × 0.5) + ([OP8EO] × 0.5)

For purposes of the TEQ calculation, use one-half of the reported detection limit for non-detected test results.

Toxic Equivalency Factors (TEFs) for NP, NPEs, OP, OPEs (relative to NP) for BC MOE prescribed substances.	
Nonylphenol (NP)	1
NPnEO (1≤n≤8)	0.5
Octylphenol (OP)	1
OPnEO (1≤n≤8)	0.5

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Lab Control Samples or Reference Materials must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement:

Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Average accuracy must be between 70–130% for all analytes.

Precision Requirement:

Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement:

Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	60–140%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤30% RPD [or within 2x reported DL for low level results]
Surrogate Compounds	All samples	50–140%

Matrix Spike	One per batch (max 20 samples)	50–140%
Internal Standards	All samples	Peak area counts for all internal standards in all injections must be within ±50% of the average peak area calculated during the initial calibration.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80–120%
Continuing Calibration Verification (CCV)	One per batch (max 20 samples)	70–130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Blank: Required. An aliquot of reagent water that is treated exactly like a sample including exposure to equipment, solvents and reagents, sample preservatives, internal standards and surrogates that are used in the analysis batch.

Laboratory Duplicates: Required. Data quality objectives are listed above.

Laboratory Control Sample (Method Spike): Required. Prepare a Laboratory Control Sample by fortifying a field sample with known concentrations of the analytes.

Surrogate Compounds: Required. Suggested: 4-n-NP-$^{13}C_6$, NP3EO-$^{13}C_6$ and/or OP1EO-$^{13}C_6$.

Calibration Verification Standard (CVS): Required. A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. A mid-point calibration standard must be analyzed throughout the instrument run at least every 20 samples and at the end of the run to monitor calibration drift.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be done by LC/MS/MS with a MRM transition for each compound, except Nonylphenol and Octylphenol may be analyzed by GC/MS or GC/MS/MS.

Confirmation of LC/MS/MS test results must be done with a second MRM transition.

All identifiable isomers of each nonylphenol substance class (branched and linear) must be included with this analysis.

Different surrogate standards must be used with ESI negative and ESI positive modes. Suggested: 4-n-NP-$^{13}C_6$, NP3EO-$^{13}C_6$ and/or OP1EO-$^{13}C_6$.

Different internal standards must be used with ESI negative and ESI positive modes. Suggested: BPA-d_{16}, NP2EO-$^{13}C_6$.

A representative portion of any particulate matter present in samples must be extracted and analyzed. Where particulate matter exceeds 1% of sample volume (by estimation), it must be separated by filtration and extracted separately, with extracts or final results combined to give a total concentration.

TEQ calculations must be conducted as specified.

If this method is utilized for seawaters or brine samples, method validation for that matrix must be conducted prior to use using Matrix Spikes and/or Reference Materials.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

All performance requirements and QC requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

ASTM D7485-09. Determination of Nonylphenol, p-tert-octylphenol, Bisphenol A, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Liquid Chromatography/Tandem Mass Spectrometry, 2009.

CCME 2002. Canadian Water Quality for the Protection of Aquatic Life, Nonylphenol and its Ethoxylates, Canadian Council of Ministers of the Environment.

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.

Nonylphenols and Ethoxylates in Soil by LC/MS/MS

Parameter Nonylphenol and Nonylphenol Ethoxylates (TEQ)

MDLs and EMS Analyte Codes

Analytes	CAS#	Approx. MDL µg/g	EMS Analyte codes
NP (Nonylphenol)	84852-15-3	0.001–0.01	N032
NP1EO (Nonylphenol Monoethoxylate)	104-35-8	0.001–0.01	
NP2EO (Nonylphenol Diethoxylate)	20427-84-3	0.001–0.01	
NP3EO (Nonylphenol Triethoxylate)		0.001–0.01	
NP4EO (Nonylphenol Tetraethoxylate)		0.001–0.01	
NP5EO (Nonylphenol Pentaethoxylate)		0.001–0.01	
NP6EO (Nonylphenol Hexaethoxylate)		0.001–0.01	
NP7EO (Nonylphenol Heptaethoxylate)		0.001–0.01	
NP8EO (Nonylphenol Octaethoxylate)		0.001–0.01	
OP (Octylphenol)	140-66-9	0.001–0.01	
OP1EO (Octylphenol Monoethoxylate)	2315-67-5	0.001–0.01	
OP2EO (Octylphenol Diethoxylate)	2315-61-9	0.001–0.01	
OP3EO (Octylphenol Triethoxylate)		0.001–0.01	
OP4EO (Octylphenol Tetraethoxylate)		0.001–0.01	
OP5EO (Octylphenol Pentaethoxylate)		0.001–0.01	
OP6EO (Octylphenol Hexaethoxylate)		0.001–0.01	
OP7EO (Octylphenol Heptaethoxylate)		0.001–0.01	
OP8EO (Octylphenol Octaethoxylate)		0.001–0.01	
Nonylphenol and Nonylphenol Ethoxylates (TEQ)		0.01–0.1	

Analytical Method SPE extraction - LC/MS/MS

Introduction

This method is for the quantitative determination of nonylphenol, octylphenol, and their ethoxylates in soils and sediments samples by LC/MS/MS.

Endocrine disruptors (EDs), such as nonylphenol, affect reproduction in humans, as well as wildlife. Thus, the need to monitor EDs is of importance for public safety. For more than forty years alkylphenols such as NP, NPE, OP, and OPE have been used as detergents, emulsifiers, wetting agents and more. Their presence in the environment is solely due to human activities. Soil contamination is mainly from pesticide applications, or sewage and pulp and paper sludge application to agricultural fields. Over 80% of alkylphenol produced are nonylphenol based compounds. The rest is mostly octylphenol based compounds.

NPEs are degraded to shorter chain nonylphenol ethoxylates as well as shorter nonylphenol ethoxycarboxylates under aerobic condition, before being biodegraded to nonylphenol. Shorter ethoxylate chain alkylphenols have greater toxicity than longer ones. CCME describes Toxic Equivalent Factors from Environment Canada for NPnEO ($1 \leq n \leq 8$) and OPnEO($1 \leq n \leq 8$) as half the relative toxicity of NP and OP.

Certified nonylethoxylate and octylethoxylate standards greater than NP3EO and OP2EO are almost nonexistent and therefore characterization of ethoxylate distribution in technical grade standards such as nonoxynol and triton-X are suitable alternatives.

Method Summary

Solid samples are extracted by successive sonication before SPE cleanup. Samples are weighed in a glass tube, spiked with a labelled surrogate solution, covered with a methanol/DCM solution, and placed in a sonic bath for 60 minutes. Extraction is repeated and extracts are recovered. After centrifugation, extracts are diluted in acidified water. SPE cleanup follows the same steps as the water extraction protocol.

Samples are cleaned up using polymeric sorbent SPE. Cartridges are cleaned with dichloromethane (DCM) to eliminate all alkylated phenols leftover from manufacturing, packaging or handling. SPE sorbents are conditioned with methanol and acidified water.

Samples are loaded onto the SPE. After washing the sorbent beds with a methanol solution in water, they are vacuum dried. Elution is done by percolating a methanol/DCM solution through the SPE cartridges. A labelled internal standard is added before LC/MS/MS analysis.

Matrices

This method is applicable for determination of selected alkylphenols from soil and sediment samples.

Interferences and Precautions

Contaminants present in solvents, reagents, sample containers, or sample processing equipment may cause interferences or yield artefacts. Plastic containers should be avoided. High purity grade solvents should be used.

Matrix dependant interferences can cause signal suppression or signal enhancement in the Electrospray Ionisation source (ESI). Extract dilution may help to damper these effects.

A method blank helps to demonstrate a contamination free procedure. Background subtraction of method blank is not allowed.

Solvent blanks should be run before and after LC/MS/MS analysis to clean the system of alkylphenol contaminants.

Solvent blanks should also be run after highly contaminated samples to eliminate carryover.

Sample Handling and Preservation

Container: Glass jars, Teflon-lined lids, 125–250 mL recommended.

Preservation: No preservatives.

Stability

Holding Time:

Sample: Extract samples within 14 days after sampling.

Extract: Analyze extracts up to 40 days after extraction.

Storage: Store samples and extracts at ≤ 6C (freezing is acceptable).

Procedure

Calibration Stock:

Individual standards can be purchased as neat material or in solution but are only available for Nonylphenol, Octylphenol and mono- and di- ethoxylates. A technical grade mix must be used to calibrate for the remainder of the ethoxylates. This requires the technical grade mix to be characterized initially by HPLC to determine the ethoxylate distribution. All identifiable isomers (branched and linear) of each substance class must be included with this analysis. Individual mono- and di-ethoxylate standards should be used as to provide a more accurate quantification than technical grade mix for the primary components.

Extraction:

Representative sub-samples are weighed in a glass tube for extraction. Sub-samples are spiked with labelled surrogate solution, covered with a methanol/DCM 90:10 solution, and placed in a sonic bath for 60 minutes. Samples are centrifuged, and supernatants are collected in different flasks. Extraction is repeated by covering the sample with a methanol/DCM solution and placed in a sonic bath for another 60 minutes. After centrifugation and supernatant collection, extracts are diluted in acidified water for SPE cleanup.

SPEs are mounted on a vacuum manifold and cleaned by percolating DCM through the cartridge. DCM is flushed away under full vacuum. SPE are conditioned with methanol and acidified water. Cartridges should not go dry during or after conditioning. Diluted extracts are loaded on to the cartridges at a rate of 2-5mL per minute.

Once all the extracts have completely passed through the SPE beds, flasks are washed with a methanol/water solution and applied to the cartridges and eluted. SPEs are dried under full vacuum for 15–30 minutes, until sorbent is visibly dry and free flowing.

Elution is done by percolating a methanol/DCM solution. Elution solution is drawn into the sorbent and left to soak for 1 minute before percolation. Extracts are diluted to volume with elution solution. A labelled internal standard solution is added to extracts before LC/MS/MS analysis.

UPLC Parameters

Column: ODS UPLC column
Mobile Phase A: Ammonium acetate in water
Mobile Phase B: Acetonitrile
Mode: Gradient elution

MS/MS Parameters

MS/MS transitions:

Analytes	Transitions (m/z)	ESI Polarity
NP	219->133;147	Neg.
NP1EO	282->127;265	Pos.
NP2EO	326->183;121	Pos.
NP3EO	370->227;353	Pos.
NP4EO	414->271;397	Pos.
NP5EO	458->315;440	Pos.
NP6EO	502->89;485	Pos.
NP7EO	546->89;529	Pos.
NP8EO	591->89;573	Pos.
OP	205->133;106	Neg.
OP1EO	268->113;250	Pos.
OP2EO	312->295;183	Pos.
OP3EO	356->339;295	Pos.
OP4EO	400->383;271	Pos.
OP5EO	444->427;315	Pos.
OP6EO	488->471;359	Pos.
OP7EO	532->515;403	Pos.
OP8EO	576->559;447	Pos.

Calculations

Nonylphenol and Nonylphenol Ethoxylates (TEQ) = ([NP] × 1) + ([NP1EO] × 0.5) + ([NP2EO] × 0.5) + ([NP3EO] × 0.5) + ([NP4EO] × 0.5) + ([NP5EO] × 0.5) + ([NP6EO] × 0.5) + ([NP7EO] × 0.5) + ([NP8EO] × 0.5)+([OP] × 1) + ([OP1EO] × 0.5) + ([OP2EO] × 0.5) + ([OP3EO] × 0.5) + ([OP4EO] × 0.5) + ([OP5EO] × 0.5) + ([OP6EO] × 0.5) + ([OP7EO] × 0.5) + ([OP8EO] × 0.5)

For the purposes of the TEQ calculation, use one-half of the reported detection limit for non-detected test results.

Toxic Equivalency Factors (TEFs) for NP, NPEs, OP, OPEs (relative to NP) for BC MOE prescribed substances.	
NP	1
NPnEO (1≤n≤8)	0.5
OP	1
OPnEO (1≤n≤8)	0.5

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Lab Control Samples or Reference Materials must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Average accuracy must be between 70–130% for all analytes.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	60–140%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤50% RPD [or within 2x reported DL for low level results]
Surrogate Compounds	All samples	50–140%
Matrix Spike or RM	One per batch (max 20 samples)	50–140%
Internal Standards	All samples	Peak area counts for all internal standards in all injections must be within ±50% of the average peak area calculated during the initial calibration.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80–120%

Continuing Calibration Verification (CCV)	One per batch (max 20 samples)	70–130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Blank: Required. An aliquot of reagent water that is treated exactly like a sample including exposure to equipment, solvents and reagents, sample preservatives, internal standards and surrogates that are used in the analysis batch.

Laboratory Duplicates: Required. Data quality objectives are listed above.

Laboratory Control Sample (Method Spike): Required. Prepare a Laboratory Control Sample by fortifying a field sample with known concentrations of analytes.

Surrogate Compounds: Required. Suggested: 4-n-NP-$^{13}C_6$, NP3EO-$^{13}C_6$ and/or OP1EO-$^{13}C_6$.

Calibration Verification Standard (CVS): Required. A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. A mid-point calibration standard must be analyzed throughout the instrument run at least every 20 samples and at the end of the run to monitor calibration drift.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be done by LC/MS/MS with MRM transition for each compound, except that Nonylphenol and Octylphenol may be analyzed by GC/MS or GC/MS/MS.

For LC/MS/MS analysis, confirmation must be done with second MRM transition.

All identifiable isomers of each nonylphenol substance class (branched and linear) must be included with this analysis.

Different surrogate standards must be used with ESI negative and ESI positive modes. Suggested: 4-n-NP-$^{13}C_6$, NP3EO-$^{13}C_6$ and/or OP1EO-$^{13}C_6$.

Different internal standards must be used with ESI negative and ESI positive modes. Suggested: BPA-d_{16}, NP2EO-$^{13}C_6$.

TEQ calculations must be conducted as specified.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

All performance requirements and QC requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

ASTM D7485-16. Determination of Nonylphenol, p-tert-octylphenol, Bisphenol A, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Liquid Chromatography/Tandem Mass Spectrometry, 2016.

CCME 2002. Canadian Water Quality for the Protection of Aquatic Life, Nonylphenol and its Ethoxylates, Canadian Council of Ministers of the Environment.

Revision History	Sept 15, 2017	First version added to BC Lab Manual in support of 2017 CSR updates.

Oil and Grease (Mineral) in Solids by Ultrasonic Dichloromethane Extraction

Parameter

Oil and Grease (Mineral)

Analytical Method

Ultrasonic extraction into dichloromethane, treat with silica gel, followed by gravimetric analysis.

Introduction

Oil and Grease is any material recovered as a substance soluble in hexane. Unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oil and greases are defined by the method used for their determination. Although this method is suitable as a screening tool or indicator for most industrial wastewaters or treated effluents, sample complexity may result in either low or high estimations due to lack of analytical specificity and potential for interference.

Summary

A 15g solid sample is mixed with anhydrous sodium sulphate in a disposable honey jar and 50 mL of Dichloromethane is added. The jar is capped with a PTFE lined cap, sonified and gently shaken. The mixture is transferred through Na_2SO_4 + silica gel into a preweighed disposable 25 mm × 200 mm test tube. A portion of the extract is removed for TPH, if required. The oil and grease is determined gravimetrically.

MDL

100 µg/g

Matrix

Soil (marine), sediment solids (concrete, wood chips, etc.).

Interferences and Precautions

It may include material other than animal fats and mineral or vegetable oils (e.g.: sulphur compounds, certain organic dyes, and chlorophyll) extracted by the solvent from an acidified sample and not volatilized during the test. It is important that this limitation be clearly understood. Caution with interpretation of results is advised. The method is not applicable to measurement of low boiling fractions that volatilize at temperatures below 105°C. A high bias will be achieved for coextractives which are not oil and grease.

Sample Handling and Preservation

Bottle in 0.3 L amber glass.

Stability

Holding Time: extract the sample within 14 days of sampling and analyze within 28 days.

Storage: at 4°C until analyzed.

Procedure Apparatus

a) Ultrasonic Bath with a minimum power of 300 W and pulsing capability.

b) 125mL honey jars with PTFE lined caps.

c) Disposable glass 25 mm × 200 mm test tubes.

d) DriBlock with 25 mm insert blocks.

e) Nitrogen Blowdown Apparatus.

Reagents

a) Take a clean 125mL honey jar and weigh out a well-mixed 15g sample and record the weight to the nearest 0.01g.

b) Use a spatula and mix in an amount of anhydrous sodium sulphate (~15g) depending on the moisture content of the sample. Very moist samples are dried overnight at 40°C to reduce the amount of sodium sulfate required.

c) Add 50mL of the DCM for gravimetric analysis and place the jars in a sample tray in the ultrasonic bath. Turn on the Ultrasonic bath for 20 minutes. Remove the sample tray and gently shake the samples on a table shaker for 10 minutes.

d) Place a Whatman No. 40 filter in a glass funnel, fill the bottom 2/3 of the filter with activated silica gel and fill the top ⅓ of the filter with Na_2SO_4. Place the funnel into a preweighed (to 0.0001g) 25 mm × 200 mm disposable glass test tube and pour the extract through the filter. Rinse the jar with 2 × 10 mL portions of DCM. Discard the jar and keep the Teflon cap for washing and reuse. Place the tubes into the DriBlock at 35°C and start a gentle stream of Nitrogen with the blow down unit. After the sample is completely dried, cool the tubes in a desiccator for at least 1 hour. Measure and record the final weight to 0.0001g and discard the test tube.

Note: Tared 125 mL Erlenmeyer flasks and hot plate may be used in place of glass tubes and DriBlock.

Calculation

O&G Measured Gravimetrically.

$$\text{Min. O\&G (µg/g)} = \frac{1{,}000{,}000 \times (\text{Final Wt,g} - \text{Initial Wt,g})}{(\text{Wt,g of Sample} \times (100 - \%\text{Moisture})/100)}$$

Precision

Authentic samples at concentrations of 21 to 16,687 µg/g measured in duplicate gave standard deviation of 67 µg/g, with an estimated coefficient of variation of 3%.

Accuracy

Synthetic samples prepared by spiking sea sand with 500 and 2000 µg/g of motor oil gave recoveries of 99 and 87% recovery respectively. Synthetic samples spiked with 1000 µg/g each of motor oil and linseed oil gave recovery of 134% expressed as mineral oil and grease. Linseed oil spike should be removed by the silica gel treatment.

Quality Control

Blanks: 1 per batch or 1 in 14.

All balances should be calibrated with Class "A" weights.

References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, Third Edition, U.S. EPA, Method 3550A, November 1.

Revision Date

November 2002: Method adopted from Supplement #1. EMS Codes assigned.

Oil and Grease in Water by Hexane Extraction and Gravimetry — PBM

Parameters

Oil and Grease
Mineral Oil and Grease

EMS Codes & MDLs

The MDLs listed below are achievable for this method in a typical laboratory environment. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Compound	Approx MDL (mg/L)	EMS Code
Oil and Grease	2	0003 X055
Mineral Oil and Grease	2	N/A

Analytical Method

Liquid-liquid extraction with hexane, treatment with silica gel (for Mineral Oil and Grease only) and gravimetric determination (PBM).

Introduction

This method is applicable to the quantitative determination of Oil and Grease (hexane extractable material, HEM) and Mineral Oil and Grease (silica gel treated hexane extractable material) in water. Oil and Grease provides a measure of hexane extractable non-volatile oils and greases which may be of either petrogenic or natural origin. Mineral Oil and Grease determines only non-volatile, non-polar oils and greases. Most natural oils and greases (e.g., vegetable oils, animal fats) are polar, and are excluded from the Mineral Oil and Grease parameter.

Method Summary

A water sample is acidified to pH < 2 and extracted three times with hexane (or "hexanes") in a separatory funnel. The extract is dried with sodium sulfate, the solvent and any volatile components are evaporated, and the residue is weighed with a 4-place balance.

For Mineral Oil and Grease, polar material is removed by treatment of the hexane extract with activated silica gel prior to filtration, solvent evaporation, and gravimetric determination.

Matrix

Fresh Water, Wastewater, Saline Water

Interferences and Precautions

Hexane extractable material recovered by the Oil and Grease method may include non-volatile petroleum hydrocarbons, waxes, animal fats, mineral and vegetable oils, soaps, sulfur compounds, organic dyes, chlorophyll, etc.

Mineral Oil and Grease may include any of the above components that are sufficiently non-polar such that they are not irreversibly adsorbed to activated silica gel.

Caution is advised with the interpretation of results. This method is designed to fully recover most organic compounds with boiling points that are equal to or greater than that of n-hexadecane (nC_{16}; b.pt. 297ºC). It is not applicable to the measurement of low boiling organics like solvents or gasoline range fuels. The lighter portions of middle distillate petroleum fuels (e.g., diesels, fuel oils) may be partially lost during the solvent removal step of this method. A high bias may be achieved from co-extractives which are not oils or greases.

Samples with high solids content, i.e., TSS > 500 mg/L may result in a low bias due to sorption of the material onto the insoluble fraction.

Sample Handling and Preservation

Container:
1L Glass Bottle, wide mouth with PTFE-lined lid. Smaller volumes may be collected and extracted provided that the detection limit is raised accordingly. Field Duplicates require a second container.

Preservation:
pH < 2 using HCl or H_2SO_4

Stability

Holding Time:
Extract within 28 days of collection. Raw samples arriving at the laboratory should be preserved to pH < 2 upon receipt to inhibit microbial degradation.

Storage:
Samples should be kept at ≤ 10ºC during transport to the laboratory. Refrigerate samples at ≤ 6ºC prior to analysis.

Analytical Procedure

Detailed procedures are not provided in this method. Refer to the EPA Method 1664 for further guidance.

Samples should be visually assessed and checked for pH prior to extraction. If not already done, adjust sample pH to < 2 using HCl or H_2SO_4.

Sample volumes are measured gravimetrically or volumetrically, to at least the nearest 10 mL.

Samples are sequentially extracted with three aliquots of hexane in a separatory funnel. Samples are shaken vigorously for 2 minutes per extraction. The first aliquot of hexane is used to rinse the sample container so that its entire contents are transferred to the extraction vessel. The ratio of solvent to sample should be no less than 1:20, i.e., 50 mL of hexane (per extraction) per 1 L of sample. The solvent extracts are passed through a drying funnel containing anhydrous sodium sulfate and combined.

Emulsions frequently occur during the extraction of many oil and grease samples. When encountered, precautions must be taken to ensure that adequate extraction efficiency is obtained. Centrifugation, ultrasonication, and the addition of NaCl are recommended to separate emulsions.

For Oil and Grease, the extract is evaporated to dryness at ambient temperature (~20–25ºC). Following evaporation, residual water, solvent, and other volatiles are removed by heating in an oven at 50–60ºC for 30–60 minutes or by continued evaporation at ambient temperature, prior to gravimetric determination of the residue using at least a 4-place balance. If the final evaporation step is done at ambient temperature, gravimetric measurements must be done to constant weight (see prescriptive elements).

For Mineral Oil and Grease, the hexane extract is cleaned up with 100% activated silica gel (60 Angstrom pore size, ~70–230 mesh) using either an in-situ or column-based process. Extracts may be cleaned up directly after extraction or may be reconstituted into hexane after an initial Oil and Grease determination. Activate silica gel by drying at 200–250°C for at least 16 hours. A default amount of 3.0 ±0.3 grams of silica gel is recommended, which is generally assumed to have an adsorptive capacity for up to 100 mg of HEM. For samples that are known or expected to exceed 100mg of HEM, additional silica gel may be used, or a suitable quantitative portion of the extract may be treated with silica gel prior to the Mineral Oil and Grease analysis (if necessary, another portion of the extract may first be tested for Oil and Grease to determine the total HEM content). After silica gel treatment, the extract is filtered and then evaporated to dryness at ambient temperature (~20–25ºC). Following evaporation, residual water, solvent, and other volatiles are removed by heating

in an oven at 50–60ºC for 30–60 minutes or by continued evaporation at ambient temperature, prior to gravimetric determination of the residue using an analytical balance (4 place minimum). If the final evaporation step is done at ambient temperature, gravimetric measurements must be done to constant weight (see prescriptive elements).

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80–120% for both Oil and Grease and Mineral Oil and Grease.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤15% relative standard deviation (%RSD) for both Oil and Grease and Mineral Oil and Grease.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Lab Control Sample (LCS)	1 per batch (max 20 samples)	70–130% recovery
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Reference Material (optional)	1 per batch (max 20 samples)	N/A
Field Duplicates	Recommended	Not specified

* Minimum DQOs apply to individual QC samples, not averages at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met.

QC Details

Method Blank:
Extract an appropriate amount of reagent water adjusted to pH < 2 (i.e., 1L).

Lab Control Sample (LCS):
Extract an appropriate amount of spiking solution added to 1L of laboratory water adjusted to pH < 2. The spike formulation must be a 1:1 mixture of mineral oil (e.g., Nujol) and canola oil, made up in acetone so that it is miscible with the aqueous sample matrix. Exclude the canola oil concentration from Mineral Oil and Grease LCS targets since canola oil is removed by activated silica gel.

Lab Duplicates:
Not applicable, due to whole sample analysis requirement.

Field Duplicates:
Recommended to assess both laboratory and sampling variability (precision).

Prescribed Elements

The following components of this method are mandatory:

Sample holding times and preservation requirements must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

The entire contents of the sample container must be extracted, and the sample container must be rinsed with hexane, which is added to the sample extraction solvent.

The extraction solvent must be hexane (either n-hexane or a mixture of "hexanes", which are typically ≥ 60% n-hexane, mixed with cyclohexane and branched hexanes).

Classical separatory funnel liquid-liquid extractions must be conducted for samples with high total suspended solids content (greater than approximately 500 mg/L of TSS), or else the solid and liquid fractions must be separated and extracted separately. Alternative extraction techniques may be utilized for low TSS samples.

Following solvent evaporation, sample extracts must be dried at 50–60ºC for 30–60 minutes, or at ambient temperature (~20–25ºC). When drying at ambient temperature, samples must be dried to constant weight (to ensure complete removal of water) prior to gravimetric determinations. Constant weight is defined as 2 consecutive measurements, taken at least 30 minutes apart, which differ by less than 2.0 mg.

For Mineral Oil and Grease, 100% activated Silica Gel 60 (60 Angstrom pore size) with an approximate particle size range of 63–200 micron must be used. This is equivalent to an approximate mesh size range of 70–230.

All stated Performance Requirements and Quality Control requirements must be met. The spike solution used for the LCS must consist of a 1:1 mixture of mineral oil and canola oil in acetone.

Apart from the above limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, February 1999. United States Environmental Protection Agency, Office of Water, Washington, D.C.

Revision History

Nov 6, 2015:	Changed LCS spike formulation from a 1:1 mixture of n-hexadecane (nC_{16}) and stearic acid to a 1:1 mixture of mineral oil and canola oil, due to spike recovery issues related to interaction of nC_{16} & stearic acid that are not representative of typical oil and grease contaminants. Method is designed for quantitative recovery of nC_{16} & stearic acid (if spiked independently).
Sept 19, 2011:	Removed requirement to dry extract at 70ºC for 4 hours to ensure recovery of nC_{16} in LCS.
April 16, 2010:	Initial Publication of Version 1.0 of PBM. Replaces several older BC Lab Manual Oil and Grease methods.

Oil and Grease, and Oil and Grease (Mineral) in Solids by Hexane Extraction

Parameter

Oil and Grease

Oil and Grease (Mineral)

Analytical Method

Solvent extraction — Gravimetric Determination.

EMS Code

Introduction

Unlike some parameters representing distinct chemical species such as elements, ions, compounds, or groups of compounds, the Oil and Grease parameter is defined by the method used for its determination. Oil and Grease is defined by this method as any material that can be extracted from a sample with hexane that is not volatile at normal room temperature. Mineral Oil and Grease is further defined by this method as those compounds that do not have an affinity for 10% deactivated silica gel. Although this method is useful as a screening tool, sample complexity may result in either low or high estimations due to lack of analytical specificity and potential for interference. The Oil and Grease and Mineral Oil and Grease procedures described here are applicable to the semi-quantitative determination of high molecular weight petroleum products in solids. The Mineral Oil and Grease procedure uses silica gel to remove naturally occuring organic materials (rootlets, leaves, humic and resin acids, etc.) which may cause false positive results.

Summary

Samples are dried with magnesium sulfate and extracted by mechanical shaking with hexane. Samples may also be extracted without drying with a mixture of hexane and acetone. This hexane-acetone mixture is then back extracted with water to isolate the hexane phase. In either case, the hexane extract is passed through sodium sulfate and collected in a preweighed aluminum pan. When determining Mineral Oil and Grease, the hexane extract is passed through a mixture of sodium sulfate and silica gel into a pre-weighed aluminum pan. The final hexane extract is evaporated to dryness at room temperature and results are determined gravimetrically.

MDL

Analyte	Detection Limit (µg/g)
Oil and Grease	50
Oil and Grease (Mineral)	50

Matrix

Soil (marine), sediment solids (concrete, wood chips, etc.).

Interferences and Precautions

Naturally occurring organic material, or any non-petroleum material present in the sample that is soluble in hexane, can cause false positive results. The silica-gel clean-up may not remove all of this material from the extract.

Sodium sulfate or silica gel may be collected in the aluminum pan with the hexane extract causing false positive results.

Sample Handling and Preservation

Container: wide mouth glass jar.

Preservation: 4°C.

Stability Samples must be extracted within 14 days of collection.

Principle or Procedure

a) Extraction

1) Option 1 — Hexane extraction of dried sample.

- Thoroughly dry a representative sub-sample with magnesium sulfate in an extraction tube.

- Extract the dried sample three times with hexane.

- Collect the hexane extracts through a glass funnel containing anhydrous sodium sulfate into an aluminum pan that has been preweighed to an accuracy of 0.00001 grams.

2) Option 2 — Hexane/Acetone extraction of wet sample.

- Weigh a representative sub-sample into an extraction tube.

- Accurately measure equal portions of hexane and acetone into the extraction tube. Leave enough room in the tube to later add one more equal volume of water. Extract by mechanically shaking the sample for approximately one hour.

- Add a volume of contaminant free water to the raw extract that is at least equal to the volume of acetone added at the beginning of the extraction. The water will separate the all of the acetone from the hexane.

- Gently mix the contents of the extraction tube by inverting several times and then centrifuge to separate the aqueous and organic phases.

- Pass an accurately measured portion of the hexane layer through a glass funnel containing anhydrous sodium sulfate into an aluminum pan that has been pre-weighed to an accuracy of 0.00001 grams.

b) Silica Gel Clean-up (Mineral Oil and Grease Only)

The Mineral Oil and Grease procedure uses silica gel to remove non-petroleum, naturally occuring hydrocarbons from the sample extract prior to quantification.

1) When collecting the extract into the pre-weighed aluminum pan, pass the extract through sodium sulfate mixed with 60–200 mesh silica gel that has been 10% de-activated with contaminant free water.

2) By convention, 3 grams of de-activated silica gel are used for every 20 grams of sample.

3) The amount of silica gel should be reduced accordingly for the hexane/acetone extraction since only a portion of the hexane extract is used.

c) Quantification

1) Leave the hexane to evaporate at room temperature.

2) When the aluminum pan reaches a constant weight, determine the weight of the residue in the pan using a balance that is accurate to 0.00001 grams.

3) Determine the concentration of Oil and Grease or Mineral Oil and Grease in the sample in milligrams per kilogram. Take into account any dilutions associated with the hexane/acetone extraction procedure.

Calculation O&G Measured Gravimetrically.

$$\text{Min. O\&G (µg/g)} = \frac{1{,}000{,}000 \times (\text{Final Wt,g} - \text{Initial Wt,g})}{(\text{Wt,g of Sample} \times (100 - \%\text{Moisture})/100)}$$

Precision Not Available.

Accuracy Not Available.

Quality Control

a) One method blank per analytical batch (10–20 samples).

b) One method spike (mineral oil) per analytical batch (10–20 samples).

c) One laboratory replicate per every 10 samples.

d) Balance should be calibrated with Class "A" weights.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th edition, 1992 Section 5520B and 5520F.

b) Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods (Revised). Publication #SW-846 Revision 1. United States Environmental Protection Agency, Washington, DC. 3rd Edition, 1990.

Revision Dates November 2002: Method adopted from Supplement #1.
EMS Codes assigned.

Oil Content (Waste) in Solids and Liquids for Hazardous Waste Regulation — PBM

Parameter

Waste Oil Content as defined by the British Columbia Hazardous Waste Regulation.

Analytical Method

Soxhlet or Liquid-Liquid Extraction using Petroleum Ether (boiling point range approximately 35–60°C), with Silica Gel Cleanup and Gravimetric Determination.

Introduction

The British Columbia Hazardous Waste Regulation defines “Waste Oil” as “automotive lubricating oil, cutting oil, fuel oil, gear oil, hydraulic oil or any other refined petroleum based oil or synthetic oil where the oils are in the waste in a total concentration greater than 3% by weight and the oils though use, storage or handling have become unsuitable for their original purpose due to the presence of impurities or loss of original properties”.

A material with Waste Oil Content by this method exceeding 3% by weight may be classified as Waste Oil under the Hazardous Waste Regulation.

Waste Oil Content as defined by this method is also used to measure compliance against the Total Oil standard under section 41.1 of the Hazardous Waste Regulation (Standards for Management of Hydrocarbon Contaminated Soil). For this application, Waste Oil Content must be expressed on a dry weight basis.

Method Summary

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

A 20 g solid waste sample is acidified, dried with magnesium sulfate and extracted with petroleum ether using a Soxhlet apparatus. Whole bottle aqueous samples are extracted with petroleum ether in a separatory funnel. An extract aliquot is treated in situ with silica gel to remove polar components (e.g., animal and vegetable oils) and is heated at 70°C to remove solvent and volatile components such as gasoline. The final residue is determined gravimetrically.

MDL and EMS Codes

Analyte	Reporting Limit	EMS Code
Waste Oil Content	0.5% by weight *	

* 0.5% is the minimum required reporting limit for the method. Lower MDLs may be obtained.

Matrix

Solids, liquids, including aqueous samples, organic phase liquids, or combinations of both, mixed-phase samples.

Interferences and Precautions

This is an aggregate test that quantifies a range of materials with similar physical and chemical characteristics. The method employs a silica gel clean up which in addition to removing non-petroleum products such as vegetable oil or animal fat can remove polar components of petroleum products. The method employs heating at 70°C to remove volatile

compounds such as gasoline and portions of kerosene and diesel. Typical Waste Oil Content measures of common petroleum and non-petroleum products are listed below as recoveries:

Product Type	Typical Recovery Range
Gasoline	0–5%
Diesel	70–85%
Motor Oils (30–50 Weight)	80–100%
Kerosene	50–60%
Vegetable Oil / Lard	0–1%
Asphalt	30–40%
Bunker	30–40%

Sample Handling and Preservation

Solids: Glass container recommended. No preservation required.

Liquids: Glass container recommended (500mL wide mouth). No preservation required.

Stability

Holding Time:

Solids: 28 days

Liquids: 28 days

Storage:

Store at 4°C

Procedure

Extraction Procedures

Solid Samples — Soxhlet Extraction

Weigh 20 g of wet soil or solids.

Acidify with approximately 0.3 mL concentrated HCl.

Dry sample using anhydrous $MgSO_4$ until mixture is free flowing.

Transfer sample to a Soxhlet apparatus taking care to include any residue remaining on weighing/mixing containers.

Extract the sample by Soxhlet for at least 4 hours using petroleum ether. Ensure that each Soxhlet apparatus cycles at least 4 times per hour.

Bulk solvent to a known volume with petroleum ether. This will generally be 100 mL.

Aqueous Samples — Liquid/Liquid Extraction

For the purposes of this method, aqueous samples include samples with up to 10% by volume of organic phase liquids and may include samples with up to 10% by volume of solids.

Sample weight (g) must be determined though this procedure. In the absence of significant solids or organic phase liquids, sample weight may be measured by volume, assuming a density of 1 g/mL.

Acidify the sample to < pH 2 using hydrochloric acid.

Transfer the sample to a separatory funnel. Any solids present must also be extracted, either separately or in combination with the aqueous portion of the sample. Separate extraction of solids with later recombination of extracts is recommended where significant emulsions form.

Determine the sample weight.

Add approximately 30 mL petroleum ether to the empty sample bottle to remove residual oil adhering to the bottle surfaces, then add to the separatory funnel. Additional rinsing may be necessary to completely remove all residual oil from the sample container.

Shake the separatory funnel vigorously for 2 minutes.

Drain the aqueous (lower) portion back into the sample bottle. Drain the solvent (upper) layer through anhydrous Na_2SO_4 into a compatible collection container.

Repeat steps 3 through 7 twice more.

Bulk combined solvent extracts to a known volume with petroleum ether. This will generally be 100 mL.

Special Case Sample Extractions:

A range of possible material types and phases can potentially be categorized as waste oil. Often the laboratory must use their best judgment when selecting an appropriate extraction procedure, noting that the overall objective is to quantify the percent (as weight / weight) of Waste Oil Content in the received material. By definition, waste oil must be soluble in petroleum ether.

For special case samples it is recommended that sample data be qualified to describe key preparation and analysis steps.

Depending on the procedures employed to address “special case” samples, calculations based on the proportion of material used for testing may be required in addition to the general calculations referenced in Sections 2 and 3, in order to obtain a final result for the entire sample.

The following steps provide guidance for commonly encountered “special case” samples:

Organic Phase and Multiphasic Liquids

For materials consisting partially or entirely of organic phase liquids, where the organic phase constitutes more than 10% of the sample by volume, first transfer the entire contents of the sample into a tared graduated cylinder and determine the sample weight (do not assume a density of 1 g/mL). Then accurately determine the volume of the organic phase liquid in the sample. In the rare case that the organic phase is immiscible with petroleum ether, treat the sample in the same manner as an aqueous sample, using the procedure in section 1.2. If the organic phase liquid is miscible in petroleum ether, dilute an accurately measured volume of the organic phase liquid into a known volume of petroleum ether. Then proceed to Section 2, Oil and Grease Determination. A filtration step may be necessary to remove materials that are insoluble in petroleum ether from the solution prior to oil and grease determination. The fraction (by volume) of the total organic phase liquid that was used to create the petroleum ether solution will be required in section 2. Note that in this procedure, the aqueous phase is not extracted, but does form a component of the bulk sample weight.

Mixed Liquid/Solid Samples

For materials containing both solid and liquid matrixes, separate and analyze each matrix independently using the matrix specific extraction procedures (Section 1.1 and 1.2). As a general guide, this approach applies where visual estimation determines more than 10% (v/v) of the secondary matrix. Combine results for each matrix to obtain a single result for the bulk sample. Determine the combined weight of waste oil found in the two sub-samples and divide by the weight of the entire sample.

Total Oil and Grease Determination

This step determines Total Oil and Grease (both petroleum and non-petroleum based) in order to determine the silica gel amount required for the clean up step.

Transfer an appropriate extract aliquot (up to ½ the total extract volume) to a pre-weighed container that has been heated in an oven at 70 ± 5°C for at least 30 minutes and desiccated.

Allow solvent to evaporate to dryness in fumehood. Alternatively, solvent may be reduced to approximately 1 mL using a rotary evaporator, followed by nitrogen blowdown to dryness.

Dry container at 70 ±5°C for 30 ±5 minutes, then desiccate to constant weight.

Reweigh the container and determine total oil and grease as follows:

$$\text{Total Oil and Grease (\%)} = \frac{\text{gain in weight (g)}}{\text{sample weight (g)}} \times \frac{\text{extract volume (mL)}}{\text{aliquot (mL)}} \times 100\%$$

Note: For classification of samples as waste oil under the Hazardous Waste Regulation, Waste Oil Content is reported by weight on an *as-received basis* (i.e., wet weight). For assessment of compliance of the Total Oil standard under section 41.1 of the Hazardous Waste Regulation (Standards for Management of Hydrocarbon Contaminated Soils), Waste Oil Content is reported on a dry weight basis.

If the sample contains less than 0.5% Total Oil and Grease, then report a result for Waste Oil of <0.5%. Otherwise proceed to Section 3, Waste Oil Content Determination.

Waste Oil Content Determination

This step is only necessary if the Total Oil and Grease result exceeds 0.5%.

Based on the Total Oil and Grease result, prepare an aliquot of the sample extract that contains no more than 100 mg of total oil and grease. Perform an in situ silica gel cleanup on the sample aliquot using 3g of 100% activated silica gel in a centrifuge tube or other suitable container. Mix thoroughly for 5 minutes (e.g., by mechanical shaker device), then filter to remove silica gel.

Transfer solvent extract to a pre-weighed container that has been heated in an oven at 70 ± 5 °C for at least 30 minutes and desiccated.

Allow solvent to evaporate to dryness in fumehood. Alternatively, solvent may be reduced to 1 mL using a rotary evaporator set at less than or equal to 35°C, followed by nitrogen blowdown to dryness.

Dry residue and container at 70 ± 5 °C for 30 ± 5 minutes then desiccate to constant weight.

Reweigh the container and determine Waste Oil Content as follows:

$$\text{Waste Oil Content (\%)} = \frac{\text{gain in weight (g)}}{\text{sample weight (g)}} \times \frac{\text{extract volume (mL)}}{\text{aliquot (mL)}} \times 100\%$$

Note: For classification of samples as waste oil under the Hazardous Waste Regulation, Waste Oil Content is reported by weight on an *as-received basis* (i.e., wet weight). For assessment of compliance of the Total Oil standard under section 41.1 of the Hazardous Waste Regulation (Standards for Management of Hydrocarbon Contaminated Soils), Waste Oil Content is reported on a dry weight basis.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) between 80 to 120% for clean matrix spikes or certified reference materials at concentrations equal to or greater than the regulatory standard of 3% Waste Oil Content. Method accuracy is determined using single weight SAE30 motor oil.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes of single weight SAE30 motor oil at concentrations equal to or above the regulatory standard of 3% Waste Oil Content.

Sensitivity Requirement: The method must support a Method Detection Limit of equal to or less than 0.5% Waste Oil Content.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per batch	Less than 0.5% Waste Oil Content
Method Spike or Ref. Material	One per batch	70–130%
Lab Duplicates	One per batch or approximately 5–10%	40% RPD

* Minimum DQOs apply to individual QC samples, not averages. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Except where whole sample analysis is employed. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5–10%, or a minimum of one per batch.

Reference Material or Method Spike: Required. Spiking material will consist of motor oil (single weigh SAE30) prepared in petroleum ether. It is recommended that routine method spikes be prepared at a concentration equal to the hazardous waste regulatory standard level of 3% Waste Oil Content by weight.

Prescribed Elements

The following components of this method are mandatory:

Petroleum ether with a boiling point range of approximately 35–60°C must be used as the extraction solvent.

Soxhlet extraction must be conducted for solid samples as described (which for wet soils must include the magnesium sulfate drying step).

Liquid/liquid extraction must be conducted for aqueous liquids as described.

Silica gel clean up must be conducted as described.

Gravimetric detection is mandatory, with a final drying step conducted at 70 $\pm$ 5°C for 30 $\pm$ 5 minutes.

Quality control efforts must be conducted as described.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

a) British Columbia Ministry of Water, Land and Air Protection, Hazardous Waste Regulation, Determination of Waste Oil as Defined by Special Waste Regulations in Solids Liquids, Petroleum Ether Extraction, October 25, 1996.

b) Development of a Standard Procedure for Waste Oil for the Special Waste Regulation Phase 2, Prepared for the British Columbia Ministry of Environment, prepare by British Columbia Research Corporation, Project 4-03-710, February 1993.

c) Standard Methods the Examination of Water and Wastewater: 5520B, Partition Gravimetric Method, 5520E Extraction Method for Sludge Samples, 5520F Hydrocarbons, APHA, 20th Edition, 1998.

Revision History

March 31, 2005: Method revised to PBM format, changed reporting parameter to Waste Oil Content.

October 30, 1996: Original Special Waste Oil and Grease Method (Determination of Waste Oil as Defined by Special Waste Regulation in Solids and Liquids, Petroleum Ether Extraction).

Organic Chlorine in Petroleum Products by Oxidative Pyrolysis and Microcoulometry

Parameter

Total Organic Halides (as Cl) in Oil
Total Halides (as Cl) in Oil

Analytical Method

Oxidative Pyrolysis and Microcoulometry

Introduction

This procedure describes the measurement of organic chloride in new and used petroleum products by oxidative pyrolysis and microcoulometry. This method is carried out in accordance with EPA SW-846 Test Method 9076, with the addition of pre-extraction with water to remove inorganic chlorides (per ASTM D7457).

Total chloride can be measured by omitting the water washing; however, the results will be biased low due to incomplete conversion of inorganic species during oxidative pyrolysis.

Method Summary

An aliquot of sample that has undergone water washing is introduced into a combustion tube maintained at 900 to 1100°C under an argon stream. Oxygen flow in the combustion tube precipitates oxidative pyrolysis, converting the organic halides into hydrogen halides which are then fed into the titration cell through a dehydrating tube. The hydrogen halides react with the silver ions in the electrolyte, which are replaced coulometrically. The total amount of electric charge required to replace the silver ions is a measure of the amount of organic halides in the sample aliquot.

Note: This is a prescriptive method and must be followed exactly as described.
Where minor deviations are permitted, this is indicated in the text

Analyte CAS No., MDL(s) and EMS Code(s)

Analyte	CAS No.	Approx. MDL mg/L	Analyte EMS Code
Total Organic Halides		1 mg/L	TOX
Total Halides		1 mg/L	

EMS Method Code(s)

…

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

New and used petroleum products and their derivatives.

Interferences and Precautions

Nitrogen and Sulfur interfere at concentrations greater than approximately 0.1%

Any Bromide and Iodide present within the sample will generate a detector response. The oxyhalides do not precipitate silver and will generate a 50% detector response in comparison to chloride.

Fluorine as fluoride does not precipitate silver and is neither an interferent nor detected.

Sample Handling and Preservation

Refer to the following method with respect to sample handling:
ASTM D4057 Standard Practice for Manual Sampling of Petroleum and Petroleum Products

Container:	See ASTM D4057
Preservation:	See ASTM D4057
Holding Time:	No holding time prescribed
Storage:	Store at room temperature

Equipment and Supplies

1. Total Organic Halides Analyzer (Combustion Analysis / Microcoulometry)
2. Analytical Balance
3. 10 µL Gas-tight syringe
4. 100 mL Class A volumetric Flask
5. 2 L Eppendorf Flask
6. Appropriate PPE (gloves, lab coat, eye protection)

Reagents

Use analytical grade or better for all reagents:

- Xylenes
- Acetic Acid
- Concentrated Sulfuric Acid
- Deionized Water
- Sodium Acetate Anhydrous
- Potassium Nitrate
- Potassium Chloride
- Pentachlorophenol
- Compressed Oxygen, 99.99% Purity
- Compressed Argon, High Purity

Standards

Calibration Standard — 1.0 µg/µL chlorine

Weigh 150 mg ±0.1 mg of pentachlorophenol. Transfer the pentachlorophenol to a 100 mL Class A volumetric flask, rinsing the vial with xylene 3 times. Add xylene to the 100 mL mark on the volumetric flask.

QC Standard — 1.0 µg/µL chlorine

Weigh 150 mg ±0.1 mg of pentachlorophenol. Transfer the pentachlorophenol to a 100 mL Class A volumetric flask, rinsing the vial with xylene 3 times. Add xylene to the 100 mL mark on the volumetric flask.

Spike Standard — 50 µg/µL chlorine

Weigh 7.5 g ±0.1 mg of pentachlorophenol in a 100 mL Class A volumetric flask, Add xylene to the 100 mL mark on the volumetric flask.

Cell Electrolyte Solution — 85% Acetic Acid

Weigh 2.70 g of sodium acetate and add to 0.3 L of deionized water. Mix the solution until the sodium acetate is dissolved. Transfer solution to 2 L Eppendorf flask and add 1.7 L of acetic acid to the sodium acetate solution and mix well.

Reference Electrode Electrolyte (Outer Chamber) — 1M KNO_3

Weigh 10.11 g of potassium nitrate in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium nitrate is dissolved.

Reference Electrode Electrolyte (Inner Chamber) — 1M KCL

Weigh 7.46 g of potassium chloride in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium chloride is dissolved.

Counter Electrode Electrolyte — 10% KNO_3

Weigh 10.11 g of potassium nitrate in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium nitrate is dissolved.

Procedure

Sample Preparation — Inorganic Chloride Extraction

It is crucial that samples are homogenized prior to analysis. For oil samples, shake thoroughly by using a paint shaker (or similar device) for at least 5 minutes.

Using a calibrated pipette: add 1.0 mL of sample, 1.0 mL of xylene and 1.0 mL of deionized water to a 4 mL glass vial.

Cap the vial and homogenize the sample via vortex mixing for a minimum of 30 seconds.

Centrifuge the samples for a minimum of 5 minutes. Place vials into a swing-bucket centrifuge rotor and set to approximately 2000 RPM. Ensure the rotor is balanced.

Separate the organic layer into a new vial and repeat the wash with deionized water. Vortex and centrifuge the vial following steps 3 and 4.

Instrument Preparation

Set up the analyzer as per manufacturer's instructions. Replace the electrolyte solutions in the reference electrode, counter electrode and reaction cell. Replace the dehydration solution (95% concentrated sulfuric acid). Allow the instrument to stabilize at the programmed set points, ensuring the pyrolysis furnace is set at a temperature within the 900 to 1100°C temperature range.

Instrument Analysis Procedure — System Recovery

Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing the Calibration Standard.

Inject 5 µL of the Calibration Standard through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.

Repeat step 2 two more times. The replicates must agree to within ±10% of the average result and the average recovery must be at least 85% of the theoretical value in order to proceed with sample analysis. The recovery factor generated (ratio of chlorine determined in the standard minus the system blank, divided by the standard content) is utilized to calculate the mass units of chloride present.

Instrument Analysis Procedure — System Blank

Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing xylene.

Inject 5 µL of xylene through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.

If the response is greater than 1 µg/mL, the cause must be delineated prior to sample analysis. The system blank should be subtracted from both standards and samples.

Instrument Analysis Procedure — Sample Analysis

Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing sample.

Inject 2–5 µL of the sample based on expected chlorine concentration through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.

Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	< 1 µg/mL
Lab Duplicate (DUP)	One per batch (max 20 samples)	10% RPD
System Recovery	1 per batch (prior analysis)	85% Recovery / ≤ 10% RPD
Continuing Calibration Verification (CCV) / System Drift	1 per batch (after analysis)	Within 13.7% of System Recovery
Matrix Spike (MS) / Matrix Spike Duplicate (MSD)	One per batch (max 20 samples)	80–120% recovery / ≤ 10% RPD
If any of the specified acceptance criteria cannot be met for the analysis of a given sample, then the data reported for that sample must be appropriately qualified.		

System Drift:
System recovery must be verified to validate generated results. Analyze the QC standard at the end of sample analysis and ensure the instrument response is within 13.7% of the average system recovery

Matrix Spike / Matrix Spike Duplicate:
Spike samples with a chlorinated organic (10 µL of 50 µg/µL spike standard). The spike recovery should be reported and should be between 80 and 120% of the expected value. Duplicate values should be within 10% RPD.

Method Validation Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation requirements specified below.

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies.

For Initial Validations, averages of at least 8 Reference Material or Laboratory Control samples must be assessed (multiple batches preferred). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy of 80–120% (measured as average recovery of reference material or Laboratory Control Sample) at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision <13.7% RPD at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

References

1. ASTM D7457 — 12 Standard Test Method for Determining Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry.

2. EPA SW-846 Test Method 9076: Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry

3. ASTM D4057 — 18 Standard Practice for Manual Sampling of Petroleum and Petroleum Products

Revision History

14-Nov-2019 Draft method for review by BCELTAC

24-Aug-2023

Perfluoroalkyl Substances (PFAS) in Soils by LC/MS/MS — PBM

Parameter

Perfluoroalkyl Substances (Perfluorobutane Sulfonate (PFBS), Perflourooctane Sulfonate (PFOS), Perfluorooctanoic Acid (PFOA)) in Soils

Analytical Method

Methanol Extraction, Solid Phase Extraction (SPE) Clean-up, LC//MS/MS

Introduction

This method is applicable to the quantitative determination of perfluorinated alkyl substances in soils and solids.

Method Summary

Soil samples are spiked with isotope dilution standards, extracted with a methanol solution, and cleaned up and concentrated by SPE. Analysis for PFBS, PFOS and PFOA is by reversed phase liquid chromatography with isotope dilution tandem mass spectrometry (LC/MS/MS).

This method may be applied to other perfluorinated alkyl acids in soils provided the performance requirements and data quality objectives are met.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/g)	EMS Analyte Code
Perfluorobutane Sulfonate (PFBS)	375-73-5	0.001–0.01	Defined on request
Perflourooctane Sulfonate (PFOS)	1763-23-1	0.001–0.01	Defined on request
Perfluorooctanoic Acid (PFOA)	335-67-1	0.001–0.01	Defined on request

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil, sediment, sludge, solid waste.

Interferences and Precautions

All reagents and solvents should be pesticide residue purity or higher to minimize interference problems. Avoid the use of all sources of Teflon®/PTFE including PFC-containing caps.

Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on variations in the sample matrices. Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers, and other apparatus that release perfluorinated compounds. These materials and supplies must be demonstrated to be free from interferences by analysis of laboratory reagent blanks under the same conditions as for tested samples. If found, take measures to remove the contamination or qualify the test results; background subtraction of blank contamination is not allowed.

Use polyethylene LC vial caps, polyethylene disposable pipettes or any other target-analyte-free materials. Check disposable pipettes for release of target analytes of interest.

The Liquid Chromatography system used should consist, as much as practical, of sample solution or eluent-contacting components free of PTFE and PFC target analytes.

Degassers are important to continuous LC operation and most commonly are made of fluorinated polymers. To enable use, an isolator column should be placed after the degasser and prior to the sample injection valve to separate the PFCs in the sample from the PFCs in the LC system.

Sample Handling and Preservation

Container: Glass or plastic (HDPE or Polypropylene recommended). Avoid PTFE.

Preservation: None. Cool samples immediately after sample collection.

Stability

Holding Time: Extract samples within 28 days of collection (Ref: ASTM D7968-14). Sample extracts may be held for up to 40 days before instrumental analysis.

Storage: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage. Storage of extracts and standards at room temperature is preferred to prevent sorption onto container surfaces when refrigerated. However, standards and extracts may be stored refrigerated if stabilized at room temperature prior to use (Ref: EPA 537).

Procedure

Calibration Standard Stock:

If possible, purchase all calibration standards as technical grade standards or neat materials. Standards or neat materials that contain only the linear isomer can be substituted only if technical grade (linear and branched isomers) standards or suitable neat technical materials cannot be purchased. PFOS calibration standards must be purchased as technical grade (containing branched and linear isomers).

Extraction:

Detailed sample extraction procedures are not provided in this method. Consult ASTM Method D7968-14 for more detailed guidance (see references). A summary of the extraction method is as follows:

Weigh and transfer a representative aliquot of the sample to a polypropylene tube.

Add isotopically-labelled isotope dilution standards to samples and quality control samples.

Extract samples with a methanol:water extraction solution.

Following extraction, centrifuge the tubes.

Filter or decant the supernatant.

Adjust the extract to pH 4–5.

Process the extract through a conditioned SPE column.

Transfer an aliquot to an autosampler vial, add isotopically-labelled injection internal standard and analyze the extract by LC/MS/MS.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. Consult EPA Method 537 or ASTM Method D7968-14 for more detailed guidance (see references).

Extracts must be analyzed by LC/MS/MS. A C_{18} column or any column that provides adequate resolution, peak shape, capacity, accuracy and precision is used.

Use a minimum five-point initial calibration over the desired working range to meet the performance requirements outlined in ASTM D7968-14.

If required, dilutions may be conducted on high level samples using the standard isotope dilution corrections if the diluted ID standards can still be accurately measured. Alternatively, a smaller (but representative) portion of sample may be extracted and analyzed, or higher amounts of the ID standards may be added prior to extraction. For highly contaminated soils, ID standards may be added to a quantitative fraction of the soil extract, rather than being added to the soil prior to extraction (e.g., add the normal amount of ID standards to 1/100th of the soil extract to accomplish a 100-fold dilution).

Most PFAAs are produced by two different processes. One process gives rise to linear PFAAs only while the other process produces both linear and branched isomers. Thus, both branched and linear PFAAs can potentially be found in the environment. For the compounds that give rise to more than one peak (particularly PFOS), all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the calibration standard.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Laboratory Control Samples or Reference Materials must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Recovery must be between 70–130% of true value.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	50–140%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	50–140%
Peak Asymmetry Factor	Calculate the peak asymmetry factor for the first two eluting chromatographic peaks in a mid-level calibration standard every time a calibration curve is generated.	0.8–1.5 (Ref: EPA 537)
Injection Internal Standard (IIS) (not used in isotope dilution calculations)	All samples	Peak area counts for all internal standards in all injections must be within ±50% of the average peak area calculated during the initial calibration and 70–140% from the most recent CCV (Ref: EPA 537).
Isotope Dilution Standards (IDS)	All samples, all regulated PFAS analytes	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%.
Calibration Verification Standard (CVS)	minimum 1 per initial calibration	70–130%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	70–130%
*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Blank (MB): Required. Prepare a Method Blank using clean oven-baked sand, treated exactly like a sample including exposure to equipment, solvents and reagents, and the internal standards (IDS and IIS) that are used in the analysis batch.

Laboratory Duplicate (DUP): Required. Data quality objectives are listed above.

Laboratory Control Sample (LCS): Required. Prepare a Laboratory Control Sample by fortifying clean sand with known concentrations of the target analytes.

Matrix Spike (MS): Required. Spike a duplicate field sample with known concentrations of the target analytes.

Injection Internal Standard (IIS): One or more injection internal standards are added to extracts at the end of the extraction process. IIS's should be stable isotopically-labelled PFAA substances representative of method analytes. They are

used to monitor the integrity of each injection, and to calculate absolute recoveries of isotope dilution standards in samples and QC.

Isotope Dilution Standards (IDS): Isotope dilution standards must be stable isotopically-labelled analogues of the parameters of interest. Isotope Dilution Standards are added to the sample prior to extraction and are used for correction of extraction recoveries and matrix effects. Isotope Dilution is required for all regulated PFAS analytes (PFOS, PFOA, PFBS), and is recommended for other PFAS analytes. If suitable labelled isotopes are unavailable for non-regulated PFAS analytes, then the use of the most chemically similar available IDS is recommended.

Calibration Verification Standard (CVS): Required. A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. A mid-point calibration standard must be analyzed throughout the instrument run at least every 12 hours and at the end of the run to monitor calibration drift. A CVS may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by LC/MS/MS. At least two MRM transitions are required to be monitored for PFOS and PFOA (only one suitable transition exists for PFBS). Labs must define appropriate criteria for confirmation of analyte identity by secondary transitions.

Initial calibrations must include at least 5 points.

PFOS test results must represent and include the sum of all branched and linear isomers that are identifiable from technical grade PFOS standards or material.

The 499 to 80 m/z MRM transition must be used for the quantitation of PFOS, unless subject to sample specific interferences.

Isotope dilution calibration and recovery correction must be used for all regulated PFAS analytes.

Blank correction is not permitted for this method.

All Performance Requirements and Quality Control requirements must be met.

Sample container materials, preservation, storage, and hold time guidance may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

ASTM D7968-14, Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), ASTM International, 2014.

US EPA Method 537, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), version 1.1, Sept/2009.

Revision History

Sept 15, 2017	First version added to BC Lab Manual in support of 2017 CSR updates.

Perfluoroalkyl Substances (PFAS) in Water by LC/MS/MS — PBM

Parameter

Perfluoroalkyl Substances (Perfluorobutane Sulfonate (PFBS), Perflourooctane Sulfonate (PFOS), Perfluorooctanoic Acid (PFOA)) in Waters

Analytical Method

Solid Phase Extraction (SPE), LC/MS/MS

Introduction

This method is applicable to the quantitative determination of perfluorinated alkyl substances in waters.

Method Summary

Water samples are fortified with isotope dilution standards and passed through an SPE cartridge to extract the target analytes. Target compounds are eluted from the solid phase with methanol and the extract is evaporated to dryness. Internal standard is added and the volume is adjusted to a known volume with methanol:water. Analysis for PFBS, PFOS and PFOA is by isotope dilution liquid chromatography tandem mass spectrometry (LC/MS/MS).

This method may be applied to other perfluorinated alkyl acids in waters provided the performance requirements and data quality objectives are met.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/L)	EMS Analyte Code
Perfluorobutane Sulfonate (PFBS)	375-73-5	0.01–0.10	Defined on request
Perflourooctane Sulfonate (PFOS)	1763-23-1	0.01–0.10	Defined on request
Perfluorooctanoic Acid (PFOA)	335-67-1	0.01–0.10	Defined on request

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Freshwater, seawater, groundwater, wastewater.

Interferences and Precautions

All reagents and solvents should be pesticide residue purity or higher to minimize interference or contamination problems. Avoid the use of all sources of Teflon®/PTFE including PFC-containing caps.

Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source, or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample.

Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers, aluminum foil, PTFE products and other apparatus that release perfluorinated compounds. These materials and supplies must be demonstrated to be free from interferences by analysis of laboratory reagent blanks under the same conditions as for tested samples. If found, take measures to remove the contamination or qualify test results; background subtraction of blank contamination is not allowed.

Relatively large quantities of preservatives may be added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks particularly when new lots of reagents are acquired.

SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

The Liquid Chromatography system used should consist, as much as practical, of sample solution or eluent-contacting components free of PTFE and PFC target analytes.

Degassers are important to continuous LC operation and most commonly are made of fluorinated polymers. To enable use, an isolator column should be placed after the degasser and prior to the sample injection valve to separate the PFCs in the sample from the PFCs in the LC system.

Sample Handling and Preservation

Container: HDPE or Polypropylene (PP). HDPE is recommended where extended lists of PFAA substances will be tested (some sorption of higher chain PFAAs to PP has been reported). Avoid PTFE.

Preservation: Chlorinated waters must be preserved with sodium thiosulfate (~80 mg/L of sodium thiosulfate is recommended, which can neutralize up to ~15 mg/L free chlorine), or with Tris base (Trizma®) at 5 g/L. Preservation is not required for non-chlorinated samples.

Storage: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage. Storage of extracts and standards at room temperature is preferred to prevent sorption onto container surfaces when refrigerated. However, standards and extracts may be stored refrigerated if stabilized at room temperature prior to use (Ref: EPA 537).

Stability

Holding Time:

Samples: Extract samples within 28 days of collection (Ref: ASTM D7979-15).

Extracts: Sample extracts may be held for up to 40 days before instrumental analysis.

Procedure

Calibration Standard Stock:

If possible, purchase all calibration standards as technical grade standards or neat materials. Standards or neat materials that contain only the linear isomer can be substituted only if technical grade (linear and branched isomers) standards or suitable neat technical materials cannot be purchased. PFOS calibration standards must be purchased as technical grade (containing branched and linear isomers).

Extraction:

Detailed sample extraction procedures are not provided in this method. Consult EPA Method 537 or ASTM Method D7979-15 for more detailed guidance (see references). A summary of the extraction method is as follows:

Transfer a representative aliquot of sample (including any particulate matter) to a suitable pre-calibrated container. An indirect measurement may be made by marking the level of the sample on the bottle or by weighing the sample and bottle. Because some PFAAs adsorb to surfaces, do not transfer the sample to a graduated cylinder for volume measurement.

Note: Where samples contain more than ~1% solids, the solids must be separated and extracted separately with extracts or test results combined to represent total sample concentrations.

Add isotopically-labelled isotope dilution (ID) internal standards to all samples and quality control samples prior to extraction.

Pass the samples through a conditioned SPE column and extract with a methanol solution.

Concentrate the extract to dryness under a gentle steam of nitrogen in a water bath to remove all the water/methanol mix.

Reconstitute to 1 mL with methanol:water solution.

Transfer an aliquot to a polypropylene autosampler vial and analyze by LC/MS/MS.

Instrumental Analysis:

Detailed instrumental analysis procedures are not provided in this method. Consult EPA Method 537 or ASTM Method D7979-15 for more detailed guidance (see references).

Extracts must be analyzed by LC/MS/MS. A C_{18} column or any column that provides adequate resolution, peak shape, capacity, accuracy and precision is used.

Use a minimum five-point initial calibration over the desired working range to meet the performance requirements outlined in US EPA Method 537.

If required, dilutions may be conducted on high level samples using the standard isotope dilution corrections if the diluted ID standards can still be accurately measured. Alternatively, a smaller portion of sample may be extracted and analyzed or higher amounts of the ID standards may be added.

Most PFAAs are produced by two different processes. One process gives rise to linear PFAAs only while the other process produces both linear and branched isomers. Thus, both branched and linear PFAAs can potentially be found in the environment. For the compounds that give rise to more than one peak (particularly PFOS), all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the calibration standard.

As noted above, PFOS (and most likely PFBS) has linear and branched isomers. In an attempt to reduce PFOS bias, it is required that the transition m/z 499 → m/z 80 be used as the quantitation transition. Some MS/MS instruments, such as conventional ion traps, may not be able to scan a product ion with such a wide mass difference from the precursor ion; therefore, they may not be used for this method if PFOS analysis is to be conducted.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Laboratory Control Samples must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Recovery must be between 80–120% of the true value.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision, measured as percent relative standard deviation (%RSD), must be ≤15% for all analytes.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Performance Requirement for Seawater Matrix: If the method will be used for seawater matrix, independent method validations must be conducted on seawater matrix samples.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	70–130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	70–130%
Peak Asymmetry Factor	Calculate the peak asymmetry factor for the first two eluting chromatographic peaks in a mid-level calibration standard every time a calibration curve is generated.	0.8–1.5 (Ref: EPA 537)
Injection Internal Standard (IIS) (not used in isotope dilution calculations)	All samples	Peak area counts for all internal standards in all injections must be within ±50% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCV (Ref: EPA 537).
Isotope Dilution Standard(s) (IDS)	All samples, all regulated PFAS analytes	Absolute recovery of all isotope dilution standards used for recovery correction must be 10–130%
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	70–130%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	70–130%

*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

Method Blank (MB): Required. An aliquot of reagent water that is treated exactly like a sample including exposure to equipment, solvents and reagents, sample preservatives, and the internal standards (IDS and IIS) that are used in the analysis batch.

Laboratory Duplicate (DUP): Required. Data quality objectives are listed above.

Laboratory Control Sample (LCS): Required. Prepare a Laboratory Control Sample by fortifying deionized water with known concentrations of target the analytes.

Matrix Spike (MS): Required. Spike a duplicate field sample with known concentrations of the target analytes.

Injection Internal Standard (IIS): One or more injection internal standards are added to extracts at the end of the extraction process. IIS's should be stable isotopically-labelled PFAA substances representative of method analytes. They are used to monitor the integrity of each injection, and to calculate absolute recoveries of isotope dilution standards in samples and QC.

Isotope Dilution Standards (IDS): Isotope dilution standards must be stable isotopically-labelled analogues of the parameters of interest. Isotope Dilution Standards are added to the sample prior to extraction and are used for correction of extraction recoveries and matrix effects. Isotope Dilution is required for all regulated PFAS analytes (PFOS, PFOA, PFBS), and is recommended for other PFAS analytes. If suitable labelled isotopes are unavailable for non-regulated PFAS analytes, then the use of the most chemically similar available IDS is recommended.

Calibration Verification Standard (CVS): Required. A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. A mid-point calibration standard must be analyzed throughout the instrument run at least every 12 hours and at the end of the run to monitor calibration drift. A CVS may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by LC/MS/MS. At least two MRM transitions are required to be monitored for PFOS and PFOA (only one suitable transition exists for PFBS). Labs must define appropriate criteria for confirmation of analyte identity by secondary transitions.

Initial calibrations must include at least 5 points.

PFOS test results must represent and include the sum of all branched and linear isomers that are identifiable from technical grade PFOS standards or material.

Test method utilized must include extraction and analysis of a representative portion of any solids or particulate matter contained in the sample. Where samples contain more than ~1% solids, the solids must be separated and extracted separately with extracts or test results combined to represent total sample concentrations.

The 499 to 80 m/z MRM transition must be used for the quantitation of PFOS, unless subject to sample specific interferences.

Isotope dilution calibration and recovery correction must be used for all regulated PFAS analytes.

Blank correction is not permitted for this method.

If this method is utilized for seawaters or brine samples, method validation for that matrix must be conducted prior to use using Matrix Spikes and/or Reference Materials.

All Performance Requirements and Quality Control requirements must be met.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

US EPA Method 537, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), version 1.1, Sept/2009.

ASTM D7979-15. Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), ASTM International, Nov 2015.

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.

Pesticide Scan, Organochlorine, Organonitrogen and Organophosphorus Compounds

Parameter Neutral Pesticide Scan

Analytical Method Extraction, GC/ECD, GC/NPD.

EMS Code (EMS code to be defined upon request)

Introduction The method is applicable to aqueous samples that may contain concentrations of pesticides ranging from trace to high levels. The number of compounds present in the sample may vary considerably depending on the history associated with the site.

Summary The sample is extracted with dichloromethane. The raw extract is concentrated, solvent-exchanged and examined on a capillary column gas chromatograph equipped with electron capture and nitrogen/phosphorus detector. If necessary, the raw extract is cleaned up on a charcoal-cellulose column.

MDL

Compound	Type	mg/L
Acephate	OP	0.0005
Alachlor	H	0.001
Aldrin	OC	0.0001
Allidochlor	H	0.0005
Atrazine	H	0.0002
Azinphos-methyl	OP	0.0005
BHC, alpha-	OC	0.00005
BHC, beta-	OC	0.00005
BHC, delta-	OC	0.0001
Bromacil	H	0.0001
Bromophos	OP	0.0001
Captan	F	0.001
Carbaryl	C	0.002
Carbofuran	C	0.0005
Carbophenothion	OP	0.0001
Chlordane, alpha-	OC	0.0001
Chlordane, gamma-	OC	0.0001
Chlordecone	OC	0.0002
Chlordene, alpha-	OC	0.0001
Chlordene, gamma-	OC	0.0001
Chlorothalonil	F	0.0001
Chlorpropham	H	0.0005
Chlorpyrifos	OP	0.0001
Chlorthal-dimethyl	H	0.0001
Coumaphos	OP	0.0005
Dazomet	F	0.0005
DDD, o,p-	OC	0.0002
DDD, p,p'-	OC	0.0002
DDE, p,p'-	OC	0.0001
DDT, o,p-	OC	0.0002
DDT, p,p'-	OC	0.0001
Diazinon	OP	0.0002
Diazinon-oxygen analog	OP	0.0002
Dichlobenil	H	0.00005
Dichlofop-methyl	H	0.0001
Dichloran	F	0.0001
Dichlorvos	OP	0.0001
Dieldrin	OC	0.0001
Dimethoate	OP	0.0002
Disulfoton	OP	0.0005
Diuron	H	0.0005
Endosulfan sulfate	OC	0.0003
Endosulfan-1	OC	0.0001
Endosulfan-2	OC	0.0001
Endrin	OC	0.0001
Eptam	H	0.001
Ethion	OP	0.0005
Fensulfothion	OP	0.0001
Fensulfothion-oxone	OP	0.0005
Fenthion	OP	0.0002
Flamprop-methyl	H	0.0001
Folpet	F	0.001
Fonofos	OP	0.0002
Fonofos-oxygen analog	OP	0.0005
Heptachlor	OC	0.00005
Heptachlor epoxide	OC	0.0001
Hexachlorobenzene	OC	0.0002
Hexazinone	H	0.0003
Iodofenphos	OP	0.0001
Lindane	OC	0.00002
Linuron	H	0.0002
Malathion	OP	0.0001
Methamidophos	OP	0.0005

Compound	Type	mg/L	Compound	Type	mg/L
Methidathion	OP	0.0002	Phosmet	OP	0.0003
Methoxychlor	OC	0.0002	Phosphamidon	OP	0.0005
Methyl Parathion	OP	0.0002	Prometryne	H	0.0002
Metolachlor	H	0.0002	Pronamide	H	0.0001
Metobromuron	H	0.0005	Propanil	H	0.0002
Metribuzin	H	0.0001	Propazine	H	0.0002
Mevinphos	OP	0.0005	Ronnel	OP	0.0005
Mirex	OC	0.0002	Simazine	H	0.0002
Monuron	H	0.0005	Sulfotep	OP	0.0002
Naled	OP	0.0001	Terbacil	H	0.0005
Nitrofen	H	0.0001	Terbofos	OP	0.0002
Nonachlor, trans-	OC	0.0001	Terbutryn	H	0.0002
Omethoate	OP	0.0003	Terbutylazine	H	0.0005
Oxychlordane	OC	0.0001	Tetrachlorvinphos	OP	0.0002
Oxyfluorfen	H	0.0001	Tetradifon	OC	0.0001
Parathion	OP	0.0002	Triallate	H	0.0001
Phorate	OP	0.0002	Trifluralin	H	0.0001
Phosalone	OP	0.0005	Vernolate	H	0.0002

OC = Organochlorine pesticide
OP = Organophosphate pesticide
H = Herbicide
C = Carbamate
F = Fungicide

Matrix Fresh water, wastewater, marine water.

Interferences and **Precautions** Any other pesticide or organic compound that responds to a nitrogen/phosphorus detector or electron capture detector may interfere in the gas chromatography step.

Sample Handling and Preservation **Bottle:** 4.5 L amber glass, narrow mouth, Teflon-lined cap.

Preservation: none required.

Stability **Holding time:** extract within 14 days, analyze within 30 days.

Storage: store at 4°C until analyzed.

Principle or Procedure None listed.

Precision None listed.

Accuracy None listed.

Quality Control **Blanks:** 1 blank per batch or 1 in 14.

Replicates: 1 duplicate per batch or 1 in 14.

References None listed.

Revision History February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: Republication. Note neither SEAM nor EMS codes had been assigned. Out of print reference deleted.

Pesticides, Organochlorine, and PCBs in Water by GC/ECD

Parameter Organochlorine Pesticide Scan

Analytical Method Extraction, Florisil, GC/ECD.

EMS Code (EMS code to be defined upon request.)

Introduction This method is applicable to the determination of a selected group of chlorinated pesticides and PCBs. Some of the pesticides have been banned while others are still in widespread use.

Summary The sample is extracted with dichloromethane, solvent exchanged into iso-octane, and partitioned on 1% deactivated Florisil, if necessary, to remove interferences and reduce chromatographic complexity. The extract is analyzed by capillary column gas chromatography with electron capture detection.

MDL

Compound	mg/L
Aldrin	0.00001
BHC, alpha-	0.00001
BHC, beta-	0.00001
BHC, delta-	0.00001
Chlordane, alpha-	0.00005
Chlordane, gamma-	0.00005
DDD, o,p-	0.00005
DDD, p,p'-	0.00005
DDE, p,p'-	0.00005
DDT, o,p-	0.00005
DDT, p,p'-	0.00005
Dieldrin	0.00005
Endosulfan I	0.00005
Endosulfan II	0.00005
Endosulfan sulfate	0.0001
Endrin	0.00005
Heptachlor	0.00001
Heptachlor epoxide	0.00002
Hexachlorobenzene (HCB)	0.000005
Lindane (gamma-BHC)	0.00001
Methoxychlor	0.0001
Mirex	0.0001
Nonachlor, trans-	0.00005
Oxychlordane	0.00005
PCBs	0.0004

Matrix Fresh water, wastewater, marine water.

Interferences and Precautions Any other pesticide or organic compound that responds to an electron capture detector may interfere in the gas chromatography step.

Sample Handling and Preservation **Bottle:** 1L or 4.5L amber glass, narrow mouth, Teflon-lined cap.Preservation: none required.

Stability **Holding time:** extract within 14 days, analyze within 30 days.

	Storage: store at 4°C until analyzed.
Principle or Procedure	**None listed.**
Precision	None listed.
Accuracy	None listed.
Quality Control	1 blank per batch or 1 in 14.
References	a) Organochlorinated Pesticides and PCB's in Water (Gas Chromatographic), Analytical Methods Manual, Inland Waters Directorate, Water Quality Branch, Ottawa, 1981, part 3, Naquadat No. 18332.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual.
	December 31, 2000: Republication. Note neither SEAM nor EMS codes had been assigned. Out of print reference deleted.

Pesticides, Organophosphate in Water by GC/NPD

Parameter Organophosphate Pesticide Scan

Analytical Method Extraction, charcoal, GC/NPD.

EMS Code (EMS code to be defined upon request.)

Introduction This method is applicable to the determination of a selected group of organophosphate pesticides. Some of the pesticides have been banned while others are still in widespread use.

Summary The sample is extracted with dichloromethane and cleaned up, if necessary, with charcoal. The extract is analyzed by gas chromatography with nitrogen/phosphorus detection.

MDL

Compound	mg/L
Acephate	0.0005
Azinphos methyl	0.0005
Bromophos	0.0001
Carbophenothion	0.0001
Chlorfenvinfos	0.0001
Chlorpyrifos	0.0001
Demeton	0.0002
Diazinon	0.0002
Dichlorvos	0.0001
Dimethoate	0.0002
Dimethoate-O	0.0002
Ethion	0.0005
Fenitrothion	0.0002
Fensulfothion	0.0001
Fenthion	0.0002
Fonofos	0.0002
Fonofos-oxygen analog	0.0005
Iodofenphos	0.0001
Malathion	0.0001
Methamidophos	0.0005
Methidathion	0.0002
Mevinphos	0.0005
Naled	0.0001
Parathion	0.0001
Parathion, Methyl	0.0002
Phorate	0.0002
Phosalone	0.0005
Phosmet	0.0003
Phosphamidon	0.0005
Sulfotep	0.0002
Tetrachlorvinphos	0.0002

Matrix Fresh water, wastewater, marine water.

Interferences and Precuations Any other pesticide or organic compound that responds to a nitrogen/phosphorus detector may interfere in the gas chromatography step.

Sample Handling and Preservation	**Bottle:** 1 L amber glass, narrow mouth, Teflon-lined cap. Preservation: none required.
Stability	**Holding time:** extract without delay, analyze within 30 days. **Storage:** store at 4°C until analyzed.
Principle or Procedure	See Reference 1, pp 139-141.
Precision	None listed.
Accuracy	None listed.
Quality Control	**Blanks:** 1 blank per batch or 1 in 14. **Replicates:** 1 duplicate sample per batch or 1 in 14.
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

Phenols, 4-Aminoantipyrine Colorimetric

Parameter	Phenols
Analytical Method	Aminoantipyrine colorimetric.
EMS Code	**0117 X142**
Introduction	Phenol, which is a hydroxy derivative of benzene, may occur in industrial, surface, and ground waters. Upon chlorination the presence of phenol leads to objectionable tastes due to the formation of various byproducts.
Summary	Phenolic compounds are removed from the sample matrix by steam co-distillation. An aliquot of the distillate is reacted with 4-aminoantipyrine in the presence of potassium ferri-cyanide at a pH of 7.9 ±0.1 to form a red antipyrine dye. The colour is extracted with dichloromethane and the absorbance is read at 460 nm. The colour development procedure may be performed either in an automated system or manually.
MDL	Typical: 0.001 mg/L.
	Range: 0.001–0.25 mg/L.
Matrix	Domestic and industrial wastewaters, natural water, and potable water supplies.
Interferences and Precautions	By acidifying the sample, interferences such as phenol-decomposing bacteria, oxidizing and reducing substances, and alkalinity are minimized. Distillation removes the phenols from most interferences in the sample matrix. Different (substituted) phenolic compounds may produce varying amounts of colour; interpret results with care.
Sample Handling	Glass (1.0 L). Add 5 mL 8% $CuSO_4$ /L and H_3PO_4 to pH <4.
and Preservation	Store cool, 4°C.
Stability	M. H. T. = 28 days.
Principle or Procedure	Autoanalyzer with phenol manifold, photometer with 460 nm filters and 10 mm tubular flow cell. A manual adaptation of this method is also acceptable.
Precision	40 wastewaters analyzed in duplicate over a range of 0.02–6.4 mg/L had an average RSD of ±12%.
Accuracy	None listed.
Quality Control	**Blanks:** one reagent blank per batch or 1 in 14.
	Replicates: one duplicate sample per batch or 1 in 14.
	Recovery control: one mid-range spike per batch or 1 in 14.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 5530 C. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Methods 420.1 and 420.2.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual.
	December 31, 2000: SEAM codes replaced by EMS codes.

Polychlorinated Biphenyls (PCBs) in Petroleum Products

Parameter PCBs, Total

Analytical Method Silicic Acid/Florisil, GC-ECD.

EMS Code **P019 X376**

Introduction Polychlorinated biphenyls have been widely used in hydraulic oils, industrial plasticizers and electrical transformer fluids. Due to the increased environmental concern over PCBs, their persistance and the costs associated with their destruction, coupled with the tendency for petroleum products, especially waste oils, to become contaminated with PCBs, there has been a growing need for a means of screening waste oils for PCBs.

Note: This method is applicable to the determination of PCBs in transformer oil.

Summary The petroleum product is diluted in hexane and an aliquot is partitioned on a combination silicic acid/Florisil column. The extract is examined on a gas chromatograph equipped with an electron capture detector.

MDL 0.5 µg/g

Matrix Petroleum products including waste lubricants and used transformer oils.

Interferences and Precautions Other halogenated organics, including organo-chlorine pesticides, may cause a response on the electron capture detecto. High levels of co-eluting nonchlorinated hydro-carbons cause quenching of the detector signal, hence the need for a means of separating PCBs from the oil matrix.

Sample Handling and Preservation 0.5 litre wide mouth brown glass bottle; acetone rinsed, heat treated.

No preservation. The samples must be handled with caution as they may contain high levels of PCBs.

Stability **Holding time:** PCBs are stable indefinitely, especially at high concentration.

Storage: Store at 4°C until analyzed.

Procedure The transformer oil is diluted in hexane and an aliquot is cleaned up on a combination silicic acid/Florisil column. The extract is examined by electron capture gas chromatography.

Apparatus

a) Centrifuge tubes, graduated, 12 mL, with ground glass stoppers.

b) Preparatory chromatographic column, 9 mm ID by 300 mm, with a 200 mL reservoir.

c) Evaporation flasks, round bottom, with 24/40 standard taper neck.

d) Rotary evaporator.

Reagents

a) Solvents, pesticide grade, glass distilled;

1) Hexane
2) Petroleum ether
3) Iso-octane (2,2,4-trimethyl pentane)
4) Ethyl acetate.

b) Florisil, PR grade, 60/100 mesh, heat treated at 650°C for 6 hours, cooled in a desiccator and deactivated with 1% water (w/w).

c) Silicic acid, heat treated at 130°C for 24 hours, cooled in a desiccator and deactivated with 1% water (w/w).

d) Sodium sulfate, granular, anhydrous, heat treated at 650°C for 4 hours minimum.

e) Glass wool, heat treated at 300°C.

Procedure

a) Weigh out 1.0 g of transformer oil (or other waste oil) in a 12 mL centrifuge tube and dilute to 10.0 mL. Vortex to ensure complete mixing.

b) Prepare a cleanup column containing 8 grams of 1% deactivated silicic acid topped by 2 grams of 1% deactivated Florisil and 1.5 to 2 cm of anhydrous sodium sulfate. Place 1.0 mL of the diluted oil onto the cleanup column and, without allowing the top of the column to go dry, fractionate using the following procedure:

1) Fraction 1: 30 mL of petroleum ether. Discard this fraction.

2) Fraction 2: 125 mL of 1% ethyl acetate (or acetone) in petroleum ether. This fraction contains the PCBs.

Note: this elution profile should be verified for each new batch of deactivated silicic acid.

c) Examine the cleaned up extract by electron capture gas chromatography. If the concentration of PCBs in the oil is suspected to be high, analyze the unconcentrated extract to establish the appropriate dilution range. To attain the stated MDL, add 2 mL of iso-octane to the extract in the evaporation flask and concentrate to 1–2 mL, then transfer to a 5 mL graduated centrifuge tube and concentrate to 1.0 mL by “blowing down” with a stream of purified nitrogen.

Precision

None listed.

Accuracy

None listed.

Quality Control

Blanks: 1 blank per batch or 1 in 14.

Replicates: 1 duplicate sample per batch or 1 in 14.

References

None listed.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

Polychlorinated Biphenyls (PCBs) in Solids

Parameter

Polychlorinated Biphenyls (PCBs)

Analytical Method

DCM extraction, Florisil cleanup, GC/ECD.

Introduction

This method is applicable to the quantitative determination of polychlorinated biphenyls in soil, sediments and other solids. PCBs were produced commercially as a series of distinct mixtures of varying chlorine content under the tradename "Arochlor". Pure PCB material is a dense liquid and was used in many applications requiring high thermal stability and dielectric constant, most notably as insulating oils in the electrical industry. Due to their environmental persistance, PCBs were banned from production in the US in 1976.

Summary

A portion of the sample is extracted, as received, with a solvent mixture that affords good contact with potentially high moisture content soils. One to one mixtures of hexane/acetone, dichloromethane/acteone or dichloromethane/ methanol are all suitable. The mixed solvent extract is back extracted with water to isolate the hexane or dichlorimethane phase. The raw extract is concentrated, cleaned up by partitioning on a Florisil column and/or treated with freshly cleaned copper to remove sulfur, as required and examined on a capillary column gas chromatograph equipped with an electron capture detector.

MDL

Polychlorinated Biphenyls (PCB's)	Detection Limit (µg/g)
Aroclor 1242	0.05
Aroclor 1248	0.05
Aroclor 1254	0.05
Aroclor 1260	0.05

Matrix

Soil (marine), sediments, other solid samples, e.g., wood chips, floor sweepings, demolition debris and etc.

Interferences and Precautions

a) Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baselines. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

b) Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The type and extent of matrix interferences will vary from source to source. Sulfur is common in anerobic sediments, phthalate esters may be prevalent in landfill samples.

Sample Handling and Preservation

Soil samples should be collected in hydrocarbon clean 0.5 litre widemouth amber glass bottles and stored in a freezer at -10°C. Minimum required sample mass is 50 grams, however preferred sample size is 250 grams or more.

Stability

Holding Time: extract the sample within 14 days of sampling and analyze within 28 days.

Storage: store samples at -10°C and extracts at 4°C until analyzed.

Procedure

a) Separatory funnels, 500 mL

Apparatus

b) Flasks, Erlenmeyer, 500 mL

c) Flasks, round bottom 250 mL and 500 mL

d) Glass filter funnels

e) Glass columns 1.4 cm × 30 cm with 150 mL reservoir

f) Pipettes, 2 mL

g) Polytron homogenizer or

h) Waring (type) blender, stainless steel, explosion proof

i) Rotary evaporator

j) Graduated centrifuge tubes with ground glass stoppers, 15 mL

k) Nitrogen 'blow down' apparatus

Reagents

a) Solvents, *distilled in glass* or pesticide grade

- Dichloromethane (Methylene chloride)
- Hexane
- Acetone
- Methanol
- Isooctane (2,2,4-trimethylpentane)
- Petroleum Ether
- Ethyl Acetate

b) Granular sodium sulphate, anhydrous, reagent grade, heat treated at 600°C for 6 hr.

c) Florisil, PR Grade, heat treated at 650°C for six hours, deactivated with 1% (weight to weight) water.

d) Glass wool, heat treated at 300°C.

e) Copper, granulated, acid cleaned and solvent rinsed.

Procedure

a) Pour 50 g of sample into a blender (Waring type or Polytron as appropriate).

b) Add 50 µL of 20 ppm surrogate (Dibromobiphenyl) and 100 mL of mixed solvent (dichloromethane (DCM)/acetone or alternative mixture). Blend for one to two minutes.

c) Decant the supernatant through glass wool supported in a glass funnel into a 500 mL separatory funnel.

d) A second extraction of the sample is carried out by adding 75 mL of dichloromethane (DCM) to the centrifuge bottle and again blending for 12 minutes.

e) Decant the supernatant into the separatory funnel.

f) Add 250 mL of water to the extract in separatory funnel and shake to remove the acetone into the water layer. Allow layers to separate.

g) Collect the solvent layer in a 500 mL erlenmeyer flask after filtering through sodium sulfate supported by glass wool in a glass filter funnel. Add 10 g of sodium sulfate to the erlenmeyer.

h) Repeat the extraction with two more aliquots of 50 mL DCM.

i) The combined organic extract is allowed to dry. If necessary, more sodium sulfate is added to the erlenmeyer until the solution clears.

j) The solution is decanted into a 500 mL round bottom flask. The erlenmeyer and sodium sulfate are rinsed with DCM and the rinse is added to the evaporating flask.

k) Add 23 mL of isooctane to the flask and evaporate the extract using a rotary evaporator to 23 mL. Add 20 mL hexane to the flask and reevaporate to 23 mL. Make up to 10 mL with hexane in a graduated centrifuge tube.

l) Place glass wool at the outlet of a glass column (1.4 × 30 cm) and add about 1 cm of heat treated sodium sulfate.

m) Add 10 g of prepared 1% Florisil to the column. Wash down the column with approximately 50 mL of petroleum ether. When the solvent is about 45 cm above the Florisil add 1 cm of heat treated sodium sulfate.

Note: Maintain the solvent level above the sodium sulfate.

n) Pipette 1.0 mL of the raw extract onto the column. Carefully rinse the walls of the column with small amounts of the solvent to ensure that the sample is quantitatively transferred to the top of the Florisil.

o) Add 100 mL of petroleum ether to the column and collect the eluate in a 250 mL round bottom flask.

p) Add 2 mL of isooctane and concentrate to 23 mL on a rotary evaporator. Do not allow the solution to go to dryness.

q) Add 10 mL of hexane and concentrate to 23 mL on a rotary evaporator.

Note: If sulphur is present in the sample, it will appear as an interference (a large broad peak) during the first portion of the chromatogram. It is removed using a copper metal cleanup procedure. If highly contaminated, the sulphur may precipitate during the rotary evaporation stage. If this occurs, transfer the extract, being careful not to transfer any solid sulphur, into another evaporation flask. Rinse the original flask three times with hexane to quantitatively transfer all PCB material. Continue to concentrate on the rotary evaporator. If precipitation occurs again, repeat the transfer procedure.

r) Pretreat the copper metal by oxidizing with dilute nitric (approximately 0.5 mL to 10 mL reagent grade water) acid for 2–3 minutes on a vortex mixer. Discard the acid, then rinse the copper with reagent grade water until pH is neutral. Wash the copper with acetone three times, then dry on an NEvap.

s) Add a small amount of copper to the sample and vortex for 3 min. If copper turns black, CuS has been formed, and more copper is required. If some copper remains unreacted then transfer the extract to a fresh concentrator tube and concentrate to 1.5 mL, exchanging to isooctane.

t) Transfer to a 15 mL graduated centrifuge tube and make up to 5 mL with isooctane or hexane.

u) Spike with 50 µL of 20 ppm hexachlorobenzene (internal standard) and analyze by GC.

Instrument Conditions

(Provided as a guide, product endorsement is not implied.)

Instrument:	HP 5880 gas chromatograph with split/ splitless injection system and electron capture detector.
Column:	DB17, 30 m × 0.25 mm i.d., 0.025 µm film thickness, or

	DB5, 30 m × 0.25 mm i.d., 0.025 µm film thickness.
Carrier gas:	Helium
Head pressure:	25 psi
Injector temperature:	250°C
Injection volume :	1 µL
Injection mode:	Splitless, 1 minute
Initial temperature:	100°C
Initial time:	1 min
Oven program:	25°C/min to 170°C, then 4°C/min to 220°C, then 10°C/min to 260°C.
Final hold:	17.5 min

GC Calibration

a) To each prepared calibration standard mixture add a known constant amount of the internal standard (hexachlorobenzene) to yield a resulting concentration of 0.2 µg/mL. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system.

b) Analyze a constant amount (usually 1 µL) of each calibration standard and tabulate the area for each PCB and internal standard, and calculate the relative response factor (RRF) for each using the following equation:

$$RRF = \frac{(A_x C_{i_s})}{(A_{i_s} C_x)}$$

where:

A_x = Area of the PCB to be measured

C_x = Area of the internal standard

A_{i_s} = Concentration of the PCB, (ng/µL)

C_{i_s} = Concentration of the internal standard, (ng/µL)

c) If the RRF value over the working range is a constant (< 20% RSD), the RRF can be assumed to be invariant and the average RRF can be used for calculations.

d) The working calibration curve or RRF must be verified on each working day by measurement of one or more calibration standards. If the RRF for any parameter varies from the predicted RRF by more than 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

e) The retention times for each compound in each calibration run should agree within 0.06 relative retention time units of the nearest internal standard.

Daily One Point Initial Calibration Check

At the beginning of each work day, a daily one-point calibration check is performed by reevaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one instead of three working standards is evaluated. Analyze the one working standard under the same conditions the initial calibration curve was evaluated. Analyze 2 µL of the midscale calibration standard and obtain the RRF. Calculate the percent difference between the current RRF and average RRF using the following equation:

$$\% \text{ Difference} = \frac{(RRF_c - RRF_i)}{RRF_i} \times 100$$

where:

RRF_i = Average relative response factor from initial calibration using midscale standard

RRF_c = Relative response factor from current verification check using midscale standard

If the percent difference for the midscale level is greater than 10%, the laboratory should consider this a warning limit. If the percent difference for the midscale standard is less than 20%, the current calibration is assumed to be valid. If the criterion is not met (>20%), then corrective action must be taken. This check must be met before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new threepoint calibration must be generated. This criterion must be met before sample analysis begins.

12-Hour Calibration Verification

A calibration standard at midlevel concentration containing selected arochlors must be performed every twelve continuous hours of analysis. Compare the RRF every 12-hours with the average RRF from the initial calibration. If the % difference for RRF is less than 20%, then the GC system is operative within initial calibration values. If the criterion is not met (>20% difference), then the source of the problem must be determined and a new threepoint curve must be generated.

Calculations

$$\text{Concentration of PCB}_x = \frac{\sum_1^8 A_x}{A_{is}} \times \frac{W_{is}}{RRF_{PCB}} \times \frac{1}{Wt}$$

where:

A_{x1} = Area of PCB peak #1 that was measured

A_{x2} = Area of PCB peak #2 that was measured

A_{x3} = Area of PCB peak #3 that was measured

A_{x4} = Area of PCB peak #4 that was measured

A_{x5} = Area of PCB peak #5 that was measured

A_{x6} = Area of PCB peak #6 that was measured

A_{x7} = Area of PCB peak #7 that was measured

A_{x8} = Area of PCB peak #8 that was measured

A_{is} = Area of internal standard

W_{is} = Amount of internal standard added to the final extract

RRF_{PCB} = Relative response factor of the total area of PCB peaks one to eight of PCB_x from a calibration run

Wt = Initial sample weight

The eight PCB peaks chosen are the eight largest and best resolved peaks that do not correspond to a retention time associated with an organochlorine pesticide.

Precision

Not available.

Accuracy

Not available.

Quality Control

Method Blank:

Analyze at a frequency of one per sample extraction batch. Blanks should contain no more than method detection limit (MDL) levels. Sample data are not corrected for blanks. If positives are detected at >5% of sample values, the samples should be repeated.

Method Spike:

Analyze at a frequency of one in 14 or one per batch, whichever is more frequent. 50 g of water is spiked with a known concentration of arochlor. The spike level should relate to the sample concentration as closely as possible. If this is not possible, then the spike level should be at a concentration ten times the minimum detection limit. Calculate the % recovery as follows:

$$\%\ \text{Recovery} = \frac{((\text{sample} + \text{spike}) - (\text{sample only}))}{\text{spiked amount}} \times 100$$

Allowed recoveries are: 50–130%. Samples for which the spike is outside the limit are to be reinjected. If it fails again, repeat the batch.

Method Duplicate:

Analyze at a frequency of one in 14 or one per batch, which ever is more frequent. The relative percent difference for the compounds detected is calculated as follows:

$$\%\ \text{Difference} = \frac{((\text{sample 1}) - (\text{sample 2}))}{(\text{average of 1 \& 2})} \times 100$$

Allowed difference: < 25% (if both samples are greater than 5 times the MDL). Replicates outside the limits are required to be repeated.

Surrogates:

Acceptable recovery: 50–130%

References

a) EPA (1986) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, SW-846, 3rd Edition, November, 1986.

b) EPA (1994) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, SW-846, 3rd Edition, Update IIA, September 1994.

c) ASTM Method D3304: Analysis of PCBs in Environmental Materials.

Revision Date

November 2002: Method adopted from Manual Supplement #1. EMS Code assigned.

Polychlorinated Biphenyls (PCBs) in Water

Parameter Polychlorinated Biphenyls

Analytical Method DCM extraction, Florisil cleanup, GC/ECD.

EMS Code

Introduction This method is applicable to the quantitative determination of polychlorinated biphenyls in water. PCB material consists of distinct mixtures (referred to as "Arochlor" mixtures). Pure PCB material is a dense liquid and was used in many applications requiring high thermal stability and dielectric constant, most notably as insulating oils in the electrical industry. Due to their environmental persistance, PCBs were banned from production in the US in 1976.

Summary An aliquot of the water sample is extracted with dichloromethane. The raw extract is concentrated and examined on a capillary column gas chromatograph equipped with an electron capture detector. If necessary the raw extract is cleaned up (partitioned) on a Florisil column.

MDL

Polychlorinated Biphenyls (PCB's)	**Detection Limit (mg/L)**
Aroclor 1242	0.0004
Aroclor 1248	0.0004
Aroclor 1254	0.0004
Aroclor 1260	0.0004

Matrix Fresh water, wastewater, marine water.

Interferences and

Precautions

a) Interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to artifacts and/or elevated baselines. All materials used should be routinely monitored and demonstrated to be free of interferences under the the conditions of the analysis.

b) Matrix interferences may be caused by contaminants that could be coextracted from the sample. The extent of the matrix interferences will vary from source to source.

Sample Handling

and Preservation Water samples should be collected in hydrocarbon clean 1 litre amber glass bottles and stores at 4°C. Minimum required volume is 1 L.

Stability **Holding Time:** extract the sample within 14 days of sampling and analyze within 28 days.

Storage: store at 4°C until analyzed.

Procedure

Apparatus

a) Separatory funnels, 1000 mL

b) Round bottom flasks, 250 and 500 mL

c) Glass filter funnels

d) Glass columns 1.4 cm × 30 cm with 150 mL reservoir

e) Pipettes, 2 mL

f) Rotary evaporator

g) Graduated centrifuge tubes with ground glass stoppers, 15 mL

h) Nitrogen 'blow down' apparatus

Reagents

a) Solvents, *distilled in glass* or pesticide grade

- Dichloromethane
- Isooctane (2,2,4-trimethylpentane)
- Hexane
- Petroleum Ether
- Ethyl Acetate

b) Granular sodium sulphate, anhydrous, reagent grade, heat treated at 600°C for 6 hr.

c) Florisil, PR Grade, heat treated at 650°C for six hours, deactivated with 1% (weight to weight) water.

d) Glass wool, heat treated at 300°C.

Procedure

a) Pour 800 mL of sample into a 1000 mL separatory funnel. Add 50 µL of 20 ppm surrogate (Dibromobiphenyl) and 60 mL of dichloromethane (DCM). Shake vigorously for one minute.

b) Allow the layers to seperate and collect the DCM in a 250 mL round bottom flask after filtering through sodium sulfate supported by glass wool in a glass filter funnel.

c) Repeat the extraction with two more aliquots of 60 mL DCM.

d) Collect all DCM and concentrate to 23 mL on a rotary evaporator.

e) Add 10 mL of hexane and concentrate to 23 mL on a rotary evaporator.

f) Transfer to a 15 mL graduated centrifuge tube and make up to 5 mL with isooctane or hexane.

g) Spike with 50 µL of 20 ppm hexachlorobenzene and analyze by GC/ECD.

Instrument Conditions: (Provided as a guide, product endorsement is not implied.)

Instrument:	HP 5880 gas chromatograph with split/splitless injection system and electron capture detector.
Column:	DB17, 30 m × 0.25 mm i.d., 0.025 µm film thickness, or DB5, 30 m × 0.25 mm i.d., 0.025 µm film thickness.
Carrier gas:	Helium
Head pressure:	25 psi
Injector temperature:	250°C
Injection volume :	1 µL
Injection mode:	Splitless, 1 minute
Initial temperature:	100°C
Initial time:	1 min
Temperature program:	25°C/min to 170°C, then 4°C/min to 220°C, then 10°C/min to 260°C.
Final hold:	17.5 min

GC Calibration

a) To each prepared calibration standard mixture add a known constant amount of the internal standard (hexachlorobenzene) to yield a resulting concentration of 0.2 µg/mL. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system.

b) Analyze a constant amount (usually 1 µL) of each calibration standard and tabulate the area for each PCB and internal standard, and calculate the relative response factor (RRF) for each using the following equation:

$$RRF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:

A_x = Area of the PCB to be measured

C_x = Concentration of the PCB, (ng/µL)

A_{is} = Area of the internal standard

C_{is} = Concentration of the internal standard, (ng/µL)

c) If the RRF value over the working range is a constant (< 20% RSD), the RRF can be assumed to be invariant and the average RRF can be used for calculations.

d) The working calibration curve or RRF must be verified on each working day by measurement of one or more calibration standards. If the RRF for any parameter varies from the predicted RRF by more than 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

e) The retention times for each compound in each calibration run should agree within 0.06 relative retention time units of the nearest internal standard.

Daily One Point Initial

Calibration Check

At the beginning of each work day, a daily one-point calibration check is performed by re-evaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one instead of three working standards is evaluated. Analyze the one working standard under the same conditions the initial calibration curve was evaluated. Analyze 2 µL of the midscale calibration standard and obtain the RRF. Calculate the percent difference between the current RRF and average RRF using the following equation:

$$\% \text{ Difference} = \frac{(RRF_c - RRF_i)}{RRF_i} \times 100$$

where:

RRF_i = Average relative response factor from initial calibration using mid-scale standard

RRF_c = Relative response factor from current verification check using mid-scale standard

If the percent difference for the mid-scale level is greater than 10%, the laboratory should consider this a warning limit. If the percent difference for the mid-scale standard is less than 20%, the current calibration is assumed to be valid. If the criterion is not met (>20%), then corrective action must be taken. This check must be met before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new three-point calibration must be generated. This criterion must be met before sample analysis begins.

12-Hour Calibration Verification

A calibration standard at midlevel concentration containing selected arochlors must be performed every twelve continuous hours of analysis. Compare the RRF every 12-hours with the average RRF from the initial calibration. If the % difference for RRF is less than 20%, then the GC system is operative within initial calibration values. If the criterion is not met (>20% difference), then the source of the problem must be determined and a new threepoint curve must be generated.

Calculations:

$$\text{Concentration of } PCB_x = \frac{\sum_1^8 A_x}{A_{is}} \times \frac{W_{is}}{RRF_{PCB}} \times \frac{1}{Vol}$$

where:

A_{x1}	=	Area of PCB peak #1 that was measured
A_{x2}	=	Area of PCB peak #2 that was measured
A_{x3}	=	Area of PCB peak #3 that was measured
A_{x4}	=	Area of PCB peak #4 that was measured
A_{x5}	=	Area of PCB peak #5 that was measured
A_{x6}	=	Area of PCB peak #6 that was measured
A_{x7}	=	Area of PCB peak #7 that was measured
A_{x8}	=	Area of PCB peak #8 that was measured
A_{is}	=	Area of internal standard
W_{is}	=	Amount of internal standard added to the final extract
RRF_{PCB}	=	Relative response factor of the total area of PCB peaks one to eight of PCB_x from a calibration run
Vol	=	Initial sample volume

The eight PCB peaks chosen are the eight largest and best resolved peaks that do not correspond to a retention time associated with an organochlorine pesticide.

Precision Not available.

Accuracy Not available.

Quality Control Method Blank:

Analyze at a frequency of one per sample extraction. Blanks should contain no more than method detection limit (MDL) levels. Sample data are not corrected for blanks. If positives are detected at >5% of sample values, the samples should be repeated.

Method Spike:

Analyze at a frequency of one in 14 or one per batch, whichever is more frequent. 800 mL of water is spiked with a known concentration of arochlor. The spike level should relate to the sample concentration as close as possible. If this is not possible then the spike level should be at a concentration five or ten times the minimum detection limit. Calculate the % recovery as follows:

$$\% \text{ Recovery} = \frac{((\text{sample} + \text{spike}) - (\text{sample only}))}{\text{spiked amount}} \times 100$$

Allowed recoveries are: 50–130%. Samples for which the spike is outside the limit are to be reinjected. If it fails again, repeat the batch.

Method Duplicate:

Analyze at a frequency of one in 14 or one per batch, which ever is more frequent. The relative percent difference for the compounds detected is calculated as follows:

$$\% \text{ Difference} = \frac{((\text{sample 1}) - (\text{sample 2}))}{(\text{average of 1 \& 2})} \times 100$$

Allowed difference: < 25% (if both samples are greater than 5 times the MDL). Replicates outside the limits are required to be repeated.

Surrogates:

Acceptable recovery: 50–130%

References

Not available.

Revision Date

November 2002: Method adopted from Manual Supplement #1. EMS Codes assigned.

Polychlorinated Dioxins and Furans in Water and Solids by GC/HRMS/SIM

Parameter

Polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) in water and in soil or solids.

Analytical Method

Extraction: waters liquid/liquid; solids soxhlet; multicolumns silica gel and alumina cleanup, GC/HRMS/SIM.

EMS Codes

Introduction

This method is applicable to the quantitative determination of poly-chlorinated dibenzo(p)dioxins and polychlorinated dibenzo-furans in water and in soil.

Summary

Water samples are extracted with dichloromethane. Soil samples are ground with anhydrous sodium sulphate (sediments can be air dried) and soxhlet extracted with toluene. The extract is then cleaned up by a series of chromatography columns containing acid silica gel, neutral silica gel, basic silica gel, silver nitrate silica gel followed by alumina column chromatography and analyzed by capillary gas chromatography - high resolution mass spectroscopy using selected ion monitoring (SIM).

MDL

The sensitivity of this method is dependent upon the level of interferences within a given matrix, detection limits are likely to be higher than those quoted below. Within each sample for each component or congener group, a sample specific method detection limit is provided. The 2,3,7,8-substituted isomers will have similar detection limits to the congener groups.

PCDDs & PCDFs	pg/L	pg/g
Total TCDD	2.5	1
Total TCDF	2.5	1
Total P5CDD	8	2
Total P5CDF	7	2
Total H6CDD	25	3
Total H6CDF	15	3
Total H7CDD	10	3
Total H7CDF	25	3
OCDD	25	4
OCDF	25	4

Matrix

Water, soil, sediment, solids.

Interferences and Precautions

a) Solvents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks must be analyzed in order to demonstrate that all laboratory materials are free from interferents under the conditions of the analysis. The use of high purity reagents and solvents helps to minimize interference problems.

b) Interferents coextracted from the sample material will vary considerably with the matrix and the diversity of the site being sample. PCDDs and PCDFs are often associated with other chlorinated organics which may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated methoxy biphenyls, polychlorinated hydroxy diphenyl ethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

c) Oftentimes, the compounds responsible for interferences may be present at concentration levels several orders of magnitude higher than any PCDDs and PCDFs which may be present. Cleanup procedures can be used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation of PCDDs and PCDFs at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If detection limits are seriously elevated by the excessive background, the sample extract will have to be reprocessed using alternative cleanup techniques.

d) Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Sample Handling and Preservation

Bottle (soils): 0.5L wide mouth amber glass, heat treated 350°C.

Preservation: none.

Bottles (water): 4 × 1L narrow mouth amber glass, precleaned.

Stability

Holding Time: extract the sample within 14 days of sampling and analyze within 28 days.

Storage: store at 4°C until analyzed.

Procedure

Apparatus

a) 250 mL glass beakers

b) 25, 50, 100, 250 mL glass micro syringes

c) 10, 25, 50 mL glass volumetric flasks

d) 250 mL wide mouth jars with Teflon lined closures

e) 10 mL glass disposable serological pipettes

f) 500 mL Pyrex flat bottom flask

g) 15 mL glass vials with closures

h) 35 mL glass vials with closures

i) 2 L separatory funnel

j) Allihn filter with coarse glass filter

k) 2 mL crimp top auto sampler vials with crimper

l) Nitrogen blow down apparatus

m) Rotary evaporator

n) 1L erlenmeyer with 20/40 ground glass joint

o) Buchner funnel

p) Solvent dispenser

q) 1L graduated cylinder

r) Glass wool

s) Steel wire

t) Sample tumbler (RollaCell)

u) Analytical balance capable of measuring to 0.0001g

v) Top loading balance capable of measuring to 0.01g

w) Vented oven set at 105°C

x) Soxhlets, minimum 200 mL bed volume

y) Glass column of dimensions 40 cm × 24 cm ID

Reagents

a) Solvents, distilled in glass or Pesticide grade

1) Dichloromethane
2) Toluene
3) Isooctane
4) Hexane
5) Methanol
6) Cyclohexane

b) Potassium hydroxide. Reagent grade.

c) Silver Nitrate. (Baker reagent grade.)

d) Sodium sulfate. Granulated, reagent grade. Purify prior to use by rinsing with dichloromethane and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

e) Sulfuric Acid. Reagent grade.

f) Sodium hydroxide, 1.0 N. Weight 40 g of sodium hydroxide into a 1 litre volumetric flask. Dilute to 1 litre with water.

g) Basic alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for at least 16 hours at 200°C. Store in the oven until used.

h) Silica gel. Bio-Sil A, 100200 mesh. This is stored in a glass container with a Teflon-lined screw cap.

i) Silica gel impregnated with sulfuric acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

j) Silica gel impregnated with sodium hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod. Store the mixture in a glass container with a Teflon-lined screw cap.

k) Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250 mL bottle with a Teflonlined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in a glass container.

l) Silica gel impregnated with silver nitrate (10%). Silver nitrate, reagent grade. Dissolve 10g of silver nitrate in a minimum amount of water. Combine this solution with 90g of cleaned and dried silica gel in a wide mouth glass container with a Teflon-lined closure. Tumble for at least 18 hr. Pack a glass wool plugged furnace tube with the mixed silver nitrate impregnated silica gel. Dry in a muffle furnace under nitrogen for 1hr at 160°C followed by 1hr at 260°C. Stored in a wide mouth glass container with a Teflon-lined closure.

m) Glass Wool. Cleaned by sequential immersion in three aliquots of hexane followed by three sequential immersions in dichloromethane. Alternatively, the glass wool may be cleaned by packing into a wide chromatography column or Buchner funnel and passing volumes of hexane and dichloromethane of at least twice the estimated volume of glass wool present. The cleaned glass wool is air dried followed by

heating to 225°C for at least 18 hr. After cooling, the clean glass wool is stored in a dichloromethane rinsed and dried glass jar with a Teflon-lined screw cap.

n) Nitrogen. Ultra high purity.

o) Hydrogen. Ultra high purity.

Procedure: extraction

a) Water samples containing particulates are extracted as waters with attention to high emulsions, which may be broken by centrifugation. Past history of particular samples or contract requirements may require filtration of water samples with the particulates extracted as solids.

b) Transfer 2 L of sample/blank (distilled water) into a 2 L separatory funnel and spike with 20 mL of the surrogate standard mixture containing the isotopically labelled surrogate standards listed in Table 1.

c) Add 80 mL dichloromethane to the sample/blank in a 2 L separatory funnel.

d) Shake sample/blank vigorously for 2 min and drain the organic phase through a 1.5 inch anhydrous Na_2SO_4 column in an Allihn filter.

e) Extract the aqueous phase twice as above with additional 70 mL aliquots of dichloromethane.

f) Rotary evaporate the combined extract to approximately 2 mL in preparation for a multicolumn cleanup procedure.

g) Soils determine the moisture content of the soil by oven drying (105°C) approximately 5 g of wet soil.

h) Accurately weigh 15–20 g (wet weight) of soil and add approximately 50 g of anhydrous sodium sulphate. Mix until it flows like dry sand and transfer to a soxhlet extractor.

i) Spike the samples with 20mL of the $^{13}C12$ dioxin and furan surrogate standards to determine recovery of typical compounds of interest.

j) Extract for 16–24 hours with toluene in a Soxhlet apparatus.

k) Separate the phases and drain the toluene extract through a 1.5 inch anhydrous Na_2SO_4 column in an Allihn filter.

l) Wash the walls of the Allihn filter with 20 mL of toluene and apply suction to recover all traces of the extract.

m) Rotary evaporate the extract to approximately 1 mL and add 1mL of isooctane in preparation for a multicolumn cleanup procedure.

Procedure: clean up

a) Use the cleanup steps that are needed for the specific sample matrix. Each column needs to be characterized for the analytes of interest and to ensure separation form interfering compounds.

b) Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm with glass wool. Add in sequence, approximately 1cm sodium sulphate, 1cm of silver nitrate silica gel, 1cm of silica gel, 2cm of sodium hydroxide silica gel, 1cm of silica gel, 4–6 cm of sulphuric acid silica gel, 1cm of silica gel, approximately 1cm sodium sulphate. The column is prewetted with 40mL of hexane. This eluate is discarded. Add the sample extract, dissolved in 1:1 toluene:isooctane, to the column with two additional 3 mL rinses of hexane followed by a 10mL rinse of hexane. Elute the column with an additional 40 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 mL using the nitrogen evaporative concentrator.

c) Basic Alumina Column. Shorten a 25 cm disposable Pasteur pipette to about 16 cm. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 11 mL of hexane producing Fraction A, followed by 7 mL of dichloromethane producing Fraction B Discard Fraction A. Collect Fraction B and concentrate it to about 0.5 mL using the nitrogen evaporative concentrator.

d) AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 inch from the tip of a 9 cm disposable Pasteur pipette. Insert a filter paper disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. Rinse the column, in sequence, with 5 mL of toluene, 1 mL of 50 percent dichloromethane in cyclohexane and 5mL of hexane. Discard these eluates. Transfer the concentrate in 1 mL of hexane from the basic alumina column to the carbon/celite column along with 1 mL of hexane rinse. Elute the column sequentially with 2 mL of 50 percent dichloromethane in hexane and 2 mL of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 mL of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50°C to about 1 mL. Transfer the concentrate to a Reactivial using a toluene rinse and concentrate to a volume of 200 mL using a stream of nitrogen. Store extracts in a freezer, shielded from light, until analysis.

Instrument Conditions:

Instrument: HP 5890 gas chromatograph with High resolution mass spectrometer

Column:	DB5, 60 m × 0.25 mm i.d. or equivalent
Carrier gas:	Helium
Head pressure:	10 psi
Column flow rate:	30 cm/s @ 100°C
Scan mode:	Selective ion monitoring (SIM)
Resolution:	1:10,000 with a stability of ±5 ppm
Injector temperature:	250°C
Injection volume:	1 mL
Injection mode:	Splitless
Initial temperature:	80°C
Initial time:	1 min
Temperature program:	40°C/min to 200°C, then 2°C/min to 235°C, then 8°C/min to 310°C
Final hold:	12.5 min

The ions monitored for each grouping of components is provided in the attached Table 2.

GC-MS Calibration

a) The concentration of each calibration standard is provided in Table 4. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GCHRMS system.

b) Analyze a constant amount (usually 1 mL) of each calibration standard. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each surrogate standard is used to quantify the indigenous PCDDs or PCDFs in its homologous series. For example, the ^{13}C-1,2,3,4-TCDD is used to calculate the concentrations of all other tetra-chlorinated isomers. Recoveries of the tetra and penta surrogate standards are calculated using the ^{13}C-1,2,3,4-TCDD. Recoveries of the hexa through octa surrogate standards are calculated using the ^{13}C-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

$$RRF_n = \frac{A_c \bullet C_{sc}}{A_{sc} \bullet C_c} \quad \text{and} \quad RRF_s = \frac{A_{sc} \bullet C_{rc}}{A_{rc} \bullet C_{sc}}$$

where:

RRF_n = relative response factor, native standard to surrogate standard

RRF_s = relative response factor, surrogate standard to recovery standard

A_c = quantification ion (single or both ions) peak area for native standard

A_{sc} = quantification ion (single or both ions) peak area for the appropriate surrogate standard

A_{rc} = quantification ion (single or both ions) peak area for ^{13}C-121,2,3,4-TCDD or ^{13}C12-1,2,3,7,8,9-H6CDD

C_c = concentration of the native standard (pg/mL)

C_{sc} = concentration of the appropriate surrogate standard (pg/mL)

C_{rc} = concentration of ^{13}C12-1,2,3,4-TCDD or ^{13}C12-1,2,3,7,8,9-H6CDD (pg/mL)

c) If the RRF value over the working range is a constant (see criteria in Table 4), the RRF can be assumed to be invariant and the average RRF can be used for calculations.

d) The working calibration curve or RRF must be verified on each working day by measurement of one or more calibration standards. If the RRF for any parameter varies from the predicted RRF by more than the percentage criteria presented in Table 4, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

e) The retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

12-Hour Calibration

Verification

A calibration standard at midlevel concentration containing all PCDD and PCDFs must be performed every twelve continuous hours of analysis. Calculate the percent difference between the current RRF and average RRF using the following equation:

$\%\ \text{Difference} = [(RRF_c - RRF_i) / RRF_i] \times 100$

where:

RRF_i = Average relative response factor from initial calibration using midscale standard

RRF_c = Relative response factor from current verification check using midscale standard

Compare the RRF every 12-hours with the average RRF from the initial calibration. If the % difference for RRF is less than the criteria in Table 4, then the GC-MS system is operative within initial calibration values. If the criterion is not met, then the source of the problem must be determined and a new 5-point curve **MUST** be generated.

Interpretation

Identification Criteria: The following identification criteria shall be used for characterization of PCDDs and PCDFs.

a) The integrated ion-abundance ratio shall be within 15 percent of the theoretical value. The acceptable ion abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 3.

b) The retention time for the analytes must be within 3 seconds for the corresponding ^{13}C-labeled internal, surrogate or alternate standard.

c) The monitored ions shown in Table 2 for a given analyte shall reach their maximum within 2 seconds of each other.

d) The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

d) The signal to noise for all monitored ions must be greater than 2.5.

Calculation

The concentration of PCDD/PCDF (C_x) is calculated as follows:

$$C(X) = \frac{\sum_{k=1}^{n} A_k \bullet Q_{ss}}{A_{ss} \bullet RRF_n \bullet V}$$

and

$$\%R(X) = \frac{A_{ss} \bullet Q_{rs} \bullet 100}{A_{rs} \bullet Q_{ss} \bullet RRF_s}$$

Where:

C(X) = recovery-corrected quantity of analyte × (pg)

A_k	=	quantification ion (single or both ions) peak area for the "k"th homologous isomer of analyte × (n = 1 for isomer-specific analysis)
V	=	Initial weight or volume of sample (g or L)
Q_{ss}	=	amount of surrogate standard × added to the sample (pg)
A_{ss}	=	quantification ion (single or both ions) peak area for surrogate standard × in sample extract
%R(X)	=	recent recovery of surrogate standard X
Q_{rs}	=	amount of $^{13}C_{12}$-1,2,3,4-TCDD (recovery standard for tetra- and penta-CDD/CDF) or $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD (recovery standard for hexa- and hepta-CDD/CDF and OCDD) in sample extract (pg)
A_{rs}	=	quantification ion (single or both ions) peak area for $^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD in sample extract

For homologues represented by more than one isomer in the calibration standard solutions, the "homologue-average" RRF is used to quantify all target analytes that are not 2,3,7,8-substituted congeners.

Precision

Not available.

Accuracy

Not available.

Quality Control

Method Blank Analysis:

Analyze at a frequency of one per sample extraction batch. Blanks should contain no more than method detection limit (MDL) levels. Sample data are not corrected for blanks.

Method Spike:

Analyze at a frequency of one in 14 or one per batch, whichever is less. 2 L of sample is spiked with a known concentration of PCDD/PCDF. The spike level should be at a concentration close to the mid-point of the calibration range. Calculate the % recovery as follows:

$$\%\ \text{Recovery} = [\text{recovered amount}] / [\text{spiked amount}] \times 100$$

Allowed recoveries are:

50–130%. Samples for which the spike is outside the limit are to be repeated. If it fails again, repeat the batch.

Laboratory duplicate:

Analyze at a frequency of one in 14 or one per batch, which ever is less. The relative percent difference for the compounds detected is calculated as follows:

$$\%\ \text{Difference} = \frac{[\text{sample 1}] - [\text{sample 2}]}{[\text{average of 1 \& 2}]} \times 100$$

Allowed difference:

< 25% (if both samples are greater than 5 times the MDC).

Replicates outside the limits are required to be repeated.

Surrogates:

Acceptable surrogate recoveries are 30–130%.

References

a) US Environmental Protection Agency. SW846 Method 3510B/3540B/8290B.

b) US Environmental Protection Agency. Method 23.

Revision Dates

November 2002: Method adopted from Manual Supplement #1. EMS Codes assigned.

TABLE 1 SAMPLE FORTIFICATION AND RECOVERY STANDARD SOLUTIONS

Surrogate Standards:	**Concentration (pg/µL)**
^{13}C-2,3,7,8-TCDD	100
^{13}C-1,2,3,7,8-PeCDD	100
^{13}C-1,2,3,6,7,8-HxCDD	100
^{13}C-1,2,3,4,6,7,8-HpCDD	100
^{13}C-OCDD	200
^{13}C-2,3,7,8-TCDF	100
^{13}C-1,2,3,7,8-PeCDF	100
^{13}C-1,2,3,6,7,8-HxCDF	100
^{13}C-1,2,3,4,6,7,8-HpCDF	100
Internal Standards:	
^{13}C-1,2,3,4-TCDD	100
^{13}C-1,2,3,7,8,9-HxCDD	100

TABLE 2

DESCRIPTOR NUMBER	ACCURATE MASS	ION TYPE	ANALYTE
1	303.9016	M	TCDF
TCDF / TCDD / HxCDPE	305.8987	M + 2	TCDF
	315.9419	M	^{13}C-TCDF
	317.9389	M + 2	^{13}C-TCDF
	319.8965	M	TCDD
	321.8936	M + 2	TCDD
	327.8850	M	^{37}Cl-TCDD
	331.9368	M	^{13}C-TCDD
	333.9339	M + 2	^{13}C-TCDD
	375.8364	M + 2	HxCDPE
	316.9824	LOCKMASS	PFK
2	339.8597	M + 2	PeCDF
PeCDF / PeCDD / HpCDPE	341.8567	M + 4	PeCDF
	351.9000	M + 2	^{13}C-PeCDF
	353.8970	M + 4	^{13}C-PeCDF
	355.8546	M + 2	PeCDD
	357.8516	M + 4	PeCDD
	367.8949	M + 2	^{13}C-PeCDD
	369.8919	M + 4	^{13}C-PeCDD
	409.7974	M + 2	HpCDPE
	366.9792	LOCKMASS	PFK
3	373.8208	M + 2	HxCDF
HxCDF / HxCDD / OCDPE	375.8178	M + 4	HxCDF
	383.8639	M	^{13}C-HxCDF
	385.8610	M + 2	^{13}C-HxCDF
	389.8157	M + 2	HxCDD
	391.8127	M + 4	HxCDD
	401.8559	M + 2	^{13}C-HxCDD
	403.8529	M + 4	^{13}C-HxCDD
	445.7555	M + 4	OCDPE
	380.976	LOCKMASS	PFK
4	407.7818	M + 2	HpCDF
HpCDF / HpCDD / NCDPE	409.7789	M + 4	HpCDF
	417.8253	M	^{13}C-HpCDF
	419.8220	M + 2	^{13}C-HpCDF
	423.7766	M + 2	HpCDD
	425.7737	M + 4	HpCDD
	435.8169	M + 2	^{13}C-HpCDD
	437.8140	M + 4	^{13}C-HpCDD
	479.7165	M + 4	NCDPE
	430.9728	LOCKMASS	PFK
5	441.7428	M + 2	OCDF
OCDF / OCDD / DCDPE	443.7399	M + 4	OCDF
	457.7377	M + 2	OCDD
	459.7348	M + 4	OCDD
	469.7779	M + 2	^{13}C-OCDD
	471.7750	M + 4	^{13}C-OCDD
	513.6775	M + 4	DCDPE
	454.9728	LOCKMASS	PFK

H	=	1.007825
C	=	12.000000
^{13}C	=	13.003355
F	=	18.9964
O	=	15.994915
^{35}Cl	=	34.968853
^{37}Cl	=	36.965903

Note: Lock masses may change with different types of PFK

TABLE 3 THEORETICAL ION ABUNDANCE RATIOS AND CONTROL LIMITS

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	lower	upper	
4	M / M + 2	0.77	0.65	0.89	
5	M + 2 / M + 4	1.55	1.32	1.78	
6	M + 2 / M + 4	1.24	1.05	1.43	
6	M / M + 2	0.51	0.43	0.59	use for ^{13}C-HxCDF only
7	M / M + 2	0.44	0.37	0.51	use for ^{13}C-HpCDF only
7	M + 2 / M + 4	1.04	0.88	1.20	
8	M + 2 / M + 4	0.89	0.76	1.02	

TABLE 4 COMPOSITION OF CALIBRATION SOLUTIONS AND THEIR CORRESPONDING INITIAL AND CONTINUING CALIBRATION REQUIREMENTS

Unlabeled Analytes:	CS1 Low pg/µL	CS2 Low pg/µL	CS3Low CS1 High pg/µL	CS4Low CS2 High pg/µL	CS5 Low CS3 High pg/µL	Initial Calibration % RSD	Continuing Calibration % RSD
2,3,7,8-TCDD	0.5	1	5	50	100	25	25
2,3,7,8-TCDF	0.5	1	5	50	100	25	25
1,2,3,7,8-PeCDD	0.5	1	5	50	100	25	25
1,2,3,7,8-PeCDF	0.5	1	5	50	100	25	25
2,3,4,7,8-PeCDF	0.5	1	5	50	100	25	25
1,2,3,4,7,8-HxCDD	0.5	1	5	50	100	25	25
1,2,3,6,7,8-HxCDD	0.5	1	5	50	100	25	25
1,2,3,7,8,9-HxCDD	0.5	1	5	50	100	25	25
1,2,3,4,7,8-HxCDF	0.5	1	5	50	100	25	25
1,2,3,6,7,8-HxCDF	0.5	1	5	50	100	25	25
1,2,3,7,8,9-HxCDF	0.5	1	5	50	100	25	25
2,3,4,6,7,8-HxCDD	0.5	1	5	50	100	25	25
1,2,3,4,6,7,8-HpCDD	0.5	1	5	50	100	25	25
1,2,3,4,6,7,8-HpCDF	0.5	1	5	50	100	25	25
1,2,3,4,7,8,9-HpCDF	0.5	1	5	50	100	25	25
OCDD	5	10	50	500	1000	25	25
OCDF	5	10	50	500	1000	30	30
Surrogate Standards:							
^{13}C-2,3,7,8-TCDD	100	100	100	100	100	25	25
^{13}C-1,2,3,7,8-PeCDD	100	100	100	100	100	25	25
^{13}C-1,2,3,6,7,8-HxCDD	100	100	100	100	100	25	25
^{13}C-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	30	30
^{13}C-OCDD	100	100	100	100	100	30	30
^{13}C-2,3,7,8-TCDF	100	100	100	100	100	30	30
^{13}C-1,2,3,7,8-PeCDF	100	100	100	100	100	30	30
^{13}C-1,2,3,6,7,8-HxCDF	100	100	100	100	100	30	30
^{13}C-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	30	30
Internal Standards:							
^{13}C-1,2,3,4-TCDD	100	100	100	100	100		
^{13}C-1,2,3,7,8,9-HxCDD	100	100	100	100	100		

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. 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:

$$\mathbf{V_A = s_A^2 / n_A} \qquad \mathbf{V_B = s_B^2 / n_B}$$

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.

Polycyclic Aromatic Hydrocarbons in Soil by GC/MS — PBM

Parameter

Polycyclic Aromatic Hydrocarbons (PAH) in soil

Analytical Method

Dichloromethane / Acetone Soxhlet extraction (PBM), GC/MS

Introduction

This method is applicable to the quantitative determination of polycyclic aromatic hydrocarbons in solids.

Method Summary

This method involves a Soxhlet extraction of a chemically dried soil using 1:1 DCM/Acetone followed by gas chromatography mass spectrometry (GC/MS) instrumental analysis.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes*

Analyte	Approx. MDL (µg/g)	CAS #	EMS Analyte Code
Acenaphthene	0.01–0.05	83-32-9	PA01
Acenaphthylene	0.01–0.05	208-96-8	PA02
Anthracene	0.01–0.05	120-12-7	PA03
Benz(a)anthracene	0.01–0.05	56-55-3	PA04
Benzo(a)pyrene	0.01–0.05	50-32-8	PA05
Benzo(b+j)fluoranthenes	0.01–0.05	205-99-2 & 205-82-3	PA39
Benzo(g,h,i)perylene	0.01–0.05	191-24-2	PA07
Benzo(k)fluoranthene	0.01–0.05	207-08-9	PA08
Chloronaphthalene, 2-	0.01–0.05	91-58-7	n/a
Chrysene	0.01–0.05	218-01-9	PA09
Dibenz(a,h)anthracene	0.01–0.05	53-70-3	PA10
Dibenzothiophene	0.01–0.05	132-65-0	PA49
Dibenzo(a,e)pyrene	0.01–0.05	191-65-4	PAD1
Dimethylbenz(a)anthracene, 7,12-	0.02–0.10	57-97-6	PA23
Fluoranthene	0.01–0.05	206-44-0	PA11
Fluorene	0.01–0.05	86-73-7	PA12
Indeno(1,2,3-cd)pyrene	0.01–0.05	193-39-5	PA13
Methylcholanthrene, 3-	0.02–0.10	56-49-5	PA24
Methylnaphthalene, 1-	0.01–0.05	90-12-0	PA29
Methylnaphthalene, 2-	0.01–0.05	91-57-6	PA28
Naphthalene	0.01–0.05	91-20-3	PA14
Phenanthrene	0.01–0.05	85-01-08	PA15
Pyrene	0.01–0.05	120-00-0	PA16
Quinoline	0.01–0.05	91-21-5	PA19

Other PAH, NPAH, or heterocyclic analytes may also be analyzed by this method, subject to validation and achievement of DQOs.

EMS Method Code(s)*	Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.
Matrix	Soil, sediment, sludge.
Interferences and Precautions	Interferences may result from contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis. Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source. Components co-eluting with and having fragments with the same mass/charge (m/z) ratio as target compounds are potential sources of interference. Alkylated PAHs commonly cause interferences on unsubstituted low molecular weight PAHs.
Sample Handling and Preservation	**Container**: Glass, with Teflon or foil lined lid. Wide-mouth sample jars recommended. **Preservation**: None.
Stability	**Holding Time:** Extract samples within 14 days after sample collection. Extracts may be held up to 40 days before instrumental analysis. **Storage:** Store samples and extracts at ≤6ºC (freezing of soil samples is acceptable but not recommended due to risk of container breakage). Store extracts at ≤6ºC away from direct light. Allow extracts to warm to room temperature prior to sub-sampling for analysis.
Procedure	Reagents: Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), Acetone, and Iso-Octane or Toluene. Silica gel, activated (optional — refer to US EPA Method 3630C for guidance). Sodium sulfate, anhydrous, reagent grade. Extraction: Accurately weigh a representative 10–20 gram sub-sample of wet soil into a beaker. Spike the sample with a minimum of 3 deuterated PAH surrogates. Refer to Quality Control section for requirements. Add 5–10 grams of granular anhydrous sodium sulfate, and mix in thoroughly with sample. Add more sodium sulfate if sample has a high moisture content. Let the sample stand for ~20 minutes while moisture adsorbs to the sodium sulfate. Mix well until the sample appears dry and free flowing. Add an appropriate amount of 1:1 DCM/Acetone to the Soxhlet apparatus. Turn on Soxhlet heaters, and allow samples to extract for at least 16 hours, ensuring that 4 to 6 cycles per hour are achieved. Cool and disassemble Soxhlet apparatus. Add about 1–2mL of a low volatility keeper solvent such as toluene or iso-octane to sample extracts prior to solvent

reduction steps to prevent loss of volatile PAH components during evaporative concentration.

Concentrate extracts to a known final volume using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator).

Silica Gel Clean Up (Optional):

Silica gel cleanup may be employed to reduce instrumental interferences by removing non-polar and/or polar materials that may co-elute with analytes or deteriorate instrument condition. Standard silica gel clean-up techniques are not suitable for nitrogen containing PAHs, e.g., quinoline or acridine.

In-situ or column silica gel cleanup using silica gel may be employed using the following reference as guidance:

USEPA Method 3630C, “Silica Gel Cleanup”, Revision 3, December 1996.

Concentrate the cleaned-up extract to a known, accurate final volume using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kudurna Danish, or equivalent), ensuring that method performance requirements are met (separate method validation of test procedure with silica gel clean-up is required where used). It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

- USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 5, July 2014 (or as updated from time to time).

GC/MS must be used. Selective ion monitoring (SIM) mode is recommended to achieve lower detection limits. Refer to USEPA Method 8270D for guidelines on establishing quantitation and confirmation ions for PAH compounds.

A five-point initial calibration over the desired working range (four-point minimum if an outlying calibration point must be rejected) is required to meet the performance requirements outlined in USEPA Method 8270D.

The use of internal standards is required. Internal standards can vastly improve method precision. Deuterium labeled PAHs are recommended (e.g., anthracene-d10, benzo(a)pyrene-d_{12}, etc.) and should be selected to encompass the mass range of the test analytes. Internal standards must not introduce significant interferences on test analytes or surrogates.

Isotope dilution techniques may be utilized to improve method performance.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average percent recovery) through repeat analysis of clean matrix spikes at concentrations above ten times the MDL. Average recovery must be between 80–120% for each of the heavy molecular weight PAH compounds (MW>175), between 70–120 % for each of the light molecular weight PAH compounds (MW<175), and between 60–120% for 3-methylcholanthrene, 7,12-dimethylbenz(a)anthracene, and any other PAH, NPAH, or heterocyclic analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50–140%
Lab Duplicates (DUP)	One per batch (max 20 samples)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material	One per batch (max 20 samples)	50–140%
Surrogate Compounds	All samples	50–140% Not applicable where valid surrogate recoveries cannot be obtained due to interferences.
Calibration Verification Standard (CVS) — 2nd source	One per batch (max 20 samples)	80–120% recovery
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run, and at the end of each run.	80–120% recovery for mid-level standards.
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50–200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards (IDS)	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%.

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to RM DQOs if targets are < 10x MDL (derive lab-specific DQOs in this case) or to MS results where sample background exceeds spike amount.

Surrogate Compounds: Required**.** At minimum, three surrogate compounds are required for each sample and quality control sample. Surrogates must include naphthalene-d_8. If nitrogen compounds are routinely reported, a deuterated nitrogen PAH must also be included (e.g., acridine-d_9, quinoline-d_7). Surrogates should be selected to encompass the mass range of the test analytes.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least every twelve hours). A control standard may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by GC/MS. At least one qualifier ion per analyte must be monitored (two recommended where possible).

Initial calibrations must include at least four points.

Internal standards must be used, except under extenuating circumstances (e.g., where interferences are evident on internal standard peaks).

All Performance Requirements and Quality Control requirements must be met.

At least three surrogates must be used, which must include naphthalene-d_8. If acridine or quinoline is reported, a deuterated nitrogen-containing PAH surrogate must be used (e.g., acridine-d_9 or quinoline-d_7).

The specified equivalence procedure must be followed for non-Soxhlet extraction procedures.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

Equivalence Procedure for Alternate Extraction Techniques

If alternative extraction techniques are employed, equivalence to the Soxhlet extraction procedure must be demonstrated by the extraction and analysis of two PAH Reference Materials (RMs) by the reference technique and by the lab's alternative technique. Equivalence is defined as where the grand average of the recoveries of all normally reported PAH analytes lies within 85–115% of the Soxhlet method, for each RM (i.e., determine the average recovery of each individual PAH analyte, and calculate a single grand average of all of these results to represent the overall method recovery for each RM), and where no single PAH analyte has a recovery outside of 50–150% of the Soxhlet method.

The following RMs may be suitable for this purpose, while available:

National Resource Council of Canada CRMs:

HS3B, HS4B, HS5 (availability may be limited)

Resource Technology Corporation CRMs:

CRM104, CRM140, CRM141, CRM170, CRM171, CRM172, CNS391

National Institute of Standards and Technology SRMs:

SRM 1941B

In-House produced RMs:

Must be sufficiently homogeneous (e.g., pulverized to < 100 um)

Must be natural materials (i.e., unspiked soils or sediments)

Prior to extraction by either method, each reference material must be wetted with water to a 25% moisture content (e.g., 7.5 g RM + 2.5 mL water). Extractions must be conducted at least in triplicate by each method. Equivalence is determined versus the results obtained using the reference method, not against the certified values of the RM.

Successful results for the equivalence procedure must be demonstrated prior to the use of any alternative method, and must be maintained on file indefinitely in case of audit by BC MOE or clients.

Each reference material assessment must include at least 80% of the laboratory's routinely reported PAH analytes (parameters where the results from both methods are below 5 times the laboratory's reported detection limit may be excluded).

Calculation of Grand Averages:

For the first RM, determine the average measured concentration of each individual PAH analyte by the alternative method and by the Soxhlet reference method (using averages of triplicates or more).

Use the results from above to calculate the average recovery of each individual PAH analyte for the alternative method versus the Soxhlet method.

Calculate the grand average of the recoveries for all analytes in the RM. For each RM, this result must be between 85–115%.

Repeat this assessment for the second RM.

The equivalence test described above need not be repeated for new substances added to the CSR as of 2017 if successful equivalence test data is available for previously listed substances.

References

USEPA SW846 Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", Revision 5, July 2014.

USEPA SW846 Method 3540C "Soxhlet Extraction", Revision 3, December 1996.

USEPA SW846 Method 3630C, "Silica Gel Cleanup", Revision 3, December 1996.

Revision History

July 10, 2017	Additional analytes added to support 2017 CSR updates. Matrix Spikes (or RM) added to QC requirements, and QC DQOs were revised to align with CCME methods guidance. Method validation DQOs were adjusted to support additional more challenging analytes and non-listed PAHs and heterocyclics. Required minimum number of surrogates reduced from four to three. Allowance for isotope dilution formally added. Format updated to 2017 version.
June 26, 2009	2002 version was replaced and converted to PBM format.
Nov 2002	Method adopted from Manual supplement #1. EMS Codes assigned.

Polycyclic Aromatic Hydrocarbons in Water by GC/MS — PBM

Parameter

Polycyclic Aromatic Hydrocarbons (PAH) in water

Analytical Method

Dichloromethane Liquid-Liquid Extraction, GC/MS

Introduction

This method is applicable to the quantitative determination of polycyclic aromatic hydrocarbons in water.

Method Summary

This method involves a liquid-liquid extraction using dichloromethane (DCM) followed by gas chromatography mass spectrometry (GC/MS) instrumental analysis.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	Approx. MDL (µg/L)	CAS #	EMS Analyte Code
Acenaphthene	0.01–0.05	83-32-9	PA01
Acenaphthylene	0.01–0.05	208-96-8	PA02
Acridine	0.01–0.05	260-94-6	PA18
Anthracene	0.01–0.05	120-12-7	PA03
Benz(a)anthracene	0.01–0.05	56-55-3	PA04
Benzo(a)pyrene	0.01–0.05	50-32-8	PA05
Benzo(b+j)fluoranthene	0.01–0.05	205-99-2 & 205-82-3	PA39
Benzo(g,h,i)perylene	0.01–0.05	191-24-2	PA07
Benzo(k)fluoranthene	0.01–0.05	207-08-9	PA08
Chloronaphthalene, 2-	0.01–0.05	91-58-7	n/a
Chrysene	0.01–0.05	218-01-9	PA09
Dibenz(a,h)anthracene	0.01–0.05	53-70-3	PA10
Dibenzothiophene	0.01–0.05	132-65-0	PA49
Dimethylbenz(a)anthracene, 7,12-	0.02–0.10	57-97-6	PA23
Fluoranthene	0.01–0.05	206-44-0	PA11
Fluorene	0.01–0.05	86-73-7	PA12
Indeno(1,2,3-cd)pyrene	0.01–0.05	193-39-5	PA13
Methylcholanthrene, 3-	0.02–0.10	56-49-5	PA24
Methylnaphthalene, 1-	0.01–0.05	90-12-0	PA29
Methylnaphthalene, 2-	0.01–0.05	91-57-6	PA28
Naphthalene	0.01–0.05	91-20-3	PA14
Phenanthrene	0.01–0.05	85-01-08	PA15
Pyrene	0.01–0.05	120-00-0	PA16
Quinoline	0.01–0.05	91-21-5	PA19
Methylated Naphthalene	0.10–0.50	n/a	n/a

Other PAH, NPAH, or heterocyclic analytes may also be analyzed by this method, subject to validation and achievement of DQOs.

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix	Fresh water, seawater, wastewater.
Interferences and Precautions	Interferences may result from contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis. Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source. Components co-eluting with and having fragments with the same mass/charge (m/z) ratio as target compounds are potential sources of interference. Alkylated PAHs commonly cause interferences on unsubstituted low molecular weight PAHs. Quinoline and acridine are nitrogen containing PAH and are subject to protonation and subsequent reduced extraction efficiency. Samples must be neutral or basic (pH 6 to 10) to ensure adequate extraction efficiency. Further, these compounds show low recovery if silica gel cleanup is employed.
Sample Handling and Preservation	Container: Amber glass, with Teflon lined lid. Preservation: Preservation with acid is preferred (e.g., use 1g solid $NaHSO_4$, 1 mL 1:1 HCl, or 1 mL 1:1 H_2SO_4 per 250 mL).
Stability	Holding Time: Extract samples within 14 days after sample collection if preserved, or within 7 days if unpreserved. Extracts may be held up to 40 days prior to instrumental analysis. Storage: Store samples and extracts at ≤6ºC (freezing of water samples is acceptable but not recommended due to risk of container breakage). Store extracts at ≤6ºC away from direct sunlight. Allow extracts to warm to room temperature prior to sub-sampling for analysis.

Procedure

Reagents:

Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), and Iso-octane or Toluene.

Silica gel, activated (optional — refer to US EPA Method 3630C for guidance).

Sodium sulfate, anhydrous, reagent grade.

Potassium Hydroxide, reagent grade or equivalent.

Extraction:

Measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials, surface film, or non-aqueous phase layer (NAPL). If solids content is too great for extraction in this manner, then the solids should be extracted separately from the water phase and the extracts combined. Ensure sample pH is between 6 to 10. If necessary, adjust pH using saturated KOH solution or phosphoric acid.

Spike the sample with a minimum of three deuterated PAH surrogates, including naphthalene-d_8. Include at least one deuterated nitrogen containing PAH surrogate (e.g., acridine-d_9, quinoline-d_7) unless acridine and quinoline isotopes are used as isotope dilution standards. Refer to the Quality Control section.

Add between 25 and 100 mL of DCM to the sample bottle and rinse contents into the separatory funnel. Shake vigorously for one minute with frequent venting. Allow layers to separate and drain the DCM (bottom layer) through sodium sulfate into a glass collection flask.

Repeat step **Error! Reference source not found.** twice more.

Concentrate the combined extracts to a known final volume using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator) ensuring that method performance requirements are met. It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Silica Gel Clean-Up (Optional):

Silica gel cleanup may be employed to reduce instrumental interferences by removing non-polar and/or polar materials from the extract that may co-elute with analytes or deteriorate instrument condition. Silica gel clean-up is generally not necessary for water samples. Standard silica gel clean-up techniques are not suitable for nitrogen containing PAHs, e.g., quinoline or acridine.

In-situ or column silica gel clean-up using silica gel may be employed following the guidelines described in the following reference:

USEPA Method 3630C, “Silica Gel Cleanup”, Revision 3, December 1996.

Concentrate the cleaned-up extract to a known final volume using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kudurna Danish, or equivalent) ensuring that method performance requirements are met (separate method validation of test procedure with silica gel clean-up is required where used). It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 5, July 2014 (or as updated from time to time).

GC/MS must be used. Selective ion monitoring (SIM) mode is commonly employed to achieve lower detection limits. Refer to USEPA Method 8270D for guidelines on establishing quantitation and confirmation ions for PAH compounds.

A five-point initial calibration over the desired working range (four-point minimum if an outlying calibration point must be rejected) is required to meet the performance requirements outlined in USEPA Method 8270D.

The use of internal standards is required. Internal standards can vastly improve method precision. Deuterium labeled PAHs are recommended (e.g., anthracene-d_{10}, benzo(a)pyrene-d_{12}, etc.) and should be selected to encompass the mass range of the test analytes. Internal standards must not introduce significant interferences on test analytes or surrogates.

Isotope dilution techniques may be utilized to improve method performance.

Analysis and Calculation of Methylated Naphthalene

For purposes of the BC approved marine water quality guidelines, methylated naphthalene refers to the aggregate summed concentration of all mono, di, tri, and tetramethyl naphthalenes.

For GCMS data acquisition and calculations, use quantitation and qualifier ions as indicated in the table below.

Isomer Type	Quantitation Ion (m/z)	Qualifier Ion (m/z)	Calibration Reference
1-Methylnaphthalene	142	141	1-Methylnaphthalene
2-Methylnaphthalene	142	141	2-Methylnaphthalene
Dimethylnaphthalenes	156	141	128 ion RF for Naphthalene
Trimethylnaphthalenes	170	155	128 ion RF for Naphthalene
Tetramethylnaphthalenes	184	169	128 ion RF for Naphthalene

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Average accuracy must be between 80–120% for heavy molecular weight PAH compounds (MW>175), between 70–120 % for light molecular weight PAH compounds (MW<175) and nitrogen containing PAHs (e.g., quinoline and acridine), and between 60–120% for 3-methylcholanthrene, 7,12-dimethylbenz(a)anthracene, and for any other PAH, NPAH, or heterocyclic analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50–140%
Field Duplicates	Recommended One per batch (max 20 samples) (requires 2nd sample bottle)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	Recommended One per batch (max 20 samples) (requires 2nd sample bottle)	50–140%
Surrogate Compounds	All samples	50–140% Not applicable where valid surrogate recoveries cannot be obtained due to interferences.
Calibration Verification Standard (CVS)	1 per initial calibration	80–120% recovery
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run.	80–120% recovery for mid-level standards.
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50–200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards (IDS)	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. No corrective actions are required for field duplicate DQO exceedances.		

Lab Duplicates: Lab Duplicates are not possible for this method, because whole sample analysis is required. Field Duplicates may be conducted using multiple sample containers.

Field Duplicates: Recommended. Replicate all components of the test from start to finish. Field Duplicate precision represents the combined variability of sampling and analysis processes.

Matrix Spike: Recommended. Requires second sample container due to whole sample analysis requirement. Matrix effects can also be evaluated in all samples using PAH surrogate results. Matrix Spikes are only necessary to evaluate parameter-specific matrix issues.

Surrogate Compounds: Required. At minimum, three surrogate compounds are required for each sample and quality control sample. Surrogates must include naphthalene-d_8. A nitrogen-heterocyclic surrogate (e.g., acridine-d_9, quinoline-d_7) is required unless acridine and quinoline isotopes are used as isotope dilution standards. Surrogates should be selected to encompass the mass range of the test analytes.

Calibration Verification Standard (CVS): Required. A control standard from a source separate from the calibration standard must be analyzed to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least every twelve hours). A control standard may serve the same purpose.

Isotope Dilution Standards (IDS): Optional. Required only if necessary to meet LCS DQOs and Accuracy Performance Requirements.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by GC/MS. At least one qualifier ion per analyte must be monitored (two recommended where possible).

Initial calibrations must include at least four points.

Internal standards must be used, except under extenuating circumstances (e.g., where interferences are evident on internal standard peaks).

The entire contents of the sample container must be analyzed, including any accompanying suspended or settled material and any surface film that may exist (with the exception that up to 20% of total sample volume may be removed from the sub-surface after inversion and mixing, if required to create room for extraction using alternate in-bottle extraction methods). Should this not be possible, the client must be contacted for direction and any method deviations must be qualified on the final report.

All Performance Requirements and Quality Control requirements must be met.

If acridine or quinoline is to be reported, a nitrogen-heterocyclic (e.g., acridine-d_9 or quinoline-d_7) must be used as surrogate or as isotope dilution standard, and sample pH must be between 6 to 10 prior to extraction. Alternative ranges for acceptable pH may be established through validation studies. Acceptable recovery of the nitrogen-heterocyclic surrogate or ID standard in a sample may be used as validation that sample pH was appropriate.

Methylated naphthalene calculation protocols are prescribed, but the listed qualifier ions are recommended.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 5, July 2014.

USEPA Method 3510C, “Separatory Funnel Liquid-Liquid Extraction”, Revision 3, December 1996.

USEPA Method 3630C, “Silica Gel Cleanup”, Revision 3, December 1996.

British Columbia Ministry of Water, Land and Air Protection, “Polycyclic Aromatic Hydrocarbons (PAHs) in Water by GC/MS/SIM”, November 2002 *(Previous version of this method prior to conversion to PBM format).*

US EPA Statement of Work for Determination of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Environmental Samples Related to BP Oil Spill, 2010 (reference for calculation protocol for methylated naphthalenes).

Revision History	July 10, 2017	Additional analytes added to support 2017 CSR updates. PAHs without CSR water standards were removed. Preservation guidance updated for consistency with current MOE preservative and hold time requirements. Definition and calculation protocols added for Methylated Naphthalene (for marine water quality guideline). DQOs for optional Matrix Spikes added. QC DQOs were revised to align with CCME methods guidance. Wider method validation DQOs added for challenging analytes and non-listed PAHs and heterocyclics. Required minimum number of surrogates reduced from four to three. Requirement for use of internal standards was added for consistency with soils method. Cancelled requirement for an NPAH surrogate if isotope dilution is used for both acridine and quinoline. Format updated to 2017 version.
	March 31, 2005	2002 version was replaced and converted to PBM format.

Resin and Fatty Acids in Water

Parameter

Resin and fatty acids

Analytical Method

Extraction, methylation, Florisil, GC/FID.

Introduction

This method is applicable to the qualitative and quantitative determination of resin and fatty acids in water.

Summary

The water sample is acidified and extracted with dichloro-methane. The raw extract is concentrated and derivatized with diazomethane to produce the corresponding methyl ester derivatives. (Suitable substitute derivatives may be produced by other available techniques.) If required, the extracts are cleaned up by Florisil column chromatography. The derivatives are analyzed by gas chromatography with flame ionization detection.

MDL

Resin Acids	EMS Code		mg/L
Abietic Acid	**A030**	**P030**	0.001
Chlorodehydroabietic Acid	**C050**	**P030**	0.001
Dichlorodehydroabietic Acid	**D053**	**P030**	0.001
Dehydroabietic Acid	**D052**	**P030**	0.001
Isopimaric Acid	**I004**	**P030**	0.001
Levopimaric Acid	**L003**	**P030**	0.001
Neoabietic Acid	**N005**	**P030**	0.001
Pimaric Acid	**P025**	**P030**	0.001
Sandaracopimaric Acid	**S006**	**P030**	0.001
Sum of Resin Acids	**0128 X380**		
Fatty Acids EMS Code		mg/L	
Arachidic Acid	**FA07**	**P030**	0.001
Behenic Acid	**FA08**	**P030**	0.001
Lauric Acid	**FA01**	**P030**	0.001
Lignoceric Acid	**FA09**	**P030**	0.001
Linoleic Acid	**FA05**	**P030**	0.001
Linolenic Acid	**FA10**	**P030**	0.001
Myristic Acid	**FA02**	**P030**	0.001
Oleic Acid	**FA11**	**P030**	0.001
Palustric Acid	**FA12**	**P030**	0.001
Palmitic Acid	**FA03**	**P030**	0.001
Stearic Acid	**FA06**	**P030**	0.001

Matrix

Fresh water, wastewater, marine water.

Interferences and Precautions

Some sample extracts contain certain co-extractives which interfere in the gas chromatography step of the analysis. The generation of diazomethane must be performed in a fume hood with appropriate safety precautions.

Sample Handling and Preservation

Bottle: 1L amber glass, narrow mouth, heat treated 350°C.
Preservation: unfiltered.

Stability

Holding Time: extract the sample within 14 days of sampling and analyze within 28 days.

Storage: store at 4°C until analyzed.

Procedure

Apparatus

a) Separatory funnels, 1000 mL

b) Graduated centrifuge tube, 15 mL

c) Round bottom flasks, 500 mL, 250 mL

d) Diazomethane generator

e) Rotary evaporator

f) Glass filter funnels (75 mm)

g) Glass chromatography column, 30 cm × 1.4 cm, with 150 mL reservoir

Reagents

a) Solvents, glass distilled, pesticide grade;

1) Dichloromethane

2) Iso-octane

3) Petroleum Ether

4) Diethylether

5) Hexane.

b) Sulfuric acid, 36 N, extracted with hexane prior to use.

c) Sodium sulfate, anhydrous, granular, reagent grade, heat treated to 650°C.

d) N-Nitrosomethylurea for diazomethane generation.

e) Sodium hydroxide (aq): 10% w/v.

f) Florisil, PR grade, heat treated at 650°C and deactivated with 1% water (w/w).

g) Acidic sodium sulfate.

h) Glass wool, solvent rinsed and heat treated at 350°C.

i) Acidic glass wool.

Procedure

a) Shake sample well before subsampling 500 mL into a separatory funnel.

b) Add 1mL of 36 N sulfuric acid to sample (pH should be <2).

c) Spike the sample with 100 µL of 500 ppm nonadecanoic acid.

d) Extract the sample three times with 100 mL of dichloro-methane each time.

e) Filter the dichloromethane extracts through acidified sodium sulfate, supported by acidified glass wool in a glass funnel, into a 500 mL round bottom flask.

f) Concentrate the combined extracts to 5 mL using a rotary evaporator.

g) Methylate with diazomethane and let stand in a fume hood for a minimum of 30 minutes.

1) In the bottom of a glass impinger place 10 mL of 10% NaOH and 10 mL of diethylether.

2) Add 50 to 100 mg of N-nitrosomethylurea (about the size of a pea).

3) Reconnect the impinger and bubble a stream of nitrogen through it. The exit of the impinger should have a long, disposable Pasteur pipet attached. The end of the pipet is submerged in the extract solvent.

4) Continue bubbling until the extract turns a definite yellow. Remove the extract from the generator and allow to stand in the fume hood for 30 minutes.

h) Remove residual diazomethane with a gentle stream of nitrogen.

i) Add 2 mL hexane to the round bottom flask and evaporate the dichloromethane using a rotary evaporator.

j) Clean up the extract on a chromatographic column containing 10 g of 1% deactivated Florisil topped with 1–2 cm of anhydrous sodium sulfate. Fractionate as follows:

1) 100 mL of petroleum ether (discard).

2) 100 mL of 2% ethyl acetate in petroleum ether. This fraction contains the resin acids.

k) Reduce the solvent to 1–2 mL using a rotary evaporator and transfer to a 15 mL graduated centrifuge tube. Blow down to 1 mL with a gentle stream of nitrogen.

l) Spike the extract with 50 µL of 1000 ppm 5-alpha-androstane.

m) Transfer to a 2 mL GC vial and top to the neck with hexane.

n) Analyze by flame ionization gas chromatography.

Precision

None listed.

Accuracy

None listed.

Quality Control

Blanks:
one method blank per analytical batch or 1 in 14.

Replicates:
one duplicate sample per batch or 1 in 14.

Recovery control:
a 500 mL reagent water sample is spiked with 100 µL of a standard solution containing 500 mg/L each of the target compounds. All samples and blanks are spiked with 100 µL of 500 mg/L nonadecanoic acid as an internal standard.

References

None listed.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: SEAM codes replaced by EMS codes. Requirement for NaOH preservative removed as suggested by PESC and confirmed by the BCQAAC Technical Subcommittee.

Rotenone (Derris Root, Noxfish, Fish-Tox) in Aqueous Samples

Parameter	Rotenone
Analytical Method	Extraction, HPLC.
EMS Code	R001 X381
Introduction	Rotenone is a controlled product generally available only to government fish and wildlife agencies. It is used to poison ponds and lakes to remove coarse fish (all fish are killed) prior to restocking with desired species. Water should be tested to ensure reduction of rotenone concentrations to subtoxic levels before restocking.
Summary	A 250 mL sample is extracted with dichloromethane and the extracts are combined and evaporated just to dryness. The extract is redissolved in petroleum ether and fractionated on a Florisil column using ethyl acetate in petroleum ether as the eluant. The fraction containing the rotenone is evaporated and redissolved in 2 mL methanol-water for analysis by high performance liquid chromatography (HPLC) using a 5 µm octadecylsilane reverse phase column and UV absorbance detection at 297 nm.
MDL	0.008 mg/L
Matrix	Fresh water.
Interferences and Precautions	Any compound that co-extracts, co-elutes under the analytical conditions and absorbs at 297 nm may interfere. Interferences in the extract may be removed or reduced by open tube Florisil chromatography after solvent exchange into a hydrocarbon solvent. The use of diode array detection or stop-flow scan techniques allows analyte confirmation by comparison of absorbance spectra of chromatographic peaks at the charactar-istic retention time.
Sample Handling and Preservation	**Sample container:** Amber glass bottle. 0.5L or larger with a Teflon-lined cap. **Preservation:** Not preserved.
Stability	**Holding time:** Not determined; samples should be extracted as soon as practical after receipt. **Storage:** Store at 4°C until analyzed.
Principle or Procedure	Rotenone is isolated from the sample matrix by liquid/liquid extraction using dichloromethane under neutral conditions. The concentrated extract is cleaned up by Florisil column chromatography. The rotenone-containing fraction is analyzed by reverse phase high performance liquid chromatography with UV absorbance detection at 297 nm.

Precision	None listed.
Accuracy	None listed.
Quality Control	Blanks: 1 per batch (10%).
	Spikes: 1 per batch (10%).
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual.
	December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

Semi-Volatile Organics Screening Method by GC/MS for TCLP Leachates — PBM

Parameter Semi-volatile organic compounds in leachate extract.

Analytical Method Leachate Extraction, GC/MS.

Introduction This method is applicable to the quantitative determination of semi-volatile waste components, including pyridine in a leachate extract.

Method Summary This method involves a leachate extraction followed by gas chromatography mass spectrometry (GC/MS) instrumental analysis.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and criteria Laboratories should strive to achieve reportable detection limits at least fivefold lower than the regulatory criterion. Laboratories must ensure that reported detection limits are sufficient to meet applicable regulatory requirements.

Analyte	Leachate criterion (mg/L)
Aldicarb	0.9
Aldrin + Dieldrin	0.07
Aldrin	
Dieldrin	
Atrazine + metabolites	0.5
Desethyl-atrazine	
Desisopropyl-atrazine	
Azinphos-methyl	2
Bendiocarb	4
Benzo(a)pyrene	0.001
Bromoxynil	0.5
Carbaryl	9
Carbofuran	9
Chlordane (total)	0.7
cis-Chlordane (alpha)	
trans-Chlordane (gamma)	
Chlorpyrifos	9
Cresols (total)	200
m-Cresol	
o-Cresol	
p-Cresol	
Cyanazine	1
DDT (total all isomers)	3
2,4'-DDT	
4,4'-DDT	
2,4'-DDE	
4,4'-DDE	

Analyte	Leachate criterion (mg/L)
2,4'-DDD	
4,4'-DDD	
Diazinon	2
Dicamba	12
2,4-Dichlorophenol	90
2,4-Dichlorophenoxyacetic acid (2,4-D)	10
Diclofop-methyl	0.9
Dimethoate	2
2,4-Dinitrotoluene	0.13
Dinoseb	1
Diquat	7
Diuron	15
Endrin	0.02
Glyphosate	28
Heptachlor + epoxide	0.3
Heptachlor	
Heptachlor epoxide	
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3
Lindane	0.4
Malathion	19
Methoxychlor	90
Metolachlor	5
Metribuzin	8

Analyte	Leachate criterion (mg/L)
1-Naphtyl-N-methyl carbamate (Carbaryl)	9
Paraquat	1
Parathion	5
Parathion-methyl	0.7
Pentachlorophenol	6
Phorate	0.2
Picloram	19
Pyridine	5
Simazine	1
Temephos	28
Terbufos	0.1
2,3,4,6-Tetrachlorophenol	10
Toxaphene	0.5

Analyte	Leachate criterion (mg/L)
Triallate	23
1,1,1-Trichloro-2,2-bis(p-methoxyphenyl) ethane (Methoxychlor)	90
2,4,5-Trichlorophenol	400
2,4,6-Trichlorophenol	0.5
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	28
2-(2,4,5-Trichlorophenoxy)propionic acid (2,4,5-TP, Silvex)	1
Trifluralin	4.5

Matrix

Leachate extract.

Interferences and Precautions

Interferences may result from contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

Components co-eluting with and having fragments with the same mass/charge (m/z) ratio as target compounds are potential sources of interference.

Sample Handling and Preservation

Container: Amber glass, with Teflon or foil lined lid.

Preservation: Unpreserved.

Stability

Holding Time: Extract the leachate solution within 7 days. Extracts may be held up to 40 days before instrumental analysis.

Storage: Store leachate solutions at <6°C. Store extracts at <6°C away from direct light.

Procedure

Reagents:

Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), and Iso-octane or Toluene.

Sodium sulfate, anhydrous, reagent grade.

Potassium Hydroxide, reagent grade or equivalent.

Sulfuric acid, reagent grade or equivalent.

Extraction:

Measure the sample volume (approximately 1 L) into a graduated cylinder and pour the entire contents into a Teflon or glass separatory funnel.

Spike the sample with the appropriate spiking solution, consisting of a minimum of 4 BNA surrogates. Refer to the Quality Control section.

Adjust pH to < 2 using 1:1 Sulfuric acid.

Add between 25 and 100 mL (average 60 ml) of DCM to the graduated cylinder and rinse contents into the separatory funnel. Shake vigorously for one minute with frequent venting. Allow layers to separate and drain the DCM (bottom layer) through sodium sulfate into a glass collection flask.

Repeat step d) twice more.

Adjust the pH to > 11 with concentrated sodium hydroxide.

Extract 3 times with dichloromethane (approx. 60 mL each) as in step d.

Concentrate the six combined extracts to a known final volume (approx 1 mL) using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator) ensuring that method performance requirements are met. It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile semi-volatile components.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

- USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 4, January 1998.

GC/MS must be used. Scanning mode is recommended. Refer to USEPA Method 8270D for guidelines on establishing quantitation and confirmation ions for the target compounds.

A five-point initial calibration (four-point minimum) over the desired working range is recommended to meet the performance requirements outlined in USEPA Method 8270D.

Whenever possible, the use of internal standards is strongly recommended. Internal standards can vastly improve method precision. Deuterium labeled internal standards are recommended (e.g., anthracene-d_{10}, benzo(a)pyrene-d_{12}, etc.) and should be selected to encompass the mass range of the test analytes. Internal standards must not introduce significant interferences on test analytes or surrogates.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Average accuracy must be between 60–140% for all analytes.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <25% for all analytes.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	1 per batch	Less than reported DL
Method Spike or Reference Material (Lab Control Sample)	1 per batch	50–150%
Field Duplicates	Optional	Not applicable
Surrogate Compounds	All samples	60–130% for MW>175 50–130% for MW<175 (e.g., naphthalene-d8) and for nitrogen containing compounds. Not applicable where valid surrogate recoveries cannot be obtained due to interferences.
Control Standard / Initial Calibration Verification (ICV)	1 per batch	70–130% recovery
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run.	70–130% recovery for mid-level standards.

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence (e.g., surrogate recoveries) demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Field Duplicates: Optional.

Method Spike or Reference Material (Lab Control Sample): Required**.** Either a clean matrix spike with known amounts of PAH levels or a certified reference material must be employed.

Surrogate Compounds: Required**.** At minimum, four surrogate compounds are required for each sample and quality control sample. Surrogates should span the volatility and mass range of the test analytes. Deuterated PAH surrogates are recommended.

Control Standard / Initial Calibration Verification (ICV): Required. A control standard from a source separate from the calibration standard must be analyzed to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least every twelve hours). A control standard may serve the same purpose.

Prescribed Elements

The following components of this method are mandatory:

Analysis must be by GC/MS. At least one qualifier ion per analyte must be monitored (two recommended where possible). Initial calibrations must include at least four points.

The entire contents of the leachate extract must be analyzed.

All Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 4, January 1998.

USEPA Method 3510C, “Separatory Funnel Liquid-Liquid Extraction”, Revision 3, December 1996.

Province of British Columbia. Amendment of the Special Waste Regulation,B.C.Reg.63/88, May 13, 2004.

Revision History

29 June, 2007:	First Draft for review. Initial PBM format.
09 January, 2009:	Final Version Endorsed by Committee for Lab Manual.

Sulfolane in Water and Soil Samples — PBM

Parameter

Sulfolane in Water and Soil

Analytical Method

Analysis by Gas or Liquid Chromatography with Mass Spectrometric detection (GC/MS or LC/MS or LC/MS/MS).

Introduction

Sulfolane is a colourless, highly polar, water miscible compound with good chemical and thermal stability. It has a low volatility and Henry's Law constant. Sulfolane can be subject to aerobic biodegradation under appropriate conditions.

Sulfolane has traditionally been used in the extraction of aromatics and in the removal of acid gases from a natural gas stream. Due to its combination of physical and chemical properties, sulfolane has also been used as an extraction distillation solvent, polymer solvent, polymer plasticizer, polymerization solvent, and in electronic/electrical applications (CCME 2006).

Method Summary

Water and soil samples are extracted using dichloromethane after addition of a known amount of deuterium labeled sulfolane-d8 isotope (used either as isotope dilution standard or surrogate).

Instrumental analysis is by Gas or Liquid Chromatography with Mass Spectrometric detection (GC/MS, LC/MS, or LC/MS/MS).

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS Number	Approx. MDL	EMS Analyte Code
Sulfolane	126-33-0	10 µg/L water 0.05 mg/kg soil	not yet defined

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Freshwater, groundwater, drinking water, soil and sediment.

Interferences and Precautions

Solvents, reagents, glassware and other sample processing materials must be demonstrated to be free form interferences by analyzing a method blank. Interferences may also be co-extracted from water samples. Chromatographic co-elution of such compounds, if they yield fragment ions common to an analyte, could potentially result in the reporting of artificially high results.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system and should take appropriate steps to prevent the occurrence of false positives.

Sample Handling and Preservation

Collect water samples in glass containers with Teflon lined lids (e.g., 250 mL amber glass).

Collect soil samples in 120 mL or 250 mL glass jars with Teflon-lined lids.

Preservation: Water samples may be preserved with solid sodium bisulfate (0.5% wt./vol).

Stability

Holding Times:

Waters: Water samples must be extracted within 7 days of the sampling if unpreserved, or within 14 days if preserved with sodium bisulfate. Extracts must be analyzed within 40 days of extraction.

Soils: Soil samples must be extracted within 14 days of sampling. Extracts must be analyzed within 40 days of extraction.

Storage: Refrigerate water and soil samples at ≤ 6°C (do not freeze). Store extracts refrigerated at ≤ 6°C or in a freezer at ≤ -10°C.

Procedure

Water Sample Extraction Procedure

1. Add 100 mL of water sample into a clean 250 mL extraction bottle.

2. Add an appropriate amount of d8-sulfolane for use either as surrogate compound or as isotope dilution internal standard. If d8-sulfolane is used for isotope dilution purposes, then also add an appropriate amount of an alternate compound with similar chemical characteristics for use as a surrogate (e.g., dimethyl sulfone or diethyl sulfone).

3. Ensure pH of water sample is < 2.

4. Add 100 mL of dichloromethane.

5. Shake sample for at least 1 hour on a vigorous mechanical shaker apparatus.

6. Allow phases to separate for approximately 5 minutes. Emulsions can be broken using a centrifuge if necessary.

7. Transfer the dichloromethane through a funnel filled with sodium sulfate into a solvent evaporation flask (e.g., turbovap tube or rotary evaporation flask).

8. Add another 100 mL of dichloromethane and repeat steps 4 to 6.

9. Add 2 mL of isooctane keeper solvent to the combined extracts and concentrate to 1.00 mL.

10. If required, add an appropriate amount of internal standard (e.g., dimethyl sulfone or diethyl sulfone). This step is not required if isotope dilution calibration with d8-sulfolane internal standard is used.

11. Analyze by GC/MS, LC/MS, or LC/MS/MS using internal standard with a minimum 4-point calibration.

Soil Sample Extraction Procedure

1. Add 10–12 g of field-moist soil sample into a 50mL centrifuge tube. Determine the dry weight extracted as a function of measured soil moisture content.

2. Add 1mL of deionized water to sample and vortex vigorously for 10 seconds.

3. Add an appropriate amount of d8-sulfolane for use either as surrogate compound or as isotope dilution internal standard. If d8-sulfolane is used for isotope dilution purposes, then also add an appropriate amount of an alternate compound with similar chemical characteristics for use as a surrogate (e.g., dimethyl sulfone or diethyl sulfone).

4. Add 10 mL dichloromethane and shake for 15 minutes using a vigorous mechanical shaker.

5. Add approximately 10 g of 1:1 anhydrous sodium sulfate and sodium chloride.

6. Shake for another 15 minutes by vigorous mechanical shaker.

7. Centrifuge sample at ~2,000 rpm for 5 minutes or until clarified.

8. Place 1.00 mL of extract into autosampler vial.

9. If required, add an appropriate amount of internal standard (e.g., dimethyl sulfone or diethyl sulfone). This step is not required if isotope dilution calibration with d8-sulfolane internal standard is used.

10. Analyze by GC/MS, LC/MS, or LC/MS/MS using internal standard with a minimum 4-point calibration.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80–120% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or ≤15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Internal Standard Area Checks	All samples and QC (not required if isotope dilution with d8-sulfolane is used)	Peak area counts for all internal standards in all injections must be 50–200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10%–130%.
Surrogate Compounds	All samples	50–140% recovery

Calibration Verification Standard (CVS) — 2nd source	1 per initial calibration	80–120% recovery
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	70–130% (waters) 60–140% (soils)
Lab Duplicates (DUP)	One per batch (max 20 samples)	30% RPD (waters) 50% RPD (soils) [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	50–140%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80–120% for mid-level standards
*If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

Mass spectrometric detection must be used. GC/MS, LC/MS, or LC/MS/MS are all acceptable.

Sulfolane-d8 must be added to all samples prior to sample preparation or extraction, either as an isotope dilution standard or as a surrogate. If sulfolane-d8 is used as an isotope dilution internal standard (i.e., for recovery correction purposes), then an alternate compound with similar chemical characteristics to sulfolane must be used as surrogate (e.g., dimethyl sulfone or diethyl sulfone).

Stated calibration requirements must be met. Calibration standards must be solvent-matched with sample extracts unless equivalency is demonstrated.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), United States Environmental Protection Agency Office Revision 5, July 2014.

Method 3511: Organic Compounds in water by Microextraction, United States Environmental Protection Agency Office November 2002.

CCME 2006. Canadian Environmental Quality Guidelines for Sulfolane: Water and Soil. Scientific Supporting Document, PN 1368.

Revision History	Sept 15, 2017	First version added to BC Lab Manual in support of 2017 CSR updates.

TCMTB (2-(Thiocyanomethylthio)-benzothiazole) in Aqueous Samples

Parameter	Thiocyanomethylthio)-benzothiazole
Analytical Method	Extraction, HPLC/UV
EMS Code	**TCMB X382**
Introduction	The use of chlorophenols (or chlorophenates) as anti-sapstain chemicals fell into disfavour due to their environmental persistence and because of the toxicity of byproducts of their manufacture (dioxins etc.). As a result of this concern, several compounds have been proposed as less harmful alternatives. One such compound is 2-(thiocyanomethylthio)-benzothiazole (TCMTB). However, TCMTB is quite toxic to aquatic biota and a sensitive and specific means of analyzing for TCMTB is required. High performance liquid chromatography (HPLC) with UV absorbance detection provides a convenient technique.
Summary	Samples are screened for high levels of TCMTB by direct injection onto a reverse phase column in a high-performance liquid chromatograph (HPLC). Samples containing low concentrations of TCMTB are extracted with dichloromethane and the extracts analyzed by HPLC after concentration and solvent exchange. If necessary, the extracts can be purified by Florisil column chromatography prior to analysis in order to reduce interferences.
MDL	Direct injection: 0.02 mg/L Extraction procedure: 0.001 mg/L
Matrix	Fresh water, wastewater.
Interferences and **Precautions**	Any compound that co-extracts, co-elutes under the analytical conditions and absorbs at 280 nm will interfere.
Sample Handling and **Preservation**	**Sample container:** Amber glass bottle, 0.5 L or larger, heat treated (300°C), aluminum foil-lined screw cap. **Preservation:** Dilute 1:1 with acetonitrile; this precludes extraction and attainment of a 0.001 mg/L MDL. Unpreserved samples should be analyzed within 36 hours of sampling.
Stability	**Holding time:** For samples diluted with acetonitrile, the maximum storage time is 3 weeks. Unpreserved samples should be analyzed within 36 hours of sampling. **Storage:** store samples at 4°C until analyzed.
Principle or **Procedure**	TCMTB can be chromatographed on a reverse phase octadecylsilane (ODS) high performance liquid chromatographic column using a water-acetonitrile gradient elution system. TCMTB exhibits a strong absorbance at 280 nm and concentration vs absorbance is linear over the analytical range. To lower the method detection limit (MDL), TCMTB is isolated from the sample matrix by liquid/liquid extraction using dichloro-methane. The concentrated extract may be purified by open tube Florisil chromatography after exchange to a hydrocarbon solvent. The purified extract is evaporated and the residue is redissolved in acetonitrile-water for analysis.

Precision

Direct Injection:

Authentic samples spiked at 0.100 and 0.400 mg/L

avg COV = 6.6%.

Extraction Procedure:

Authentic samples spiked at 0.010 and 0.001 mg/L

avg COV = 3.7%.

Accuracy

Direct Injection:

Authentic samples spiked at 0.100 and 0.400 mg/L

avg recovery = 101%.

Extraction Procedure:

Authentic samples spiked at 0.010 and 0.001 mg/L

avg recovery = 97%.

Quality Control

Blanks: 1 per batch (10%).

Spikes: 1 per batch (10%).

References

None listed.

Revision History

March 1990: Method Development for 2-(Thiocyanomethylthio)-benzothiazole (TCMTB), prepared by British Columbia Research Corporation for the Data Standards Group, British Columbia Ministry of Environment, Vancouver, B.C.

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

Tetraethyllead (TEL) in Soil — PBM

Parameter

Tetraethyllead (TEL)

Analytical Method

Solvent Extraction, GC-MS/MS, GC-ICPMS

Introduction

This method is applicable to the quantitative determination of Tetraethyllead in Soil.

Alkylated lead compounds are anthropogenic organometallic substances which have been in use since the 1920's, primarily associated with their use in leaded gasolines as anti-knock agents, which protect against engine damage due to premature ignition. Tetraethyllead was the primary alkyl lead substance used in gasolines, but tetramethyllead was also used for this purpose. Due to its link to severe health risks and issues, TEL was banned for automotive use across North America in the early to mid 1990's, and an almost total global ban was achieved by the early 2000's. TEL is still used with aviation fuels.

TEL is a moderately volatile substance with a boiling point of approximately 200°C (decomposition occurs at ~200°C according to the CRC handbook), which puts it on the cusp between semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). For purposes of sample handling and preservation protocols, this method treats TEL as an SVOC.

Method Summary

Solvent extraction (with isotope dilution and derivatization if necessary) followed by GC-MS/MS or GC-ICPMS instrumental analysis.

This is a performance-based method (PBM); laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

Analyte CAS No., MDL(s) and EMS Code(s)

Analyte	CAS No.	Approx. MDL mg/kg	Analyte EMS Code
Tetraethyllead	78-00-2	0.0005 mg/kg	to be determined

EMS Method Code(s)

To be determined

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil, Sediment, and other solids

Interferences and Precautions

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

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

TEL is thermally labile, with decomposition reported to occur beginning at temperatures as low as 110°C. It has also been shown to be inherently unstable in acidic conditions.

GC-MS/MS and GC-ICPMS are both highly selective analytical techniques with very limited potential for positive interferences.

Sample Handling and Preservation

Container and preservation requirements

Sampling Containers:	Collect samples in glass jars (clear or amber) with Teflon-lined silicone septa (recommended: minimum 60–250 mL wide mouth jars) with minimal headspace.
Preservation:	No preservation required.
Holding Time:	14 days to extraction. Extract hold time is 40 days.
Storage:	Sample temperature should be chilled to ≤ 10°C after sampling and for transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C.

Procedure

Reagents:

a) Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), Acetone and Iso-Octane or Toluene.

Extraction:

a) Accurately weigh a representative 10–20 gram sub-sample of wet soil into a beaker.

b) Spike the sample with at least 1 non-naturally occurring surrogate compound with physical properties (e.g. boiling point) similar to TEL (e.g. d8-acenaphthylene). Refer to Quality Control section for requirements.

c) To prevent evaporation and loss of TEL, do not dry soil sample with anhydrous drying agents prior to extraction.

d) Add an appropriate amount of 1:1 DCM/Acetone to the Soxhlet apparatus.

e) Turn on Soxhlet heaters, and allow samples to extract for at least 16 hours, ensuring that 4 to 6 cycles per hour are achieved.

f) Cool and disassemble Soxhlet apparatus. Add about 1–2 mL of a low volatility keeper solvent such as toluene or iso-octane to sample extracts prior to solvent reduction steps to prevent loss of tetraethyllead during evaporative concentration.

g) Concentrate extracts to a known final volume using an appropriate concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator)

Instrumental Analysis:

This method requires gas chromatography to physically separate organolead species from any potential interferences. Detailed gas chromatographic conditions are not provided in this method. Refer to US EPA 8270E for more detailed guidance. The on-column injection technique may reduce potential degradation issues due to the thermal lability of TEL.

For GC-MS/MS detection and quantitation, at least two multiple reaction monitoring (MRM) transitions are monitored to ensure a very high degree of specificity and freedom from interferences. The recommended MRM transitions for quantitation and confirmation are as follows:

Quantitation: Precursor ion 295 amu > Product ion 237 amu

Confirmation: Precursor ion 237 amu > Product ion 209 amu

For GC-ICPMS detection and quantitation, the recommended quantitation mass for lead is 208 amu (52.4% isotopic abundance). Two qualifier ions should be monitored for confirmation purposes, at 206 amu (24.1% isotopic abundance) and 207 amu (22.1% isotopic abundance). The high temperature of the ICPMS plasma destroys all organic molecules and acts as a highly specific elemental detector for this application.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement:

Laboratories must demonstrate method accuracy (measured as average recovery) of 50–130% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement:

Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement:

Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Calibration Verification Standard (CVS) — 2nd source	1 per initial calibration	20%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	20% for mid-level standards
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50–130%
Field Duplicate (DUP)	One per batch (max 20 samples)	see below [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	40–130%
Surrogate Compounds	All samples	50–130%
If DQOs are not met, repeat testing, or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Field Duplicates:

A minimum of 1 field duplicate or 10% of samples per submission (whichever is greater) is recommended to be submitted to the laboratory. Recommended DQO is 50% RPD for field splits (greater for co-located field duplicates), or within 2x reported DL for low level results.

Surrogate Compound(s):

Acenaphthylene-d8 is recommended as a GC-MS/MS surrogate (boiling point is similar to TEL and can be analyzed without derivatization). For GC-ICPMS any semi-volatile organometallic or ICPMS-measurable non-naturally occurring surrogate with similar physical properties to TEL (e.g., boiling point) may be used.

Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by Triple Quadrupole GC-MS/MS or GC-ICPMS. For GC/MSMS, at least one qualifier ion must be monitored for confirmation purposes
2. Initial calibrations must include at least 5 points.
3. All specified Sample Handling and Preservation requirements, Performance Requirements, and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

1. US EPA Method 3540C Soxhlet Extraction, Revision 3, December 1996.
2. US EPA Method 8270E Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June 2018.

Revision History

20-Dec-2019	Draft method, reviewed by BCELTAC, for public comment
19-Jul-2022	Updated to new Performance-Based Method Template Format
24-Aug-2023	

Tetraethyllead (TEL) in Water — PBM

Parameter

Tetraethyllead (TEL)

Analytical Method

Solvent Extraction, GC-MS/MS, GC-ICPMS

Introduction

This method is applicable to the quantitative determination of Tetraethyllead (TEL) in Water.

Alkylated lead compounds are anthropogenic organometallic substances which have been in use since the 1920's, primarily associated with their use in leaded gasolines as anti-knock agents, which protect against engine damage due to premature ignition. Tetraethyllead was the primary alkyl lead substance used in gasolines, but tetramethyllead was also used for this purpose. Due to its link to severe health risks and issues, TEL was banned for automotive use across North America in the early to mid 1990's, and an almost total global ban was achieved by the early 2000's. TEL is still used with aviation fuels.

TEL is a moderately volatile substance with a boiling point of approximately 200°C (decomposition occurs at ~200°C according to the CRC handbook), which puts it on the cusp between semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). For purposes of sample handling and preservation protocols, this method treats TEL as an SVOC.

Method Summary

Solvent extraction (with isotope dilution and derivatization if necessary) followed by GC-MS/MS or GC-ICPMS instrumental analysis.

This is a performance-based method (PBM); laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

Analyte CAS No., MDL(s) and EMS Code(s)

Analyte	CAS No.	Approx. MDL (µg/L)	Analyte EMS Code
Tetraethyllead	78-00-2	0.0005 µg/L	to be determined

EMS Method Code(s)

To be determined

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Fresh Water, Wastewater, Marine water.

Interferences and Precautions

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

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

TEL is thermally labile, with decomposition reported to occur beginning at temperatures as low as 110°C. It has also been shown to be inherently unstable in acidic conditions.

GC-MS/MS and GC-ICPMS are both highly selective analytical techniques with very limited potential for positive interferences.

Container and preservation requirements

Sample Handling and Preservation	**Sampling Containers:**	Collect samples in amber glass bottles with Teflon-lined silicone septa (e.g., 250 mL bottles, 2 per sample: contact laboratory for lab-specific sample requirements). Collect samples with zero headspace. A small air bubble of up to 5% of sample volume may appear after sampling and is acceptable.
	Preservation:	All samples must be field preserved by addition of base to pH ≥ 12 using NaOH or KOH as a microbial inhibitor and stabilizer. Field preservation with 2 mL 6N NaOH or KOH per 250 mL sample is recommended.
	Holding Time:	14 days to extraction if field preserved to pH ≥ 12. Extract hold time is 40 days.
	Storage:	Sample temperature should be chilled to ≤ 10°C after sampling and for transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C. Avoid freezing to prevent sample breakage.

Procedure

Reagents:

a) Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), and Iso-Octane or Toluene.

b) Sodium sulfate, anhydrous, reagent grade.

Extraction:

a) Accurately measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials, surface film, or non-aqueous phase layer (NAPL). If solids content is too great for extraction in this manner, then the solids should be extracted separately from the water phase and the extracts combined. Ensure sample pH is ≥ 10. If necessary, adjust pH using KOH or NaOH solution.

b) Spike the sample with at least 1 non-naturally occurring surrogate compound with physical properties (e.g., boiling point) similar to TEL. Refer to Quality Control section for requirements.

c) For a 250 mL sample, add 15 mL of DCM to the sample bottle and rinse contents into the separatory funnel (i.e., use 60 mL DCM / liter of sample). Shake vigorously for at least one minute with frequent venting. Allow layers to separate and drain the DCM (bottom layer) through anhydrous sodium sulfate into a glass collection flask.

d) Repeat step c) twice more, combining all extracts.

e) Concentrate the combined extracts to a known final volume using an appropriate concentration apparatus (e.g., rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator) ensuring that method performance requirements are met. It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of tetraethyllead during concentration. Use care during solvent concentration due to the volatility of TEL. Avoid concentration to dryness or near dryness.

Instrumental Analysis:

This method requires gas chromatography to physically separate organo-lead species from any potential interferences. Detailed gas chromatographic conditions are not provided in this method. Refer to US EPA 8270E for more detailed guidance. The on-column injection technique may reduce potential degradation issues due to the thermal lability of TEL.

For GC-MS/MS detection and quantitation, at least two multiple reaction monitoring (MRM) transitions are monitored to ensure a very high degree of specificity and freedom from interferences. The recommended MRM transitions for quantitation and confirmation are as follows:

Quantitation: Precursor ion 295 amu > Product ion 237 amu

Confirmation: Precursor ion 237 amu > Product ion 209 amu

For GC-ICPMS detection and quantitation, the recommended quantitation mass for lead is 208 amu (52.4% isotopic abundance). Two qualifier ions should be monitored for confirmation purposes, at 206 amu (24.1% isotopic abundance) and 207 amu (22.1% isotopic abundance). The high temperature of the ICPMS plasma destroys all organic molecules and acts as a highly specific elemental detector for this application.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year).
A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement:

Laboratories must demonstrate method accuracy (measured as average recovery) of 50–130% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement:

Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement:

Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Calibration Verification Standard (CVS) — 2nd source	1 per initial calibration	80–120%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80–120% for mid-level standards
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50–130%
Field Duplicate (DUP)	Greater of 1 per submission or 10% of samples recommended	see below [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	40–130%
Surrogate Compounds	All samples	50–130%
If DQOs are not met, repeat testing, or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Field Duplicates:

A minimum of 1 field duplicate or 10% of samples per submission (whichever is greater) is recommended to be submitted to the laboratory. Recommended DQO is 40% RPD for field splits (greater for co-located field duplicates), or within 2x reported DL for low level results.

Surrogate Compound(s):

Acenaphthylene-d8 is recommended as a GC-MS/MS surrogate (boiling point is similar to TEL and can be analyzed without derivatization). For GC-ICPMS any semi-volatile organometallic or ICPMS-measurable non-naturally occurring surrogate with similar physical properties to TEL (e.g., boiling point) may be used.

Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by Triple Quadrupole GC-MS/MS or GC-ICPMS. At least one additional qualifier ion or MRM transition must be monitored for confirmation purposes.
2. Initial calibrations must include at least 5 points.
3. All specified Sample Handling and Preservation requirements, Performance Requirements, and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

1. US EPA Method 3510C Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.
2. US EPA Method 8270E Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June 2018.

Revision History

20-Dec-2019	Draft method, reviewed by BCELTAC, for public comment
24-Aug-2023	Updated to new Performance-Based Method Template Format

Total Organic Halides in Petroleum Products by Oxidative Pyrolysis and Microcoulometry

Parameter

Total Organic Halides (TOX) (as Cl) in Oil
Total Halides (as Cl) in Oil

Analytical Method

Oxidative Pyrolysis and Microcoulometry

Introduction

This procedure describes the measurement of organic chlorine in new and used petroleum products by oxidative pyrolysis and microcoulometry. This method is carried out in accordance with EPA SW-846 Test Method 9076, with the addition of pre-extraction with water to remove inorganic chlorides (per ASTM D7457).

Total chloride can be measured by omitting the water washing; however, the results will be biased low due to incomplete conversion of inorganic species during oxidative pyrolysis.

Method Summary

An aliquot of sample that has undergone water washing is introduced into a combustion tube maintained at 900 to 1100°C under an argon stream. Oxygen flow in the combustion tube precipitates oxidative pyrolysis, converting the organic halides into hydrogen halides which are then fed into the titration cell through a dehydrating tube. The hydrogen halides react with the silver ions in the electrolyte, which are replaced coulometrically. The total amount of electric charge required to replace the silver ions is a measure of the amount of organic halides in the sample aliquot.

Note: This is a prescriptive method and must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text

Analyte CAS No., MDL(s) and EMS Code(s)

Analyte	CAS No.	Approx. MDL mg/L	Analyte EMS Code
Total Organic Halides		1 mg/L	TOX
Total Halides		1 mg/L	

EMS Method Code(s)

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

New and used petroleum products and their derivatives.

Interferences and Precautions

Nitrogen and Sulfur interfere at concentrations greater than approximately 0.1%

Any Bromide and Iodide present within the sample will generate a detector response. The oxyhalides do not precipitate silver and will generate a 50% detector response in comparison to chloride.

Fluorine as fluoride does not precipitate silver and is neither an interferent nor detected.

Sample Handling and Preservation

Refer to the following method with respect to sample handling:
ASTM D4057 Standard Practice for Manual Sampling of Petroleum and Petroleum Products

Container: See ASTM D4057

Preservation: See ASTM D4057

Holding Time: No holding time prescribed

Storage: Store at room temperature

Equipment and Supplies

1. Total Organic Halides Analyzer (Combustion Analysis/Microcoulometry)
2. Analytical Balance
3. 10 µL Gas-tight syringe
4. 100 mL Class A volumetric Flask
5. 2 L Eppendorf Flask
6. Appropriate PPE (gloves, lab coat, eye protection)

Reagents

Use analytical grade or better for all reagents:

- Xylenes
- Acetic Acid
- Concentrated Sulfuric Acid
- Deionized Water
- Sodium Acetate Anhydrous
- Potassium Nitrate
- Potassium Chloride
- Pentachlorophenol
- Compressed Oxygen, 99.99% Purity
- Compressed Argon, High Purity

Standards

Calibration Standard — 1.0 µg/µL chlorine

Weigh 150 mg ±0.1 mg of pentachlorophenol. Transfer the pentachlorophenol to a 100 mL Class A volumetric flask, rinsing the vial with xylene 3 times. Add xylene to the 100 mL mark on the volumetric flask.

QC Standard — 1.0 µg/µL chlorine

Weigh 150 mg ±0.1 mg of pentachlorophenol. Transfer the pentachlorophenol to a 100 mL Class A volumetric flask, rinsing the vial with xylene 3 times. Add xylene to the 100 mL mark on the volumetric flask.

Spike Standard — 50 µg/µL chlorine

Weigh 7.5 g ±0.1 mg of pentachlorophenol in a 100 mL Class A volumetric flask, Add xylene to the 100 mL mark on the volumetric flask.

Cell Electrolyte Solution — 85% Acetic Acid

Weigh 2.70 g of sodium acetate and add to 0.3 L of deionized water. Mix the solution until the sodium acetate is dissolved. Transfer solution to 2 L Eppendorf flask and add 1.7 L of acetic acid to the sodium acetate solution and mix well.

Reference Electrode Electrolyte (Outer Chamber) — 1M KNO_3

Weigh 10.11 g of potassium nitrate in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium nitrate is dissolved.

Reference Electrode Electrolyte (Inner Chamber) — 1M KCL

Weigh 7.46 g of potassium chloride in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium chloride is dissolved.

Counter Electrode Electrolyte — 10% KNO_3

Weigh 10.11 g of potassium nitrate in a 100 mL Class A volumetric flask and add 100 mL of deionized water to the mark. Mix the solution until the potassium nitrate is dissolved.

Procedure

Sample Preparation — Inorganic Chloride Extraction

1. It is crucial that samples are homogenized prior to analysis. For oil samples, shake thoroughly by using a paint shaker (or similar device) for at least 5 minutes.
2. Using a calibrated pipette: add 1.0 mL of sample, 1.0 mL of xylene and 1.0 mL of deionized water to a 4 mL glass vial.
3. Cap the vial and homogenize the sample via vortex mixing for a minimum of 30 seconds.
4. Centrifuge the samples for a minimum of 5 minutes. Place vials into a swing-bucket centrifuge rotor and set to approximately 2000 RPM. Ensure the rotor is balanced.
5. Separate the organic layer into a new vial and repeat the wash with deionized water. Vortex and centrifuge the vial following steps 3 and 4.

Instrument Preparation

1. Set up the analyzer as per manufacturer's instructions. Replace the electrolyte solutions in the reference electrode, counter electrode and reaction cell. Replace the dehydration solution (95% concentrated sulfuric acid). Allow the instrument to stabilize at the programmed set points, ensuring the pyrolysis furnace is set at a temperature within the 900 to 1100°C temperature range.

Instrument Analysis Procedure — System Recovery

1. Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing the Calibration Standard.
2. Inject 5 µL of the Calibration Standard through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.
3. Repeat step 2 two more times. The replicates must agree to within ±10% of the average result and the average recovery must be at least 85% of the theoretical value in order to proceed with sample analysis. The recovery factor generated (ratio of chlorine determined in the standard minus the system blank, divided by the standard content) is utilized to calculate the mass units of chloride present.

Instrument Analysis Procedure — System Blank

1. Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing xylene.
2. Inject 5 µL of xylene through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.
3. If the response is greater than 1 µg/mL, the cause must be delineated prior to sample analysis. The system blank should be subtracted from both standards and samples.

Instrument Analysis Procedure — Sample Analysis

1. Using a 10 µL gas-tight syringe, prime the syringe by aspirating and dispensing sample.
2. Inject 2–5 µL of the sample based on expected chlorine concentration through the septum into a cool sample boat, ensuring displacement of the last drop by touching the boat with the needle tip. Using the manual boat loader, move the boat to the vaporization zone (inlet) to volatilize light ends. Use the change in glow intensity of the furnace as a visual indication of solvent vaporization. Do not push the boat too quickly into the furnace, as incomplete combustion will generate deposits within the system. Once the solvent has volatilized, move the boat into the center of the combustion tube.
3. Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max 20 samples)	< 1 µg/mL
Lab Duplicate (DUP)	One per batch (max 20 samples)	10% RPD
System Recovery	1 per batch (prior analysis)	85% Recovery / ≤ 10% RPD
Continuing Calibration Verification (CCV) / System Drift	1 per batch (after analysis)	Within 13.7% of System Recovery
Matrix Spike (MS) / Matrix Spike Duplicate (MSD)	One per batch (max 20 samples)	80–120% recovery / ≤ 10% RPD
If any of the specified acceptance criteria cannot be met for the analysis of a given sample, then the data reported for that sample must be appropriately qualified.		

System Drift:
System recovery must be verified to validate generated results. Analyze the QC standard at the end of sample analysis and ensure the instrument response is within 13.7% of the average system recovery

Matrix Spike / Matrix Spike Duplicate:
Spike samples with a chlorinated organic (10 µL of 50 µg/µL spike standard). The spike recovery should be reported and should be between 80 and 120% of the expected value. Duplicate values should be within 10% RPD.

Method Validation Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation requirements specified below.

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies.

For Initial Validations, averages of at least 8 Reference Material or Laboratory Control samples must be assessed (multiple batches preferred). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy of 80–120% (measured as average recovery of reference material or Laboratory Control Sample) at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision <13.7% RPD at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

References

1. ASTM D7457 — 12 Standard Test Method for Determining Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry.

2. EPA SW-846 Test Method 9076: Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry

3. ASTM D4057 — 18 Standard Practice for Manual Sampling of Petroleum and Petroleum Products

Revision History

14-Nov-2019 Draft method for review by BCELTAC

24-Aug-2023

Volatile Halogenated Hydrocarbons in Water

Parameter Volatile halogenated hydrocarbons

Analytical Method Extraction, GC/MS or GC/ECD.

EMS Code (EMS code will be defined upon request).

Introduction This analysis is applicable to the class of compounds called volatile halogenated hydrocarbons. For simplicity this method will target the following compounds:

1,2-Dichlorobenzene	1,2,4-Trichlorobenzene
1,3-Dichlorobenzene	2,4,5-Trichlorobenzene
1,4-Dichlorobenzene	Hexachlorobenzene
1,2,3,4-Tetrachlorobenzene	Hexachlorobutadiene
1,2,3,5-Tetrachlorobenzene	Hexachlorocyclopentadiene
1,2,4,5-Tetrachlorobenzene	Hexachloroethane
1,2,3-Trichlorobenzene	Pentachlorobenzene

Summary The sample is placed in a separatory funnel and extracted with dichloromethane (EPA METHOD 3510A). The final extract is solvent exchanged then analyzed using one of the following procedures:

- Capillary column gas chromatography with mass spectrometry detection (EPA method 8270B).
- Dual capillary column gas chromatography with electron capture detector (EPA method 8120).

MDL Actual MDL will vary depending on the instrument sensitivity and matrix effects.

Note: The following detection limits were obtained from the Ontario Regulation 695/88 under the Environmental Protection Act "Effluent Monitoring — General".

Parameter Group MISA 23	Detection Limits (µg/L) for Standards in Reagent Water	
1,2-Dichlorobenzene	*	(1.14)
1,3-Dichlorobenzene	1.1	(1.19)
1,4-Dichlorobenzene	1.7	(1.34)
1,2,3,4-Tetrachlorobenzene	0.01	(*)
1,2,3,5-Tetrachlorobenzene	0.01	(*)
1,2,4,5-Tetrachlorobenzene	0.01	(*)
1,2,3-Trichlorobenzene	0.01	(*)
1,2,4-Trichlorobenzene	0.01	(0.05)
2,4,5-Trichlorobenzene	0.01	(*)
Hexachlorobenzene	0.01	(0.05)
Hexachlorobutadiene	0.01	(0.34)
Hexachlorocyclopentadiene	0.01	(0.40)
Hexachloroethane	0.01	(0.03)
Pentachlorobenzene	0.01	(*)

* was not determined in study.

(*) values obtained from EPA Method 612 and 8120.

Matrix Fresh water, wastewater, marine water.

Interferences and Precautions

Analysis of method blanks will identify interferences from glassware, solvent, reagents, etc. Interfering co-extractives will vary depending on the sample matrix, source, and method of detection. The extract clean-up procedure will eliminate many of these, but unique samples may require additional work, or be subject to higher detection limits. Certain of these compounds are very light sensitive and samples should be collected in amber glass containers and protected from direct light.

Sample Handling and Preservation

Bottle: 1 litre amber glass, with Teflon- or foil-lined lid.
Preservation: 80 milligrams of sodium thiosulfate per litre if residual chlorine is present; keep cool at 4°C.

Collect a representative sample in a wide mouth glass bottle that has been rinsed with solvent and oven dried. Do not rinse bottle with sample. If duplication is required, a separate one litre sample should be collected.

Stability

Holding time: extract within 7 days of collection. Analyze within 40 days of extraction.

Storage: store at 4°C from time of collection to extraction in amber glass or foil wrapped jars.

Principle or Procedure

See EPA Methods:

Extraction	- 625	3510A
Analysis	- 625	8270B (GC/MS)
	- 612	8120 (GC/ECD)

Precision

See appropriate method for data.

Accuracy

See appropriate method for data.

Quality Control

Samples: batch size 1 to 15 samples.

Blanks: 1 method blank per analytical batch.

Replicates: 1 sample duplicate if available; if not, an instrument duplicate per analytical batch.

Recovery control: 1 sample spike per analytical batch.

Note — instrument or solvent blanks should be run behind samples that contain high concentrations of analytes.

- surrogate standard recoveries should be reported.

References

a) EPA (1986) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, SW-846, 3rd Ed. (November 1986).

b) EPA (1984) Federal Register, Part VIII, Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act. U.S. Environmental Protection Agency, 40 CFR Part 136 (October 26, 1984).

c) Ontario Regulation 695/88 under the Environmental Protection Act "Effluent Monitoring — General".

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.

December 31, 2000: Republication. Note neither SEAM nor EMS codes had been assigned.

Volatile Hydrocarbons in Soil by GC/FID

Parameter

Volatile Hydrocarbons$_{(nC_6-nC_{10})}$ in soil or solids

Analytical Method

Methanol Extraction - Gas Chromatography with Flame Ionization Detection (GC/FID).

Introduction

This method measures the aggregate concentration of Volatile Hydrocarbons in soils or other solids (VH_s). Volatile Hydrocarbons (VH) are quantitated in two sub-ranges, using either *meta*-xylene or a mixture of *meta*- and *para*-xylenes (m,p-X) for the first sub-range, and using 1,2,4-trimethybenzene (1,2,4-TMB) for the second sub-range. VH_{s6-10} measures hydrocarbons that elute between n-hexane and n-decane, roughly equivalent to a boiling point range of 69 ˚C to 174 ˚C.

Volatile Hydrocarbons (VH_{s6-10}) is the precursor to the calculation of Volatile Petroleum Hydrocarbons (VPH). Specified Monocyclic Aromatic Hydrocarbon (MAH) results are subtracted from VH concentrations to arrive at VPH, using the procedure outlined in the British Columbia Lab Manual method “Calculation of Volatile Petroleum Hydrocarbons in Solids, Waters, or Air (Vapour) — VPH”.

Petroleum products that are predominantly captured by VH are those whose primary components are within the boiling point range of nC_6 through nC_{10}, for example gasolines, mineral spirits, and petroleum naphtha. The volatile fraction of some heavier petroleum products like kerosenes, jet fuels, and diesels can also be partially captured by VH.

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

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e., VOCs). However, the methanol extract produced by this method can and should be used for the analysis of targeted VOCs by selective detector (GC/MS is strongly recommended).

Method Summary

Solid samples are either field-extracted/preserved in methanol (typically ~ 5 grams of wet soil is extracted into exactly 10.0 mL methanol), or core samples of wet soil (typically 5 grams) are collected in the field using a hermetic sampler prior to methanol extraction at the laboratory.

Extracts are directly analyzed by capillary column gas chromatography with flame ionization detection (purge and trap or headspace sample introduction may also be used).

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approximate MDL	EMS Code
VH_{s6-10}	20 mg/kg (Direct Injection) 5 mg/kg (Purge and Trap, Headspace)	VHC- F084

Matrix

Soil, sediment, solids.

Interferences and Precautions

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

Where the proportion of water in a methanol extract exceeds 20–25%, the solubility of non-polar organics in the extract is substantially diminished (especially when refrigerated). A ratio of 2:1 methanol to wet solids is targeted to minimize the water content of methanol extracts. With the use of field methanol extraction and hermetic samplers, it is difficult to precisely control this ratio, but the laboratory must add methanol if necessary to ensure this ratio is at least 1.5:1. A higher ratio of approximately 2:1 or more is recommended for high moisture samples (e.g., > 50% moisture content).

Detection limits increase for samples with high moisture contents.

Pure petroleum samples are not applicable to the extraction and preservation components of this method but may be analyzed by the VH analytical procedures. Most middle-distillate or heavier petroleum products (diesels, oils, etc.) are immiscible with methanol, but can be dissolved in acetone, which can then be diluted with methanol prior to analysis by standard VH analytical protocols, if blanks are analyzed to control any interferences from acetone.

Soil samples that are highly contaminated with heavy oils (e.g., oil-soaked soils) may be poorly extracted by methanol. If such samples are encountered and identified, they should alternatively be extracted with acetone or with a mixture of acetone and methanol. Dilution of acetone or acetone/methanol extracts prior to analysis may be necessary. Analyze an appropriate blank to control interferences from acetone.

Sample Handling and Preservation

Samples must be collected and processed by one of the following two options:

Field Methanol Preservation Option: A representative sub-sample of soil (typically ~ 5 grams wet weight) is collected in the field and is extracted and preserved into an exactly known volume of high purity methanol (typically 10.0 mL). Two preserved sub-sample vials per sample are recommended as a precaution against leaks, breakage, or error.

Hermetic Sampler Option: A representative sub-sample of soil (typically ~ 5 grams wet weight) is collected in the field using a hermetically sealed soil sampling device.

Soil samples or methanol may become contaminated if exposed to or stored in the presence of gasoline or solvent vapours or automotive exhaust.

Immediately after sampling, hermetic samples and methanol preserved samples should be refrigerated or stored in coolers with sufficient quantities of ice or ice packs to ensure that sample temperatures will not exceed 10 ˚C during transit to the laboratory and must be refrigerated at ≤ 6 ˚C after receipt by the laboratory (preferably frozen at ≤ -7 ˚C).

Verification of Field Methanol Preservatives

Laboratories must ensure that Quality Control procedures are in place to ensure that Field Methanol preservatives they provide are fit for purpose. On a routine or batch basis, tare weights and methanol volumes of pre-dispensed and pre-weighed methanol vials must be verified (recommended specifications are ±2% of

methanol volume and ±0.1 grams for pre-weights). Small errors in methanol volume or tare weights can cause larger errors in final test results.

Stability

Holding Time — Hermetic Samplers: Hermetic samplers must be methanol extracted within 48 hours of sampling. Hold time prior to methanol extraction can be extended to 7 days from sampling if sample is frozen (≤ -7 ˚C) within 48 hours of sampling, but frozen samples must be extruded into methanol while still predominantly or partially frozen.

Holding Time — Methanol Extract: 40 days from sampling date.

Storage Conditions: Methanol extracts must be stored in the laboratory at ≤ 6 ˚C (preferably ≤ -7 ˚C).

Sample Preparation

This procedure is required for the analysis of both targeted VOCs and the aggregate parameter, $VH_{S_{6-10}}$. The same extract should normally be used to analyze all of these parameters.

Take an aliquot of the soil sample from the soil jar to perform an accurate moisture determination on the sample, so final results can be provided in dry weight units.

Hermetically Sealed Samplers

Keep hermetic samplers at ≤ 6 ˚C (preferably frozen) until immediately prior to extraction. Frozen samples should be extruded to methanol while still predominantly or partially frozen (warm for ~2–3 minutes at room temperature to facilitate extrusion).

Transfer the entire contents of the hermetic sampler to a tared vessel and accurately weigh the contents to at least the nearest 0.01 grams.

Add an exact volume of high purity methanol (typically 10 mL per 5 gram sample), equal to approximately 2 times the wet weight of the soil sample (but no less than 1.5 times the wet weight of the soil sample). Pre-charged methanol vials of known weight may be used.

Field Methanol Preserved Samples

Weigh field methanol preserved sample vials at the laboratory to at least the nearest 0.01 grams. Determine the accurate weight of wet soil or solids in each sample from the weight (*vial + methanol + soil sample)* minus the pre-weight *(vial + methanol)*.

Prior to weighing, carefully clean the outside of the sample vials to remove any adhered soil or residues. The weights of any labels that may have been affixed to sample vials must be considered when calculating sample weights.

Confirm that the ratio of methanol to wet weight of soil is at least 1.5:1. If not, accurately add additional methanol, targeting a ratio of approximately 2:1 (or higher). Record the volume of additional methanol added to at least the nearest 0.1 mL.

Methanol Extraction and Agitation (All Samples)

Prepare appropriate and required Method QC samples as described in the Method QC section.

At least one surrogate compound is recommended for VH analysis. VH surrogates may be combined with surrogates required for VOC/BTEX analyses (if required). Surrogates should be added to every sample (in methanol solution) prior to agitation. Surrogates will highlight possible problems with analyses, or

with limitations of the extraction process (e.g., adsorption of VOCs by charcoal or organic carbon in soil samples).

2,4-Dichlorotoluene is recommended as a VH surrogate compound, but any suitable surrogate compound may be used (2,4-Dichlorotoluene lies slightly beyond the VH range, which simplifies the integration of VH peak areas). Because VH surrogates are measured by GC-FID, which is less selective and less sensitive than GCMS, it is recommended for VH surrogate concentrations to be 10–100 times higher than GCMS surrogates.

Field methanol preserved samples must be physically agitated using a mechanical shaker (e.g., wrist shaker or platform shaker) for at least 15 minutes.

Hermetic samples that are methanol extracted in the laboratory must be physically agitated using a mechanical shaker (e.g., wrist shaker or platform shaker) for at least 60 minutes.

After the agitation process, let suspended solids settle by gravity or centrifuge if necessary. Transfer all or a portion of the extract to a vial for refrigerated storage. Store remaining extract at ≤ 6 ˚C for at least 40 days in case re-analysis is required.

GC-FID Analysis

28BAnalyze methanol extracts by GC-FID. The simplest technique for this analysis is direct injection GC-FID, for which conditions are described below.

Direct injection GC-FID is appropriate where reported detection limits of approximately 20 mg/kg or higher are required. Purge and trap GC-FID analysis is suitable where reported detection limits of lower than approximately 20 mg/kg are required. Headspace GC-FID may also be used if all performance specifications of the method are met. Refer to the BC Lab Manual method for VH in Water for detailed purge and trap conditions.

Samples must be matrix-matched with calibration standards and QC samples in terms of the amount of methanol present.

Caution: Refrigerated extracts must be warmed to room temperature and mixed gently before use or before sub-sampling (non-polar aliphatic sample components are insoluble in methanol at cold temperatures).

Recommended Direct Injection GC-FID Conditions

Column:	100% dimethylpolysiloxane (e.g., DB-1), 30 m, 0.53 mm id, 1.5 um phase
Carrier Gas:	helium
Head pressure:	5.0 psi @ 36˚C (with column dimensions as specified)
Column flow:	7.5 mL/min (50 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	200˚C
Injection solvent:	methanol
Injection volume:	1 µL (higher volumes tend to cause GC backflash)
Injection mode:	splitless or on-column
GC liner type:	4mm id splitless liner with silanized glass wool
Inlet purge on time:	0.3 minutes (splitless)
FID temperature:	250˚C
Oven program:	Initial Temp 36˚C (hold 3.0 minutes) 46B5˚C /min to 150˚C (no hold) 47B15˚C/min to 240˚C (hold 6.0 minutes)
FID gas flows:	as recommended by manufacturer

Aliphatic hydrocarbons are poorly soluble in methanol, especially when cold. 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. Storage in a freezer is preferable.

Standards

Calibration Standards

Prepare a minimum of 3 levels of Calibration Standards in methanol, each containing n-hexane (nC_6), n-octane (nC8), n-decane (nC_{10}), benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene (optional), *ortho*-xylene, and 1,2,4-trimethylbenzene (1,2,4-TMB). For the direct injection method, concentrations of 20, 50, and 250 µg/mL are recommended. If both *meta*- and *para*-xylenes are included in calibration standards, it is recommended that they be present at half the concentration of the other constituents.

Control Standard

Prepare a Control Standard containing *meta*-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene in methanol at a concentration near the middle of the calibration curve. It must be prepared from a source independent from the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions).

Gasoline Stock Solution

Prepare a stock solution of gasoline in methanol (e.g., 10,000 µg/mL). Prepare the solution by weight (e.g., weigh 0.250 g gasoline into a 25 mL volumetric flask). Record the source of the gasoline used. A gasoline source that does not contain ethanol is recommended. Note that the nominal concentration of gasoline (weight gasoline / volume) is not equal to the concentration of VH_{s6-10} (the nominal gasoline concentration is higher).

Detection Limit Check Standard

Dilute the Gasoline Stock Solution to prepare a Detection Limit (DL) Check Standard in methanol. Prepare the standard at a concentration that is approximately equal to the extract concentration that corresponds to the Reporting Detection Limit for VH_{s6-10}. This standard is required for Initial Calibration QC.

Quality Control

Table I-14 summarizes all required calibration and QC components of this method. Each of these components is described in detail in this section.

Table I-14: Summary of VH_s 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 all components.
Calibration QC and Verification		
Instrument blank	1 per initial calibration	None; required for background correction.
Control Standard	1 per initial calibration	Within 15% of expected concentration
Detection Limit Check Standard	1 per initial calibration	50–150% of VH target.
Ongoing Verification of Calibration	Every 12 hours, and at end of analysis batch if	Within 20% of initial calibration

	>6 hrs from previous check.	
Method QC		
Method Blank	1 per 20 samples (1 per batch minimum)	< Reported Detection Limit.
Laboratory Control Sample (Gasoline Method Spike)	1 per 20 samples (1 per batch minimum)	70–130% recovery.
Laboratory Duplicates	1 per 20 samples (1 per batch minimum)	40% RPD.
Field QC		
Travel or Field Blank (Field Methanol Technique only)	Strongly Recommended (1 per sampling event)	< Reported Detection Limit.
Field Duplicates	Recommended	None.

*Minimum DQOs apply at levels above 10x MDL. Report qualified data if DQOs are not met.

Instrument Performance QC

Initial Performance Check

REQUIRED. Perform this check whenever a Calibration Standard or Verification Standard is analyzed. See the Ongoing Verification of Calibration (Verification Standards) section for required frequency.

Instrument Performance Check are used to do the following:

Measure and control relative response ratios of specified VH components,

Determine retention time windows for VH integration ranges, and

Confirm resolution of hexane (nC_6) from the solvent peak.

The essential purpose of the Instrument Performance Check is to ensure that the GC/FID response factors of VH components throughout its boiling point range are roughly equal. If excessive relative bias exists among VH components due to differences in their polarity, mass, boiling point, or chemical composition, then calculated results will be biased, and interlaboratory inconsistency will result.

For each component of the Calibration Standard, determine the relative response ratio (by peak area) against the appropriate reference compound. Compare the peak areas of hexane (nC_6), octane (nC8), benzene, toluene, and ethylbenzene against *meta*-xylene. Compare the peak areas of decane (nC_{10}) and *o*-Xylene against 1,2,4-trimethylbenzene. Acceptance criteria for relative response ratios are 0.7–1.3. If any relative response ratio fails these acceptance criteria, 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.

Initial Calibration QC

Instrument Blank

REQUIRED. Minimum 1 per initial calibration. Inject a methanol solvent blank to the GC system to establish the chromatographic baseline.

Control Standard

REQUIRED. Minimum 1 per initial calibration.

Analyze a Control Standard (see the Control Standard section) containing *meta*-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene, which has been

prepared from a different source than the Calibration Standard. The Control Standard is used to confirm the integrity of the calibration standard.

If the calculated concentration of *meta*-xylene or 1,2,4-trimethylbenzene in the Control Standard varies by more than 15% from the expected target, then the calibration is invalid. Discrepancies must be corrected before any sample results for the analysis batch may be reported. Correction may require any or all of:

Re-analysis of Control Standard and/or Calibration Standard.

Re-preparation and re-analysis of Control Standard and/or Calibration Standard.

GC maintenance (if discrepancy is due to calibration non-linearity).

Detection Limit Check

REQUIRED. Minimum 1 per initial calibration. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low-level solution of gasoline.

Analyze a Detection Limit Check Standard that contains VH_{s6-10} at a concentration that is approximately equivalent to the VH_{s6-10} Reported Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50–150 % of the VH_{s6-10} target.

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.

Method Blank

REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Prepare a Method Blank using a clean soil/sediment matrix (or using reagents only).

If a Method 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 Method Blank result).

Laboratory Control Sample

REQUIRED. Minimum 1 per 20 samples. Prepare a Gasoline LCS by fortifying a clean soil matrix (containing approximately 20% water) with an accurate volume of a Gasoline Method Spike Solution, which should be prepared at a concentration at least 10x the laboratory's reported detection limit.

Determine the target for VH_{s6-10} by directly analyzing several replicates of the Gasoline Method Spike Solution diluted to a concentration that equals the amount of gasoline spiked (in µg) divided by the final extract volume for the spike (i.e., the volume of methanol plus volume of water).

Laboratory Duplicates

REQUIRED. Minimum 1 per 20 samples. Laboratory duplicates should be conducted by sub-sampling the same methanol extract from a single field sample (e.g., from a single field methanol extraction vial or from a single hermetic sampler).

Surrogate Compounds

RECOMMENDED. The use of one or more Surrogate Compounds for VH is recommended. Surrogate(s) should be added to each sample prior to the extraction or mechanical agitation process. Surrogates that elute outside the VH retention time range are recommended so that they do not need to be subtracted from integrated VH peak areas (2,4-dichlorotoluene is recommended as a suitable

surrogate compound).

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. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

Field QC

Travel Blank or Field Blank (Field Methanol Technique only)

STRONGLY RECOMMENDED. Travel Blanks and/or Field Blanks are important to verify purity of supplied methanol vials including storage, transit, and field effects. Travel Blanks can identify problems with tare weights of vials (including leakage issues), methanol contamination issues, methanol volume errors, and contamination that could be introduced during travel or storage. Field Blanks (which must be opened and handled similarly to a sample in the field) can potentially also identify contamination due to the field sampling environment (e.g., due to high concentrations of hydrocarbon or gasoline vapours). Field Blanks are recommended for sampling environments where hydrocarbon or solvent vapours may be present at time of sampling.

Field Duplicates

RECOMMENDED.

Instrument QC

Instrument blank

REQUIRED. Minimum 1 per initial calibration. Inject a methanol solvent blank to the GC system to establish the chromatographic baseline.

Control Standard

REQUIRED. Minimum 1 per initial calibration. Analyze a Control Standard (see the Control Standard section) containing *meta*-xylene and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The Control Standard is used to confirm the integrity of the calibration standard. Acceptance criteria are 85–115%.

Detection Limit Check

REQUIRED. Minimum 1 per initial calibration. Analyze a Detection Limit Check Standard that contains VH_{s6-10} at a concentration that is approximately equivalent to the VH_{s6-10} Reporting Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50–150 % of the VH_{s6-10} target.

Calibration and Analysis Procedure

Initial Calibration

A minimum 3-point linear external standard calibration is required for this method. 20, 50, and 250 µg/mL concentrations of *meta*-xylene (or m- and p-xylenes) and 1,2,4-trimethylbenene are recommended for the direct injection method (see the Calibration Standard section).

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

Calculate the Calibration Factors (CFs) for *meta*-xylene and 1,2,4-trimethylbenzene in the Calibration Standard using the equation below:

CF_{m-x} (mL/µg) = m-X area / [m-X] (µg/mL)

$CF_{1,2,4-TMB}$ (mL/µg) = 1,2,4-TMB area / [1,2,4-TMB] (µg/mL)

Ongoing Verification of Calibration (Verification Standards)

After initial calibration, the Calibration Factors ($CF_{m\text{-}X}$ and $CF_{1,2,4\text{-}TMB}$) 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.

An initial calibration is valid as long as both Calibration Factors remain within 20% of their initial values.

See the Instrument Performance Check section for Instrument Performance QC requirements that must be satisfied with each Calibration Standard and Verification Standard.

Integration of Total Areas for VH_{s6-10}

VH_{s6-10} is defined to include all GC/FID peaks eluting between hexane (nC_6) and decane (nC_{10}). VH_{s6-10} is quantitated by summing the results for two sub-ranges within the nC_6–nC_{10} range. The first VH sub-range falls between the retention times of hexane and *ortho*-xylene. The second VH sub-range falls between the retention times of *ortho*-xylene and decane. Each sub-range is integrated and quantitated separately, and VH_{s6-10} is then calculated by summing the two results.

Note: Calculating VH using two sub-ranges reduces the impact of relative response biases which may exist between higher and lower volatility VH components. The two-range calculation mechanism was intended to simplify the development of purge and trap methods that may be equivalent to the direct injection method described here.

Determine the total integrated peak area of each VH sub-range, where:

The $VH_{s(6-oX)}$ range begins at the apex of the nC_6 peak and ends at the apex of the *o*-Xylene peak.

The $VH_{s(oX-10)}$ range begins at the apex of the *o*-Xylene peak and ends at the apex of the nC_{10} peak.

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

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

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

VH_{s6-10} is the sum of the calculated concentrations for $VH_{s(6-oX)}$ and $VH_{s(oX-10)}$. $VH_{s(6-oX)}$ is quantitated against the *meta*-xylene (or *meta*- and *para*-xylene) calibration standard. $VH_{s(oX-10)}$ is quantitated against the 1,2,4-trimethylbenzene calibration standard.

It is highly recommended that the Surrogate Compounds used for VH analysis elute slightly outside the VH range of nC_6–nC_{10}. If any Surrogate Compounds are added to samples within the VH range, the contribution to VH of those Surrogates must be subtracted from calculated VH results.

Use the following equations to calculate VH_{s6-10}:

VH_{s6-10} (µg/g) = $VH_{s(6-oX)}$ (µg/g) + $VH_{s(oX-10)}$ (µg/g)

$VH_{s(6-oX)}$ (µg/g) = ($A_{(6-oX)}$ × TEV × Dil) / ($CF_{m\text{-}X}$ × DryWt)

$VH_{s(oX-10)}$ (µg/g) = ($A_{(oX-10)}$ × TEV × Dil) / ($CF_{1,2,4-TMB}$ × DryWt)

where:

$A_{(6-oX)}$ = Total area between nC_6 and *ortho*-xylene

$A_{(oX-10)}$ = Total area between *ortho*-xylene and nC_{10}

$CF_{m\text{-}X}$ = Calibration Factor for m-X or m,p-X standard (mL/µg)

$CF_{1,2,4-TMB}$ = Calibration Factor for 1,2,4-TMB standard (mL/µg)

Dil = Dilution factor of sample extract (unitless)

DryWt = Dry weight of sample extracted (g)

TEV = Total Extract Volume, including sample moisture, H_2O_{samp} (mL)

H_2O_{samp} = Sample Wet Weight Extracted × %Moisture (mL)

TEV is approximated by summing the volumes of water due to moisture + methanol, as follows:

TEV = (water due to sample moisture, H_2O_{samp}, mL) + (methanol volume, mL)

Report test results for VH_{s6-10} in solids samples in units of mg/kg (ppm, dry weight basis).

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 (for purge and trap or headspace, dilution normally entails re-analysis using a smaller aliquot of the methanol extract).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate VH_{s6-10} results for unknown samples.

Initial Verification of Relative Response Requirements

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

Calculation of Actual [VH_s] of a Gasoline Reference Solution

This procedure describes how to calculate the *Actual VH_{s6-10} Concentrations* for solutions of petroleum products where only the total weight/volume concentration of the petroleum product is explicitly known. *Actual VH_{s6-10} concentrations* of a petroleum product solution can only be measured experimentally, whereas the nominal concentration of the

petroleum product in the solution is simply determined by dividing the weight of product by the volume of solvent in which it is prepared.

Actual VH_{s6-10} Concentrations are required within this method for the following purposes:

Determination of GC/FID linear range for VH_{s6-10} (i.e., calibration range).

Determination of VH_{s6-10} Instrument Detection Limits (IDLs).

Preparation of DL Check Standards and Method Spike Solutions.

Calculation of VH_s targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual VH_{s6-10} Concentration* of a reference gasoline:

Prepare a reference gasoline solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for VH_{s6-10} (see the Establishing Instrument Calibration Working Range and Estimated IDLs section). A petroleum product concentration of at least 5,000 µg/mL is recommended for this purpose. This concentration is referred to in the example below as *[Gasoline].*

Perform a minimum of 3 replicate analyses of the petroleum product solution prepared in (a) using the selected GC-FID method conditions. In the example below, the measured VH_{s6-10} concentration is denoted as *[$VH_{s6-10,measured}$]*.

Calculate the percentage that the VH_{s6-10} range represents of the total petroleum product concentration. Example (for a given source of gasoline):

%VH_{s6-10} in gasoline = 100% × *[$VH_{s6-10,measured}$]* / *[Gasoline]*

where:

[$VH_{s6-10,\ measured}$] = measured VH_{s6-10} concentration (µg VH_{s6-10} / mL methanol)

[Gasoline] = nominal gasoline concentration (µg gasoline /mL methanol)

Note: The percentage of VH_{s6-10} in gasoline is less than 100% (typically about 50%) because not all components of gasoline fall within the nC_6–nC_{10} boiling point range.

To calculate the *Actual VH_{s6-10} Concentrations* of other concentrations of the same gasoline source, multiply the nominal gasoline concentration of the solution by the %VH_{s6-10} determined above.

Establish Instrument Calibration Working Range and Estimated IDLs

Establish the linear working range of the GC/FID system for VH_{s6-10} using a series of dilutions of the Gasoline Stock Solution prepared in methanol. Analyze Gasoline

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 direct injection method, the following solution concentrations are recommended as an approximate guide: 25, 50, 100, 200, 500, 1,000, 2,500, 5,000, 10,000, 20,000, and 50,000 µg/mL of gasoline. Calculate VH_{s6-10} results for each solution using the procedure described in the Calculations section.

At the Limit or Reporting, VH_{s6-10} should be measureable at 50–150% of the expected concentration.

The upper range of the validated linear range must be used to determine when over-range samples must be diluted.

Note: Validation of upper linear range is particularly important for purge and trap methods.

Establishing Method Detection Limits

Determine the Method Detection Limits (MDLs) at the 99% confidence level for VH_{s6-10}, using the procedure outlined in the British Columbia Environmental Laboratory Manual [e] or a comparable reference.

Consider the normal total extract volume produced by this method (including sample moisture) and select a concentration for method spikes of gasoline into a clean soil matrix (containing at least 20% moisture) that should result in extracts with concentrations of between one and three times the estimated IDL for VH_{s6-10} (as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section). Prepare, extract, and analyze at least 7 method spikes at this concentration. Use a Gasoline Method Spike Solution to prepare these method spikes.

Calculate the Method Detection Limit (MDL) at the 99% confidence level for VH_{s6-10}.

Average recoveries of the MDL Method Spikes for VH_{s6-10} must be between 60 – 140%, where recovery is defined as calculated VH_{s6-10} result / target VH_{s6-10} concentration, as determined in the Calculation of Actual VHS Concentration of a Petroleum Reference Solution section. If this condition is not met, repeat the MDL determination at a higher spike level.

Determination of DL Check Standard Concentration and VH_{s6-10} Target

Use the procedure that follows to select a suitable concentration of gasoline in methanol for the DL Check Standard. This procedure involves two separate conversions of units:

Gasoline product concentration units must be converted to (and from) VH_{s6-10} concentration units.

Sample concentration units (e.g., µg/g of solids) must be converted to sample extract concentration units (e.g., µg/mL of methanol).

Results from the Calculation of Actual VH_s Concentration of a Petroleum Reference Solution section and the Establishing Instrument Calibration Working Range and Estimated IDLs section may initially be used for step (a), but this determination should be repeated if the source of the gasoline changes:

Calculate the percentage of the total gasoline concentration that VH_{s6-10} represents, using the procedure described in the Calculation of Actual VH_s Concentration of a Petroleum Reference Solution section. Typically, VH_{s6-10} represents about 50% of the total gasoline concentration, because not all components of gasoline fall within the nC_6–nC_{10} boiling point range.

Determine the concentration of gasoline in methanol that corresponds to the VH_{s6-10} Reporting Detection Limit. Use the calculated percentage from (a) to calculate this gasoline concentration. The normal sample volume extracted, an "average" sample moisture content, and the normal methanol extract volume are all required to convert method units to the *equivalent* solution concentration units. Use an average sample moisture content of 20% for calculation purposes:

[Gasoline] equiv. to VH_{s6-10} DL = 100 × (Reporting DL for VH_{s6-10}) / (%VH_{s6-10} in Gasoline) × Avg. Sample Dry Weight / Avg. Total Extract Volume

where:

Units for [Gasoline] = ppm (µg/mL of methanol)

Units for Reporting DL for VH_{s6-10} = ppm (e.g., µg/g dry weight of sample)

Units for Sample Weight = grams (dry weight)

For 20% moisture, 5 wet gram sample weights, and 10 mL Methanol volumes:

Average Dry Sample Weight = 4.0 grams

Average Total Extract Volume = 11.0 mL

Select a concentration for the Gasoline DL Check Standard that is approximately equal to the concentration determined above. The DL Check Standard can then be routinely used to verify that the Reporting Detection Limit for VH_{s6-10} remains valid.

Calculate the target for VH_{s6-10} in the Detection Limit Check Standard by multiplying the concentration selected in (b) by the VH_{s6-10} percentage from (a).

Target for VH_{s6-10} = (DL Std. gasoline concentration in methanol) × (%VH_{s6-10} in gasoline).

Accuracy and Precision

A minimum of 8 Laboratory Control Samples prepared from unweathered gasoline must be used to assess the accuracy and precision of the method. Determine Method Spike targets using *Actual VH_{s6-10} Concentrations* of the spike solution by following the procedure outlined in section the Calculation of Actual VH_s Concentration of a Petroleum Reference Solution section. The minimum accuracy requirement for Initial Validation is an average recovery of 85–115%. The minimum precision requirement for Initial Validation is a Relative Standard Deviation of ≤ 15%.

Method Performance Data

Single laboratory and interlaboratory performance data for this method were published in previous versions of the BC Lab Manual. Refer to the 2013 version or earlier versions of the BC Lab Manual to access this information.

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 method-defined aggregate parameters like Volatile Hydrocarbons, where many components are calculated against single calibration reference standards. This method has been specifically designed to minimize the relative bias among responses of common VH components, and among VH_{s6-10} results generated by different laboratories.

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

Prescribed Elements

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

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

"REQUIRED" QC elements from the Quality Control section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.

Sample Handling and Preservation guidelines may not be modified.

Methanol extraction is required (except for samples that form 2 liquid phases with methanol, in which case acetone must be used — see the Interferences and Precautions section).

The ratio of methanol to wet weight of solids being extracted must always be at least 1.5:1.

Gas Chromatography with Flame Ionization Detection is required for VH_{s6-10}.

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

Meta-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene must be used as the calibration standards for VH_{s6-10}. Minimum 3-point linear calibration is required.

GC calibration standard must be prepared in the same solvent as sample extracts, unless equivalence (within 2%) can be demonstrated for component responses and retention times of Instrument Performance Checks in alternative solvents.

Calibration stability must be monitored as described in the Ongoing Verification of Calibration (Verification Standards) section.

Soil moisture content must be considered within data calculations for the total methanol extract volume for each sample.

VH_{s6-10} method detection limits and reporting limits must be based on unweathered gasoline (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. This information must be available in the event of audit by BC MOE.

The Instrument Performance Checks of this method are designed to identify 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 Prescribed Elements section or elsewhere, changes to the following components of this method are permitted if all specified quality control requirements of the method are achieved:

Reagents and Standards

Gas Chromatograph Conditions — including the use of Headspace or Purge and Trap analysis.

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

References

US EPA Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003.

US EPA Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.

US EPA Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 1, June 2003.

ASTM D6418-09, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis.

Revision History

Aug 15, 2014:	Revised to reflect new requirements for field methanol extraction or hermetic samplers. Minimum ratio of methanol to wet soil changed from 2:1 to 1.5:1. Relative response requirements changed to 0.7–1.3 to coincide with CCME method. Requirement to run Method Performance Spike was replaced with new requirement to run Laboratory Control Standards (gasoline) with each batch. *Meta*-xylene calibration standard was clarified such that *meta*-/*para*-xylene mixtures may also be used. Maximum batch size changed from 50 to 20 samples to coincide with industry standard practice. Calibration changed to minimum 3 point linear with narrower 20% CCV requirement. Laboratory Duplicate DQO changed from 30 to 40% RPD as per QA section guidelines and VOC soil method. Effective date for this revision is Nov 1, 2014.
April 2007:	Revision of hold times and preservation requirements.
Dec 31, 2000:	SEAM codes replaced by EMS codes. Out of print reference deleted. Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; Mandatory tests made bold.
July 1999:	Finalization of method (revised by ALS under contract to BC MOE) based on results of round robin vetted by BCLQAAC.
March 1997:	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Solids.

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 [g]. 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:

$$\mathbf{V_A = s_A^2 / n_A} \qquad \mathbf{V_B = s_B^2 / n_B}$$

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.

Volatile Hydrocarbons in Waters by GC/FID — PBM

Parameters

Volatile Hydrocarbons (nC_6–nC_{10}) in waters

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Analyte Code
VH_{w6-10}	100 µg/L	VHC-

*** Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Analytical Method

Purge and Trap or Headspace (Static or Dynamic) - Gas Chromatography with Flame Ionization Detection (GC/FID), Performance Based Method.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

Introduction

This method measures the aggregate concentration of Volatile Hydrocarbons in water (VH_W). Volatile Hydrocarbons (VH) are quantitated in two sub-ranges, using either *meta*-xylene or a mixture of *meta*- and *para*-xylenes (m,p-X) for the first sub-range, and 1,2,4-trimethylbenzene (1,2,4-TMB) for the second sub-range. VH_{w6-10} measures hydrocarbons that elute between n-hexane and n-decane, roughly equivalent to a boiling point range of 69°C to 174°C.

Volatile Hydrocarbons (VH_{w6-10}) is the precursor to the calculation of Volatile Petroleum Hydrocarbons (VPH). Specified Monocyclic Aromatic Hydrocarbon (MAH) results are subtracted from VH concentrations to arrive at VPH, using the procedure outlined in the British Columbia Ministry of Environment, Lab Manual method “Calculation of Volatile Petroleum Hydrocarbons in Solids, Waters or Air (Vapour)”.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC_6 through nC_{10}, for example gasolines, mineral spirits, and petroleum naphtha). The volatile fraction of some heavier petroleum products like kerosenes, jet fuels, and diesels can also be partially captured by VH.

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e., MAHs). GC/MS is strongly recommended for quantitation of target VOC compounds.

Method Summary

Purge and trap: A portion of the sample is transferred to a purging chamber. Volatile Hydrocarbons are purged from the sample with an inert gas, and are trapped on a solid sorbent trap. The trap is heated and VH components are directed into a gas chromatograph equipped with a flame ionization detector (FID).

Headspace: A portion of the extract is transferred to a headspace vial containing water and appropriate matrix modifying salts. The vial is then sealed and heated to a pre-determined equilibration temperature for a given period of time. After equilibration, a portion of the headspace above the sample is introduced into a GC/FID. If required, the sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column.

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

Matrix	Fresh water, wastewater, seawater.
Interferences and Precautions	Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. All of these must be monitored and demonstrated to be free of interferences under the conditions of the analysis by the 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. This method requires the analysis of a representative sub-sample of the total contents of each sample container, including any hydrocarbons which may be adsorbed to solids within the sample container. Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carry-over that occurs on their instrument and should take appropriate steps to prevent the occurrence of false positives. Excessive methanol concentration in samples can decrease purge efficiency or headspace partitioning of VOC analytes, may prevent resolution of hexane from the solvent peak, and may cause difficulties with adsorptive traps or with chromatography. Ensure that all samples and calibration standards are closely matrix matched with respect to methanol concentration.
Sample Handling and Preservation	Collect samples in glass screw-cap vials (clear or amber) with Teflon-lined silicone septa (recommended: 40mL or 60mL vials, 2 per sample). Collect samples with zero headspace (A small air bubble of up to ~ 2 mL volume or 5% of sample volume may appear after sampling and is acceptable). Preserve all samples using one of the following procedures: a) Preserve by acidification to pH ≤ 2 with sodium bisulfate ($NaHSO_4$), as a microbial inhibitor. 200 mg of solid $NaHSO_4$ per 40 mL sample is recommended. Acidification to pH ≤ 2 using HCl or H_2SO_4 is also permitted. b) For chlorinated waters, samples preserved with sodium thiosulfate (for purposes of VOC preservation) may be utilized for this test. 3 mg $Na_2S_2O_3$ per 40 mL sample is normally utilized for VOC preservation in chlorinated waters and is sufficient to reduce up to 15 ppm of free chlorine.
Stability	**Holding Time:** Maximum holding time prior to analysis is 14 days after sampling if preserved as described. Where holding times are exceeded, data must be qualified. **Storage Conditions:** Store samples at ≤ 10°C during shipment to lab, and at ≤ 6° at the laboratory in an area free from organic solvent vapors.

Apparatus

Glassware and Support Equipment

Purge and Trap or Headspace sample introduction system

Gas Chromatograph (GC)

A temperature programmable capillary gas chromatograph is required. A heated split/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 VH_{W6-10}. The FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

Sample Introduction Mechanism

Purge and Trap conditions: SW846 Method 5030C

Static Headspace conditions: SW846 Method 5021A

Chromatographic Column

The reference column for this method is a 30-meter, 0.53 mm internal diameter capillary column with a 1.5um coating of 100% dimethyl siloxane (e.g., DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified.

Procedure

Headspace: An appropriate amount of sample is added to a clean headspace vial. Internal standards and a matrix modifying salt solution are added, either manually or automatically by the headspace system. Sample vials are sealed with a cap and Teflon-lined septum, and are introduced to the headspace heating system, where they are allowed to establish a partition equilibrium. Mechanical vibration may be used to accelerate the process. The vial may be pressurized with an inert gas. A representative fraction of headspace is transferred to the analytical trap or directly to the GC column via a heated transfer line or syringe. Consult US EPA Method 5021A for additional guidance.

Purge and Trap: An appropriate amount of sample is added to a clean purge and trap vial. Internal standards are added, either manually or automatically by the purge and trap system. Sample vials are sealed with a cap and Teflon-lined septum and are loaded onto the autosampler. VH components are purged from samples with an inert gas and are trapped on a solid sorbent trap. The trap is rapidly heated and the contents are transferred to the GC column via a heated transfer line. Consult US EPA Methods 5030C and 5035A for additional guidance.

Samples must be matrix-matched with calibration standards and QC samples in terms of methanol amounts and any matrix modifying salts used.

GC-FID Analysis

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

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).

Example GC-FID Conditions

The following GC-FID conditions are provided as an example only. Any conditions 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, 0.53 mm id, 1.5 µm phase.
Carrier Gas:	helium
Head pressure:	9.0 psi @ 40˚C (with column dimensions as specified)
Column flow:	15 mL/minute @ 40°C (88 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	200˚C
Injection mode:	split
GC liner type:	2 mm id splitless liner no glass wool
Inlet purge on time:	1.0 minute (splitless)
FID temperature:	250˚C
Oven program:	Initial Temp 40°C (hold 4.0 minutes)
	5°C /min to 140°C (no hold)
	25°C /min to 220°C (hold 2.0 minutes)

Reagents and Standards

Reagents

Acetone (2-propanone)

Methanol — Purge and Trap grade

Organic-free reagent water — Refer to US EPA Method 524.2, section 7.2.2.

Preservatives — one of the following is required:

200mg sodium bisulfate per 40mL sample

Hydrochloric acid (HCl), diluted 1:1 with reagent water

Sulfuric acid (H_2SO_4), diluted 1:1 with reagent water

Sodium thiosulfate ($Na_2S_2O_3$), approximately 3mg per 40mL sample (this preservative is intended for VOC preservation, but may also be used for VH)

Standards — Cautionary Note

Aliphatic hydrocarbons are poorly soluble in methanol, especially when cold. Ensure that all calibration standards and reference solutions are warmed to room temperature and mixed well prior to use to ensure complete dissolution of all components. Store all standards refrigerated at ≤ 6 ˚C. Storage in a freezer is preferable.

Calibration Standards

Prepare a minimum of 3 levels of Calibration Standards in methanol, each containing n-hexane (nC_6), n-octane (nC8), n-decane (nC_{10}), benzene, toluene, ethylbenzene, *meta*-xylene, *para*-xylene (optional), *ortho*-xylene, and 1,2,4-trimethylbenzene (1,2,4-TMB). If both *meta*- and *para*-xylenes are included in calibration standards, it is recommended that they each be present at half the concentration of the other constituents.

Calibration Verification Standard

Prepare a Calibration Verification Standard containing *meta*-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene in methanol at a concentration near the middle of the calibration curve, from a source independent from the Calibration Standard.

Gasoline Stock Standard

Prepare a stock solution of gasoline in methanol (e.g., 10,000 µg/mL). Prepare the solution by weight (e.g., weigh 0.250 g gasoline into a 25 mL volumetric flask). Record the source of the gasoline used. A gasoline source that does not contain ethanol is recommended. Note that the nominal concentration of gasoline (weight gasoline / volume) is not equal to the concentration of VH_{w6-10} (the nominal gasoline concentration is higher).

Detection Limit Check Standard

Dilute the Gasoline Stock Solution to prepare a Detection Limit (DL) Check Standard in methanol. Prepare the standard at a concentration that is approximately equal to the extract concentration that corresponds to the Reporting Detection Limit for VH_{w6-10}. 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 VH_W 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 all components.
Calibration QC and Verification		
Instrument Blank	1 per initial calibration	None; required for background correction.
Calibration Verification Standard (CVS)	1 per initial calibration	Within 15% of expected concentration.
Detection Limit Check Standard	1 per initial calibration	50–150% of VH target.
Continuing Calibration Verification (CCV)	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Within 20% of initial calibration
Method QC		
Method Blank	1 per 20 samples (1 per batch minimum)	< Reported Detection Limit.
Laboratory Control Sample (Gasoline Method Spike)	1 per 20 samples (1 per batch minimum)	70–130% recovery
Laboratory Duplicates	1 per 20 samples (1 per batch minimum)	30% RPD [or within 2x reported DL for low level results]
Surrogate Compounds	All samples	70–130% recovery
Field QC		
Field Duplicates	Recommended	Not specified
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. 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 repeated at least every 24 hours during continuous operation.

Instrument Performance Checks serve the following purposes:

Measure and control relative response ratios of specified VH components,

Determine retention time windows for VH integration ranges, and

Confirm resolution of hexane (nC_6) from the solvent peak.

The primary purpose of the Instrument Performance Check is to ensure that the GC/FID response factors of VH components throughout its boiling point range are roughly equal. If excessive relative bias exists among VH components due to differences in their polarity, mass, boiling point, or chemical composition, then calculated results will be biased, and interlaboratory inconsistency will result.

For each component of the Calibration Standard, determine the relative response ratio (by peak area) against the appropriate reference compound. Compare the peak areas of hexane (nC_6), octane (nC8), benzene, toluene, and ethylbenzene against *meta*-xylene (or *meta*- and *para*-xylenes). Compare the peak areas of decane (nC_{10}) and *o*-Xylene against 1,2,4-trimethylbenzene. Acceptance criteria for relative response ratios are 0.7–1.3. If any relative response ratio fails these acceptance criteria, 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.

Calibration QC

Instrument Blank (IB)

REQUIRED. Minimum 1 per initial calibration. Inject a matrix matched blank to the GC system to establish the chromatographic baseline.

Calibration Verification Standard (CVS)

REQUIRED. Minimum 1 per initial calibration.

Analyze a CVS (see the Calibration Verification Standard section) containing *meta*-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The Calibration Verification Standard is used to confirm the integrity of the calibration standard.

If the calculated concentration of *meta*-xylene (or *meta*- and *para*-xylenes) or 1,2,4-trimethylbenzene in the Calibration Verification Standard varies by more than 15% from the expected target, then the calibration is invalid. Discrepancies must be corrected before any sample results for the analysis batch may be reported. Correction may require any or all of:

Re-analysis of Calibration Verification Standard and/or Calibration Standard.

Re-preparation and re-analysis of Calibration Verification Standard and/or Calibration Standard.

GC maintenance (if discrepancy is due to calibration non-linearity).

Detection Limit Check

REQUIRED. Minimum 1 per initial calibration. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low-level solution of gasoline.

Analyze a Detection Limit Check Standard that contains VH_{W6-10} at a concentration that is approximately equivalent to the VH_{W6-10} Reported Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50–150 % of the VH_{W6-10} target.

Method QC

Method Blank (MB)

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

If a Method 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 Method Blank result).

Laboratory Control Sample (LCS)

REQUIRED. Minimum 1 per 20 samples. Prepare a Gasoline LCS by fortifying reagent water with an accurate volume of a Gasoline Method Spike Solution, which should be prepared at a concentration at least 10x the laboratory's reported detection limit.

Determine the target for VH_{w6-10} by directly analyzing several replicates of the Gasoline Method Spike Solution diluted to a concentration that equals the amount of gasoline spiked (in µg) divided by the volume of reagent water used for the spike.

Acceptable performance for the Laboratory Control Sample is between 70–130 % of the VH_{w6-10} target.

Laboratory Duplicates

REQUIRED. Minimum 1 per 20 samples. Laboratory duplicates should be conducted by sub-sampling a second aliquot from a single field sample. Laboratory Duplicates must be subjected to all sample preparation steps experienced by samples. Acceptable performance for the laboratory duplicate sample is between 30 % Relative Percent Difference (RPD), or within 2 times the reported detection limit for low level results.

Surrogate Compounds

REQUIRED. The use of one or more surrogate compounds for VH is required. Surrogate(s) must be added to each sample prior to the extraction or instrumentation process. Surrogates that elute outside the VH retention time range are recommended so that they do not need to be subtracted from integrated VH peak areas (2,4-Dichlorotoluene is recommended as a suitable VH surrogate compound for detection by FID).

Surrogates from VOC/BTEX analyses by GCMS may be utilized as an alternative to a GC-FID surrogate for VH, when running in dual simultaneous GCMS/FID mode.

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. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

Field QC

Field Duplicates

RECOMMENDED.

Instrument QC

Instrument Blank

REQUIRED. Minimum 1 per initial calibration. Inject a matrix matched blank to the GC system to establish the chromatographic baseline.

Calibration Verification Standard (CVS)

REQUIRED. Minimum 1 per initial calibration. Analyze a Calibration Verification Standard (see the Calibration Verification Standard section) containing *meta*-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The Calibration Verification Standard is used to confirm the integrity of the calibration standard. Acceptance criteria are 85–115%.

Detection Limit Check

REQUIRED. Minimum 1 per initial calibration. Analyze a Detection Limit Check Standard that contains VH_{W6-10} at a concentration that is approximately equivalent to the VH_{W6-10} Reporting Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50–150 % of the VH_{W6-10} target.

Calibration & Analysis Procedure

Initial Calibration

A minimum 3-point linear external standard calibration is required for this method.

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

Calculate the Calibration Factors (CFs) for *meta*-xylene and 1,2,4-trimethylbenzene in the Calibration Standard using the equation below:

$CF_{m\text{-}X}$ (mL/µg) = m-X area / [m-X] (µg/mL)

$CF_{1,2,4\text{-}TMB}$ (mL/µg) = 1,2,4-TMB area / [1,2,4-TMB] (µg/mL)

Continuing Calibration Verification (CCV)

After initial calibration, the Calibration Factors ($CF_{m\text{-}X}$ and $CF_{1,2,4\text{-}TMB}$) 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.

An initial calibration is valid as long as both Calibration Factors remain within 20% of their initial values.

Integration of Total Areas for VH_{w6-10}

VH_{w6-10} is defined to include all GC/FID peaks eluting between hexane (nC_6) and decane (nC_{10}). VH_{w6-10} is quantitated by summing the results for two sub-ranges within the nC_6–nC_{10} range. The first VH sub-range falls between the retention times of hexane and *ortho*-xylene. The second VH sub-range falls between the retention times of *ortho*-xylene and decane. Each sub-range is integrated and quantitated separately, and VH_{w6-10} is then calculated by summing the two results.

Note: Calculating VH using two sub-ranges reduces the impact of relative response biases which may exist between higher and lower volatility VH components. The two-range calculation mechanism was intended to simplify the development of purge and trap methods that may be equivalent to alternate methods such as the headspace injection method.

Determine the total integrated peak area of each VH sub-range, where:

The $VH_{w(6-oX)}$ range begins at the apex of the nC_6 peak and ends at the apex of the *o*-Xylene peak.

The $VH_{w(oX-10)}$ range begins at the apex of the *o*-Xylene peak and ends at the apex of the nC_{10} peak.

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

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

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

VH_{w6-10} is the sum of the calculated concentrations for $VH_{w(6-oX)}$ and $VH_{W(oX-10)}$. $VH_{w(6-oX)}$ is quantitated against the *meta*-xylene (or *meta*- and *para*-xylene) calibration standard. $VH_{w(oX-10)}$ is quantitated against the 1,2,4-trimethylbenzene

calibration standard.

It is highly recommended that the Surrogate Compounds used for VH by FID analysis elute slightly outside the VH range of nC_6–nC_{10}. If any Surrogate Compounds are added to samples within the VH range, the contribution to VH of those Surrogates must be subtracted from calculated VH results.

Use the following equations to calculate VH_{w6-10}:

VH_{W6-10} (µg/mL) = $VH_{W(6-oX)}$ (µg/mL) + $VH_{W(oX-10)}$ (µg/mL) - Actual Surr. Conc* (µg/mL)

* Only Surrogates (if any) that elute within the VH_{W6-10} range are subtracted.

$$VH_{W(6-oX)}\ (\mu g/mL) = \frac{A_{(6-oX)} \times Vol}{CF_{m\text{-Xylene}}}$$

$$VH_{W(oX-10)}\ (\mu g/mL) = \frac{A_{(oX-10)} \times Vol}{CF_{1,2,4-TMB}}$$

where:

$A_{(6-oX)}$ = Total area between nC_6 and *ortho*-xylene for the sample chromatogram.

$A_{(oX-10)}$ = Total area between *ortho*-xylene and nC_{10} for the sample chromatogram.

$CF_{m\text{-Xylene}}$ = Calibration Factor for *meta*-xylene standard (μg^{-1}).

$CF_{1,2,4-TMB}$ = Calibration Factor for 1,2,4-trimethylbenzene standard (μg^{-1}).

Vol = Volume of sample purged (mL).

Dilution Requirement for High Level Sample Extracts

All valid sample analyses must lie within the validated linear range of the GC/FID system, based on initial validation. Any samples that exceed the validated linear range must be diluted and re-analyzed (for purge and trap or headspace, dilution normally entails re-analysis using a smaller aliquot of the sample).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate VH_{W6-10} 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 VH_W Concentrations of a Gasoline Reference Solution

This procedure describes how to calculate the Actual VH_{W6-10} Concentrations for aqueous solutions of petroleum products where only the total weight/volume concentration of the petroleum product in the water is explicitly known. Actual VH_{W6-10} concentrations of a petroleum product solution can only be measured experimentally, whereas the concentration of the petroleum product in the water is simply determined by dividing the weight of product by the volume of water in which it is prepared.

Actual VH_{W6-10} Concentrations are required within this method for the following purposes:

Determination of GC/FID linear range for VH_{W6-10} (i.e., calibration range).

Determination of VH_{W6-10} Instrument Detection Limits (IDLs).

Preparation of DL Check Standards and Method Spike Solutions.

Calculation of VH_W targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual VH_{W6-10} Concentration* of a reference gasoline:

Prepare the reference gasoline solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for VH_{W6-10}. A petroleum product concentration of at least 5 µg/mL in water is recommended for this purpose.

Perform a minimum of 3 replicate analyses of the reference gasoline solution prepared in (a) using the selected GC-FID method conditions. In the example below, the measured VH_{W6-10} concentration is denoted as $[VH_{W6-10,measured}]$.

Calculate the percentage that the VH_{W6-10} range represents of the total nominal gasoline concentration. Example (for a given source of gasoline):

$\%VH_{W6-10}$ in gasoline = 100% × $[VH_{W6-10,measured}]$ / $[Gasoline_{grav}]$

where:

$[VH_{W6-10}, measured]$ = measured concentration of VH_{W6-10} of a solution of gasoline in water.

$[Gasoline_{grav}]$ = actual gasoline concentration in weight of gasoline / volume water for the same solution

Units = same for both concentrations (e.g., µg/mL).

Note: The percentage of VH_{W6-10} in gasoline is considerably less than 100% (typically about 50–60%) because not all components of gasoline fall within the nC_6–nC_{10} boiling point range.

To calculate the *Actual VH_{W6-10} Concentrations* of other concentrations of the same product, multiply the nominal gasoline concentration of the solution by the $\%VH_{W6-10}$ determined above.

Establish Instrument Calibration Working Range and Estimated IDLs

Establish the linear working range of the GC/FID system for VH_{W6-10} using a series of dilutions of the 50,000 µg/mL Gasoline Stock Solution into water. Analyze gasoline solutions at concentrations ranging from below the estimated Instrument Detection Limit to above the estimated maximum calibration concentration in approximately 2-fold increments. The following aqueous concentrations are recommended as an approximate guide: 0.02, 0.05, 0.1, 0.5, 1, 2, 5, 10, 25, 50, and 100 µg/mL of the gasoline solution. Calculate VH_{W6-10} results for each solution using the procedure described in the Calculations section.

At the Limit of Reporting, VH_{W6-10} should be measurable at 50–150% of the expected concentration.

The upper range of the validated linear range must be used to determine when over-range samples must be diluted.

Note: Validation of upper linear range is particularly important for purge and trap methods.

Establishing Method Detection Limits

Determine the Method Detection Limits (MDLs) at the 95% confidence level for VH_{W6-10}, using the procedure outlined in the British Columbia Environmental Laboratory Manual.

Select a concentration for method spikes of gasoline into reagent water of between one and three times the estimated IDL for VH_{W6-10}. Prepare and analyze at least 7 method spikes at this concentration. Use a Gasoline Spike Solution to prepare these method spikes (see Method QC section).

Calculate the Method Detection Limit (MDL) at the 99% confidence level for VH_{W6-10}.

Average recoveries of the MDL Method Spikes for VH_{W6-10} must be between 60 –140%, where recovery is defined as calculated VH_{W6-10} result / target VH_{W6-10} concentration, as determined in the Calculation of Actual VH_W Concentration of a Petroleum Reference Solution section. If this condition is not met, repeat the MDL determination at a higher spike level.

Determination of DL Check Standard Concentration and VH_{W6-10} Targets

Use the procedure that follows to select a suitable aqueous concentration of gasoline for the DL Check Standard. This procedure involves the conversion of gasoline in nominal concentration units to (and from) VH_{W6-10} concentration units (in aqueous solution).

Calculate the percentage of the total nominal gasoline concentration that VH_{W6-10} represents, using the procedure described above. Typically, VH_{W6-10} represents about 50–60% of the nominal gasoline concentration. This percentage is less than 100% because not all components of gasoline fall within the nC_6–nC_{10} boiling point range.

Determine the concentration of gasoline in water that corresponds to the VH_{W6-10} Reporting Detection Limit. Use the percentage value from (a) to calculate this gasoline concentration:

[Gasoline in water] equiv. to VH_{W6-10} DL = 100 × $\frac{\text{(Reporting DL for } VH_{W6-10})}{(\%VH_{W6-10} \text{ in Gasoline})}$

Where [Gasoline] and VH_{W6-10} Reporting DLs must be in the same units (e.g., µg/mL of water).

Select a concentration for the Detection Limit Check Standard that is approximately equal to the concentration determined above.

Example: For a Reporting Detection Limit of 100 µg/L VH_{W6-10} with a sample size of 5 mL, add 10 µL of a 100 µg/mL solution of gasoline to 5 mL of reagent water to achieve a 200 µg/L aqueous concentration of gasoline in the check standard, if the proportion of VH_{W6-10} in the gasoline is 50%. The aqueous concentration of VH_{W6-10} in the Detection Limit Check Standard will be 100 µg/mL.

Calculate the target for VH_{W6-10} in the DL Check Standard by multiplying the concentration selected in (b) by the VH_{W6-10} percentage from (a).

VH_{W6-10} target = (DL Std. gasoline conc. in water) × ($\%VH_{W6-10}$ in gasoline)

Accuracy and Precision Requirements:

A minimum of 8 Laboratory Control Samples prepared from unweathered gasoline must be used to assess the accuracy and precision of the method. Determine Method Spike targets using *Actual VH_{W6-10} Concentrations* of the spike solution by following the procedure outlined in the Calculation of Actual VH_W Concentration of a Petroleum Reference Solution section. The minimum accuracy requirement for Initial Validation is an average recovery of 85–115%. The minimum precision requirement for Initial and Ongoing Validations is a Relative Standard Deviation of ≤ 15%. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Method Performance Data

Single laboratory and interlaboratory performance data for this method were published in previous versions of the BC Lab Manual. Refer to the 2013 version or earlier versions of the BC Lab Manual to access this information.

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 method-defined aggregate parameters like Volatile Hydrocarbons, where many components are calculated against single calibration reference standards. This method has been specifically designed to minimize the relative bias among responses of common VH components, and among VH_{W6-10} results generated by different laboratories.

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

Prescribed Elements

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

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

"REQUIRED" QC elements from the QC section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.

Gas Chromatography with Flame Ionization Detection is required for $VH_{W_{6-10}}$.

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

Meta-xylene (or *meta*- and *para*-xylenes) and 1,2,4-trimethylbenzene must be used as the calibration standards for $VH_{W_{6-10}}$. Minimum 3-point linear calibration is required.

GC calibration standard must be matrix matched, unless equivalence (within 2%) can be demonstrated for component responses and retention times of Instrument Performance Checks in alternative solvents.

$VH_{W_{6-10}}$ method detection limits and reporting limits must be based on unweathered gasoline (see the Establishing Method Detection Limits section).

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

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. This information must be available in the event of audit by BC MOE.

The Instrument Performance Checks of this method are designed to identify 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.

The required QC elements contained within this method are deemed sufficient to identify potential biases introduced by permitted modifications within these areas of the method

References

US EPA Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003.

US EPA Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.

US EPA Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 2, July 2014.

US EPA Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, 1995.

Revision History

Sept 15, 2017	Revised to new format. Removed Purge & Trap as prescriptive element, and formally allowed for Headspace analysis, which was previously approved on a per-laboratory basis. Requirement for Method Performance Spike was replaced with new requirement to run Laboratory Control Samples (gasoline) with each batch. *Meta*-xylene calibration standard was clarified such that *meta*-/para-xylene mixtures may be used. Requirement added for CVS to be second source. Maximum batch size changed from 50 to 20 samples to coincide with industry standard practice. Calibration changed to minimum 3 point linear with narrower 20% CCV requirement. Minimum Instrument Performance Check frequency changed to once daily. Preservation options were updated to reflect current BC MOE requirements. Adopted newer standardized nomenclature for QC terminologies (LCS, CCV, CVS). Added new initial validation performance requirements for accuracy and precision.
April, 2007	Hold time updated.
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.
Jul 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.
Mar 1997	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Water.

Volatile Organic Compounds (VOCs) in Soil — PBM

Parameter Volatile Organic Compounds (VOCs) in solids

Analytical Method Purge and Trap, Headspace (Static or Dynamic), or Direct Injection - GC/MS or GC/PID (PBM)

Introduction This method is applicable to the quantitative determination of volatile organic compounds in soil and other solids, when appropriately sampled and extracted with methanol. Analysis for $VH_{S_{6-10}}$ is often conducted concurrently.

Method Summary To minimize loss of VOCs during sampling and transport to the laboratory, samples must be either preserved in the field with methanol or collected using hermetically sealed sampling devices. Another aliquot of sample is required for moisture content determination. A field/travel blank (an additional vial pre-charged with methanol) is highly recommended.

Purge and trap: A portion of the extract is transferred to a vial containing water. The VOCs are purged from the sample with an inert gas and are trapped on a solid sorbent trap. The trap is heated and the VOCs are directed into a gas chromatograph equipped with a mass spectrometric detector (GC/MS). GC/PID is acceptable for a subset of analytes, e.g., BTEX and styrene.

Headspace: A portion of the extract is transferred to a headspace vial containing water. The vial is then sealed and heated to a pre-determined temperature for a given period. After equilibration, a portion of the headspace above the sample is introduced into a GC/MS. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column. GC/PID is acceptable for a subset of analytes, e.g., BTEX and styrene.

Direct Injection: A portion of the extract is transferred to an autosampler vial, and is injected into a GC inlet (typically a split/splitless or on-column inlet), for direct analysis by GC/MS.

The analytical portion of this method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes The analytes listed below represent the volatile substances regulated in the 2017 CSR. The MDLs listed below are achievable by GC/MS in a typical laboratory environment, but may vary by laboratory, and with the sample introduction technique used. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Analyte	Approx. MDL (mg/kg)	CAS Number	EMS Analyte Code
acetone	0.2*	67-64-1	A005
acrolein	0.1*	107-02-8	-
acrylonitrile	0.1*	107-13-1	-
allyl alcohol	0.1*	107-18-6	-
allyl chloride	0.1*	107-05-1	C056
benzene	0.01	71-43-2	B020

Analyte	Approx. MDL (mg/kg)	CAS Number	EMS Analyte Code
benzyl chloride	0.1*	100-44-7	-
bromobenzene	0.01	108-86-1	B005
bromodichloromethane	0.01	75-27-4	B012
bromoform	0.01	75-25-2	B013
bromomethane	0.02*	74-83-9	-
butadiene, 1,3-	0.05*	106-99-0	-
butanol, n-	0.1*	71-36-3	-
butylbenzene, n-	0.01	104-51-8	B034
butylbenzene, sec-	0.01	135-98-8	B035
butylbenzene, tert-	0.01	98-06-6	B036
carbon disulfide	0.05*	75-15-0	-
carbon tetrachloride	0.01	56-23-5	C034
chlorobenzene	0.01	108-90-7	C010
chlorobutane, 1-	0.01	109-69-3	-
chloroethanol, 2-	0.1*	107-07-3	-
chloroform	0.01	67-66-3	C032
chloroprene	0.05	126-99-8	-
chlorotoluene, 2-	0.01	95-49-8	2CLT
chlorotoluene, 4-	0.01	106-43-4	C047
crotonaldehyde, trans-	0.1*	4170-30-3	-
dibromo-3-chloropropane, 1,2-	0.02*	96-12-8	B038
dibromochloromethane	0.01	124-48-1	C033
dibromoethane, 1,2-	0.01	106-93-4	B029
dichlorobenzene, 1,2-	0.01	95-50-1	-
dichlorobenzene, 1,3-	0.01	541-73-1	-
dichlorobenzene, 1,4-	0.01	106-46-7	-
dichlorodifluoromethane	0.02*	75-71-8	-
dichloroethane, 1,1-	0.01	75-34-3	C021
dichloroethane, 1,2-	0.01	107-06-2	C022
dichloroethylene, 1,1-	0.01	75-35-4	C024
dichloroethylene, cis-1,2-	0.01	156-59-2	C063
dichloroethylene, trans-1,2-	0.01	156-60-5	C023
dichloromethane	0.05	75-09-2	M041
dichloropropane, 1,2-	0.01	78-87-5	C025
dichloropropane, 1,3-	0.01	142-28-9	-
dichloropropene, cis-1,3-	0.01	10061-01-5	C027
dichloropropene, trans-1,3-	0.01	10061-02-6	C028
diethyl ether	0.1*	60-29-7	-
dioxane, 1,4-	0.2*	123-91-1	-
ethyl acetate	0.1*	141-78-6	-
ethylbenzene	0.01	100-41-4	B021
hexachlorobutadiene	0.05*	87-68-3	HCBD
hexachloroethane	0.05*	67-72-1	-
hexanone, 2-	0.1*	597-78-6	H024
isobutanol	0.1*	78-83-1	-
isopropanol	0.1*	67-63-0	-
isopropylbenzene	0.01	98-82-8	I008
methacrylonitrile	0.1*	126-98-7	M028
methyl acetate	0.1*	79-20-9	-
methyl ethyl ketone [MEK]	0.1*	78-93-3	B033
methyl methacrylate	0.1*	80-62-6	M054
methyl-tertiary butyl ether [MTBE]	0.02	1634-04-4	MTBE

Analyte	Approx. MDL (mg/kg)	CAS Number	EMS Analyte Code
propylbenzene, 1-	0.01	103-65-1	P030
styrene	0.02*	100-42-5	S010
tetrachloroethane, 1,1,1,2-	0.01	630-20-6	-
tetrachloroethane, 1,1,2,2-	0.01	79-34-5	C080
tetrachloroethylene	0.01	127-18-4	T030
toluene	0.02	108-88-3	T001
trichloro-1,2,2-trifluoroethane, 1,1,2-	0.02*	76-13-1	-
trichloroethane, 1,1,1-	0.01	71-55-6	T016
trichloroethane, 1,1,2-	0.01	79-00-5	T017
trichloroethylene	0.01	79-01-6	T029
trichlorofluoromethane	0.02*	75-69-4	T070
trichloropropane, 1,1,2-	0.01	598-77-6	-
trichloropropane, 1,2,3-	0.01	96-18-4	T067
trichloropropene, 1,2,3-	0.01	96-19-5	-
trimethylbenzene, 1,3,5-	0.02	108-67-8	T069
vinyl acetate	0.05*	108-05-4	-
vinyl chloride	0.05*	75-01-4	C004
xylene, *meta*- +*para*-	0.02	108-38-3 106-42-3	X003
xylene, *ortho*-	0.01	95-47-6	X002

*Analytes with an asterisk in the MDL exhibit known difficulties with reproducibility, response, recovery, stability, and/or chromatography that may reduce the overall quality or confidence in the result. Refer to EPA reference methods 5030/5021/8260 for additional information.

Where appropriate, the method may be used for other compounds not listed here, subject to validation and achievement of data quality objectives (DQOs).

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Soil, sediment, and other solids

Interferences and Precautions

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

Where the proportion of water in a methanol extract exceeds 20–25%, the solubility of non-polar organics in the extract is substantially diminished (especially when refrigerated). A ratio of 2:1 methanol to wet solids is targeted to minimize the water content of methanol extracts. With the use of field methanol extraction and hermetic samplers, it is difficult to precisely control this ratio, but the laboratory must add methanol if necessary to ensure this ratio is at least 1.5:1.

Detection limits may be elevated for samples with high moisture content (~ > 50%).

Calibration standards are prepared using methanolic standard solutions. Ensure that samples and standards are matrix-matched as closely as possible with respect to methanol content, unless it can be demonstrated that performance is not compromised. Excessive amounts of methanol can compromise the performance of sorbent traps and/or the mass spectrometer.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. If possible, when an unusually high-level 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 a Reporting Detection Limit is suspected.

Sample Handling and Preservation

Samples must be collected and processed by one of the following two options:

Field Methanol Preservation: A representative sub-sample of soil (typically ~ 5 g wet weight) is collected (typically with a disposable coring device) and extruded into a known volume of high purity methanol (typically 10 mL) contained in a pre-weighed vial.

Hermetic Sampler: A representative sub-sample of soil (typically ~ 5 g wet weight) is collected in the field using a hermetically sealed soil sampling device.

Methanol extracts and hermetic samplers must be immediately chilled at time of collection to ≤ 10˚C for shipment to the laboratory.

Stability

Holding Time — Methanol Extract: 40 days from sampling date.

Holding Time — Hermetic Samplers: Hermetic samplers must be methanol extracted within 48 hours of sampling. Hold time prior to methanol extraction can be extended to 7 days from sampling if sample is frozen (≤ -7 ˚C) within 48 hours of sampling, but the sample must be extruded into methanol while still predominantly or partially frozen (warm for ~2–3 minutes at room temperature to facilitate extrusion).

Storage Conditions: Methanol extracts must be stored in the laboratory at ≤ 6˚C (preferably ≤ -7˚C).

Verification of Field Methanol Preservatives

Laboratories must ensure that Quality Control procedures are in place to ensure that Field Methanol preservatives they provide are fit for purpose. On a routine or batch basis, tare weights and methanol volumes of pre-dispensed and pre-weighed methanol vials must be verified (recommended specifications are ±2% of methanol volume and ±0.1 grams for pre-weights). Small errors in methanol volume or tare weights can cause larger errors in final test results.

Sample Preparation

This procedure is required for the analysis of both targeted VOCs and the aggregate parameter, $VH_{S_{6-10}}$. The same extract should normally be used to analyze these parameters.

Take an aliquot of the soil sample from the soil jar to perform an accurate moisture determination on the sample, so final results can be provided in dry weight units.

Hermetically Sealed Samplers

Keep hermetic samplers at ≤ 6 ˚C (preferably frozen) until immediately prior to extraction. Frozen samples should be extruded to methanol while still predominantly or partially frozen (warm for ~2–3 minutes at room temperature to facilitate extrusion).

Transfer the entire contents of the hermetic sampler to a tared vessel and accurately weigh the contents to at least the nearest 0.01 grams.

Add an exact volume of high purity methanol (typically 10 mL per 5 g sample), equal to approximately 2 times the wet weight of the soil sample (but no less than

1.5 times the wet weight of the soil sample). Pre-charged methanol vials of known weight may be used.

Field Methanol Preserved Samples

Weigh field methanol preserved sample vials at the laboratory to at least the nearest 0.01 grams. Determine the accurate weight of wet soil or solids in each sample from the weight (vial + methanol + soil sample) minus the pre-weight (vial + methanol).

Prior to weighing, carefully clean the outside of the sample vials to remove any adhered soil or residues. The weights of any labels that may have been affixed to sample vials must be considered when calculating sample weights.

Confirm that the ratio of methanol to wet weight of soil is at least 1.5:1. If not, accurately add additional methanol, targeting a ratio of approximately 2:1. Record the volume of additional methanol added to at least the nearest 0.1 mL.

Methanol Extraction and Agitation (All Samples)

Prepare appropriate and required Method QC samples as described in the Method QC section.

At least two surrogate compounds are required for VOC/BTEX analysis. VH surrogates may be combined with surrogates required for VOC/BTEX analyses (if required). Surrogates must be added to every sample (in methanol solution) prior to agitation. Surrogates will highlight possible problems with analyses, or with limitations of the extraction process (e.g., adsorption of VOCs by charcoal or organic carbon in soil samples).

Field methanol preserved samples must be physically agitated using a mechanical shaker (e.g., wrist shaker or platform shaker) for at least 15 minutes.

Hermetic samples that are methanol extracted in the laboratory must be physically agitated using a mechanical shaker (e.g., wrist shaker or platform shaker) for at least 60 minutes.

After the agitation process, let suspended solids settle by gravity or centrifuge if necessary. Transfer all or a portion of the extract to a vial for refrigerated storage. Store remaining extract at ≤ 6 ˚C for at least 40 days in case re-analysis is required.

Analysis Procedure

A summary of the analytical procedure follows. Detailed instrumental procedures are described in the following US Environmental Protection Agency methods:

Purge and Trap conditions:	SW846 Method 5030C
Static Headspace conditions:	SW846 Method 5021A
GC/MS conditions:	SW846 Method 8260C
GC/PID conditions:	SW846 Method 8120B

Headspace: An appropriate amount of water is added to a clean headspace vial, followed by an aliquot of sample methanol extract. Addition of salts to equalize aliphatic/aromatic headspace partitioning equilibria is recommended. Internal standards are added, either manually or automatically by the headspace system. Sample vials are sealed with a cap and Teflon-lined septum, and are introduced to the headspace heating system, where they establish a partition equilibrium. Mechanical vibration may be used to accelerate the process. The vial may be pressurized with an inert gas. A representative fraction of headspace is transferred to the analytical trap or directly to the GC column via a heated transfer line or syringe.

Purge and trap: An appropriate amount of water is added to a clean purge and trap vial, followed by an aliquot of methanol extract. Internal standards are added, either manually or automatically by the purge and trap system. Sample vials are sealed with a cap and Teflon-lined septum and are loaded onto the autosampler. VOCs are purged from the samples with an inert gas and are trapped on a solid sorbent trap. The trap is rapidly heated and the contents are transferred to the GC column via a heated transfer line.

Direct Injection: An appropriate volume of internal standards is added to a known volume of sample methanol extract. Samples are dispensed to autosampler vials and are injected into a GC/MS inlet (typically a split/splitless or on-column inlet), either manually or by autosampler.

Note: For samples containing concentrations of VOCs where one or more analytes exceed the linear range of the analytical system, use a smaller aliquot of methanol extract. It is recommended that additional methanol be added so that the total amount of methanol in the vial remains consistent.

Initial GC/MS calibrations must be five points or more (no more than one point may be excluded). At least two Internal Standards must be used. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Raw results (i.e., µg/L or µg purged) are converted into final results (mg/kg) by accounting for the sample dry weight, total extract volume (amount of methanol + sample moisture), and analysis aliquot and/or dilution factor. VOCs in solids are normally reported on a dry-weight basis.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80–120%, except 75–125% for the asterisked VOCs (refer to MDL column in analyte table), and any other VOC analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline,

standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Internal Standard Area Checks	All samples and QC	Area counts must be 50–200% of the initial calibration CVS
Surrogates	All samples and QC	60–140% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80–120% recovery
Field Blank or Trip Blank (Field Methanol Technique only)	Strongly Recommended 1 per sampling event	Less than reported DL
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	1 per batch (max 20 samples)	60–140% recovery (50–150% for asterisked and non-listed analytes — see analyte table)
Matrix Spike (MS) or Reference Material (RM)	1 per batch (max 20 samples)	60–140% recovery (50–150% for asterisked and non-listed analytes — see analyte table)
Lab Duplicates	1 per batch (max 20 samples)	≤ 50% RPD [or within 2x reported DL for low level results]
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80–120% recovery for mid-level standards (70–130% for asterisked and non-listed analytes — see analyte table)
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to RM DQOs if targets are < 10x MDL (derive lab-specific DQOs in this case) or to MS results where sample background exceeds spike amount.		

Internal Standards: Recommended internal standards include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs.

Surrogates: Appropriate Surrogate Compounds must be added to each sample prior to extraction. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs (must differ from internal standards).

Calibration Verification Standard (CVS): Analysis of a second source VOC standard to ensure validity (accuracy) of the calibration. All calibrated and reported parameters must be included.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the

instrument run to monitor calibration drift. Run a CCV at least every 12 hours (maximum 20 samples), and at the end of each batch.

Method Blank: A clean solid matrix (or methanol and reagents only) that is processed through the entire extraction and analysis process in the same manner as a sample. Analyze an aliquot of methanol extract equivalent to the default sample amount.

Lab Control Sample: A clean solid matrix (e.g., oven baked sand) that is spiked and processed through the entire extraction and analysis process in the same manner as a sample. Analyze an aliquot of methanol extract equivalent to the default sample amount. All calibrated and reported parameters must be included. This spike provides a means to assess for the accuracy of the extraction procedure and performance of the analytical system in the presence of methanol.

Matrix Spike Sample: Analysis of a second aliquot of an equal amount of methanol extract that is taken from the same vial and spiked prior to analysis. It is recommended to spike with the same standard used for the LCS at a concentration that is slightly less than or equal to the mid-point of the calibration. Used for assessing sample matrix effects.

Lab Duplicates: Analysis of a second aliquot of an equal amount of methanol extract that is taken from the same vial to assess laboratory variability.

Field Duplicates: Recommended to assess sampling variability (precision). Frequency as per sampling plan.

Travel Blank or Field Blank (Field Methanol Technique only): Strongly Recommended. Travel Blanks and/or Field Blanks are necessary to verify purity of supplied methanol vials including storage, transit, and field effects. Travel Blanks can identify problems with tare weights of vials (including leakage issues), methanol contamination issues, methanol volume errors, and contamination that could be introduced during travel or storage. Field Blanks (which must be opened and handled similarly to a sample in the field) can potentially also identify contamination due to the field sampling environment (e.g., due to high concentrations of hydrocarbon or gasoline vapours). Field Blanks are recommended for sampling environments where hydrocarbon or solvent vapours may be present at time of sampling.

Prescribed Elements

The following components of this method are mandatory:

Samples must be either preserved in the field with methanol or collected using hermetically sealed sampling devices. Results must otherwise be qualified.

Methanol extraction is required with minimum 1.5 mL to 1 g ratio of methanol volume to wet weight of solids extracted.

Field methanol preserved samples must be physically agitated using a mechanical shaker for at least 15 minutes. Hermetic samples that are methanol extracted in the laboratory must be physically agitated using a mechanical shaker for at least 30 minutes.

When using GC/MS, at least two surrogates are required to be added to all samples prior to analysis. Stated calibration and internal standard requirements must be met. Initial GC/MS calibrations must be five points or more (no more than one point may be excluded).

Wherever possible, the same sample extract must be used for the analysis of both VH_{S6-10} and targeted VOC compounds, so that sub-sampling variability does not affect the calculated VPH result.

All target compound analysis must be conducted by GC/MS, except that BTEX, Styrene, and MTBE analysis may alternatively be conducted by GC-PID (Photoionization Detection). GC-PID is less selective than GC/MS, and is much more subject to false positives and false negatives than GC/MS.

Soil moisture content must be considered within data calculations for the total methanol extract volume for each sample.

Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

EPA 8260D, Test Methods for Evaluating Solid Wastes — Physical / Chemical Methods, SW-846, 3rd Edition, Method 8260D, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Revision 4, February 2017. United States Environmental Protection Agency, Washington, D.C.

EPA 5030C, Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003. United States Environmental Protection Agency, Washington, D.C.

EPA 5035A, Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002. United States Environmental Protection Agency, Washington, D.C.

EPA 5021A, Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 2, July 2014. United States Environmental Protection Agency, Washington, D.C.

ASTM D6418-09, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis.

EPA 8021B, Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 8021B, Aromatic and Halogenated Volatiles by Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors, Revision 3, July 2014. United States Environmental Protection Agency, Washington, D.C.

Revision History	Sept 15, 2017	Significantly expanded list of analytes to cover volatile substances in 2017 CSR. Added reference to EPA 8021B for PID parameters and updated EPA 8260 and EPA 5021 reference methods. Updated QC and internal standard acceptance criteria to support broader list of VOC analytes. Matrix spike (or RM) added to QC requirements. Minimum methanol shake times were added to prescriptive elements (15 mins for field methanol preserved samples, 30 mins for hermetic samples).
	Apr 9, 2014.	Draft version for review and comment by BCELTAC and stakeholders. Revised to reflect new requirements for field methanol extraction or hermetic samplers. Minimum ratio of methanol to wet soil changed from 2:1 to 1.5:1. CVS frequency changed to once per initial calibration.
	Oct 1, 2013	New method added to BC Lab Manual. Effective date for this method is October 1, 2013.

Volatile Organic Compounds (VOCs) in Water — PBM

Parameter

Volatile Organic Compounds (VOCs) in water

Analytical Method

Purge and Trap, Headspace (Static or Dynamic) - GC/MS or GC/PID (PBM)

Introduction

This method is applicable to the quantitative determination of volatile organic compounds in water samples. Analysis for VH_{W6-10} is often conducted concurrently.

Method Summary

To minimize loss of VOCs during sampling and transport to the laboratory, samples must be collected with no headspace in glass vials containing preservative.

Purge and trap: The VOCs are purged from the sample with an inert gas and are trapped on a solid sorbent trap. The trap is heated and the VOCs are directed into a gas chromatograph equipped with a mass spectrometric detector (GC/MS). GC/PID is acceptable for a subset of analytes, e.g., BTEX and styrene.

Headspace: A portion of the sample is transferred to a headspace vial. The vial is then sealed and heated to a pre-determined temperature for a given period. After equilibration, a portion of the headspace is introduced into a GC/MS. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column. GC/PID is acceptable for a subset of analytes, e.g., BTEX and styrene.

The analytical portion of this method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

The analytes listed below represent many of the volatile substances regulated in the 2017 Contaminated Site Regulations (CSR). The MDLs listed below are achievable by GC/MS in a typical laboratory environment, but may vary by laboratory, and with the sample introduction technique used. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Analyte	Approx. MDL (µg/L)	CAS Number	EMS Analyte Code
acetone	10*	67-64-1	A005
acrolein	5*	107-02-8	-
acrylonitrile	5*	107-13-1	-
allyl alcohol	5*	107-18-6	-
allyl chloride	5*	107-05-1	C056
benzene	0.5	71-43-2	B020
benzyl chloride	5*	100-44-7	-
bromobenzene	0.5	108-86-1	B005
bromodichloromethane	0.5	75-27-4	B012
bromoform	0.5	75-25-2	B013
bromomethane	1*	74-83-9	-
butadiene, 1,3-	1*	106-99-0	-
butanol, n-	5*	71-36-3	-
butylbenzene, n-	0.5	104-51-8	B034
butylbenzene, sec-	0.5	135-98-8	B035
butylbenzene, tert-	0.5	98-06-6	B036
carbon disulfide	2*	75-15-0	-

Analyte	Approx. MDL (µg/L)	CAS Number	EMS Analyte Code
carbon tetrachloride	0.5	56-23-5	C034
chlorobenzene	0.5	108-90-7	C010
chlorobutane, 1-	0.5	109-69-3	-
chloroethanol, 2-	5*	107-07-3	-
chloroethylvinyl ether, 2-	5*	110-75-8	-
chloroform	0.5	67-66-3	C032
chloroprene	2	126-99-8	-
chlorotoluene, 2-	0.5	95-49-8	2CLT
chlorotoluene, 4-	0.5	106-43-4	C047
crotonaldehyde, trans-	5*	4170-30-3	-
dibromo-3-chloropropane, 1,2-	1*	96-12-8	B038
dibromochloromethane	0.5	124-48-1	C033
dibromoethane, 1,2-	0.5	106-93-4	B029
dichlorobenzene, 1,2-	0.5	95-50-1	-
dichlorobenzene, 1,3-	0.5	541-73-1	-
dichlorobenzene, 1,4-	0.5	106-46-7	-
dichlorodifluoromethane	1*	75-71-8	-
dichloroethane, 1,1-	0.5	75-34-3	C021
dichloroethane, 1,2-	0.5	107-06-2	C022
dichloroethylene, 1,1-	0.5	75-35-4	C024
dichloroethylene, cis-1,2-	0.5	156-59-2	C063
dichloroethylene, trans-1,2-	0.5	156-60-5	C023
dichloromethane	2	75-09-2	M041
dichloropropane, 1,2-	0.5	78-87-5	C025
dichloropropane, 1,3-	0.5	142-28-9	-
dichloropropene, cis-1,3-	0.5	10061-01-5	C027
dichloropropene, trans-1,3-	0.5	10061-02-6	C028
diethyl ether	5*	60-29-7	-
dioxane, 1,4-	5*	123-91-1	-
ethyl acetate	5*	141-78-6	-
ethylbenzene	0.5	100-41-4	B021
hexachlorobutadiene	2*	87-68-3	HCBD
hexachloroethane	2*	67-72-1	-
hexanone, 2-	5*	597-78-6	H024
isobutanol	5*	78-83-1	-
isopropanol	5*	67-63-0	-
isopropylbenzene	0.5	98-82-8	I008
methacrylonitrile	5*	126-98-7	M028
methyl acetate	5*	79-20-9	-
methyl ethyl ketone [MEK]	5*	78-93-3	B033
methyl methacrylate	5*	80-62-6	M054
methyl-tertiary butyl ether [MTBE]	1	1634-04-4	MTBE
propylbenzene, 1-	0.5	103-65-1	P030
styrene	1*	100-42-5	S010
tetrachloroethane, 1,1,1,2-	0.5	630-20-6	-
tetrachloroethane, 1,1,2,2-	0.5	79-34-5	C080
tetrachloroethylene	0.5	127-18-4	T030
toluene	0.5	108-88-3	T001
trichloro-1,2,2-trifluoroethane, 1,1,2-	1	76-13-1	-
trichloroethane, 1,1,1-	0.5	71-55-6	T016
trichloroethane, 1,1,2-	0.5	79-00-5	T017
trichloroethylene	0.5	79-01-6	T029

Analyte	Approx. MDL (µg/L)	CAS Number	EMS Analyte Code
trichlorofluoromethane	1*	75-69-4	T070
trichloropropane, 1,1,2-	0.5	598-77-6	-
trichloropropane, 1,2,3-	0.5	96-18-4	T067
trichloropropene, 1,2,3-	0.5	96-19-5	-
trimethylbenzene, 1,3,5-	1	108-67-8	T069
vinyl acetate	1*	108-05-4	-
vinyl chloride	1*	75-01-4	C004
xylene, *meta*- + *para*-	1	108-38-3 106-42-3	X003
xylene, *ortho*-	0.5	95-47-6	X002

*Analytes with an asterisk in the MDL exhibit known difficulties with reproducibility, response, recovery, stability, and/or chromatography that may reduce the overall quality or confidence in the result. Refer to EPA reference methods 5030/5021/8260 for additional information.

Where appropriate, the method may be used for other compounds not listed here, subject to validation and achievement of data quality objectives (DQOs).

EMS Method Code(s)

Refer to EMS Parameter Dictionary on the Ministry of Environment and Climate Change Strategy website for all current EMS codes.

Matrix

Fresh water, wastewater, marine water, sludge.

Interferences and Precautions

Preservation is necessary to prevent microbial degradation of VOC analytes, notably some aromatic compounds (BTEX), and/or to prevent reactions with residual chlorine. Residual chlorine reacts with organic matter to produce trihalomethanes, and can react with and degrade some VOC analytes, notably styrene.

Use extreme caution to prevent losses due to evaporation. Keep samples cold until they are dispensed. Avoid the application of vacuum to VOC water samples prior to analysis (syringes with restrictive inlets or needles are not recommended for sub-sampling). Anytime a second analysis is required for dilution purposes, a second sample vial which has not been opened should be used.

Calibration standards are prepared using methanolic standard solutions. Ensure that samples and standards are matrix-matched as closely as possible with respect to methanol content (within ~20 µL methanol).

Samples can potentially be contaminated during storage by diffusion of volatile organics through the septum (particularly fluorocarbons and dichloromethane).

A transportation blank can be prepared from reagent water and carried through the sampling and handling protocol as a check on contamination from external sources.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system, and should take appropriate steps to prevent the occurrence of false positives.

2-chloroethylvinylether often decomposes on purge and trap systems, sometimes completely. It also rapidly decomposes under acidic conditions; presence of the breakdown product 2-chloroethanol may be sufficient to demonstrate the absence of this compound in samples.

Cis- and trans-1,3-dichloropropene and bromomethane decompose over time in the solutions containing sodium thiosulfate. Analysis of these analytes is not recommended from samples preserved with sodium thiosulfate.

Alcohols, ketones, ethers and other water-soluble compounds typically have low responses. This can be partially rectified by elevating the sample temperature, but this may impact the performance of other compounds such as MTBE.

Dehydrohalogenation may result in degradation of aqueous solutions of some halogenated compounds such as 1,1,2,2-tetrachloroethane if the sample pH is greater than 4. The use of hydrogen as a carrier gas may also cause dehydrohalogenation.

Aldehydes such as acrolein have poor stability under the analytical conditions used in this method.

Heavier target compounds such as naphthalene may exhibit low responses and greater variability.

Gaseous compounds such as chloromethane are prone to loss during the handling process. Also, compounds that co-elute with water and methanol will have lower responses.

Vinyl chloride and styrene are subject to loss due to chemical reactivity, regardless of preservation.

Sample Handling and Preservation

Use 40 mL clear or amber glass VOC vials with Teflon-lined septa.

If no residual chlorine is present, preserve to a pH of less than 2 with sodium bisulfate ($NaHSO_4$) in aqueous solution or as a solid. Approximately 200 mg of $NaHSO_4$ per 40 mL sample is recommended.

If the sample is recently chlorinated, and is likely to contain residual chlorine (e.g., freshly sampled chlorinated water supplies); add sodium thiosulfate to reduce the chlorine to unreactive chloride (3 mg $Na_2S_2O_3$ per 40 mL sample is recommended, in aqueous solution or as a solid, and is sufficient for up to 5 ppm Cl2).

Do not pre-rinse the vial with sample (to avoid loss of preservative). Collect the sample with as little aeration as possible, filling to just overflowing. Cap the vial and try to ensure that no bubbles are present. A small air bubble of up to ~ 2 mL volume (5% of the sample volume) may appear after sampling and is acceptable.

It is recommended that all VOC samples be collected in duplicate to allow for re-analyses or dilutions.

HCl or H_2SO_4 are permitted as alternatives to the use of $NaHSO_4$ to preserve non-chlorinated samples, but $NaHSO_4$ is recommended. Degradation of styrene by HCl preservative has been reported, and other unsaturated VOCs may react similarly.

Acid preservative may not be used for the analysis of 2-chloroethylvinylether. This analyte rapidly decomposes in acidic solution. For this analyte, collect unpreserved samples, or preserve with sodium thiosulfate.

Sodium thiosulfate preservation is not recommended for cis- and trans-1,3-dichloropropene and bromomethane as these analytes decompose over time. If analysis is required in sodium thiosulfate preserved samples, analyze as soon as possible and verify potential decomposition losses with field spikes or lab studies.

One investigator has reported the formation of bromomethane artifacts in some groundwater samples where preservation with copper sulfate had been used.

For a full discussion of the merits of various VOC preservation techniques, refer to Appendix A of Draft EPA Method 5035A, entitled “The Collection and

Preservation of Aqueous and Solid Samples for Volatile Organic Compound (VOC) Analysis".

Stability

Holding Time: Analyze samples as soon as possible, but within 14 days of sampling. The 14-day holding time applies to correctly preserved, unopened samples with essentially zero headspace. After any significant volume has been removed, samples are quickly compromised. See interferences section regarding chemical incompatibilities of some analytes with preservatives.

Storage: Store at ≤6°C until dispensed to sealed analysis vessels.

Procedure

A summary of the analytical procedure follows. Detailed instrumental procedures are described in the following US Environmental Protection Agency methods:

Purge and Trap conditions:	SW846 Method 5030C
Static Headspace conditions:	SW846 Method 5021A
GC/MS conditions:	SW846 Method 8260C
GC/PID conditions:	SW846 Method 8021B

Headspace: An appropriate amount of sample is added to a clean headspace vial. Addition of salts to equalize aliphatic/aromatic headspace partitioning equilibria is recommended. Internal standards are added, either manually or automatically by the headspace system. Sample vials are sealed with a cap and Teflon-lined septum, and are introduced to the headspace heating system, where they establish a partition equilibrium. Mechanical vibration may be used to accelerate the process. The vial may be pressurized with an inert gas. A representative fraction of headspace is transferred to the analytical trap or directly to the GC column via a heated transfer line or syringe.

Purge and trap: An appropriate amount of sample is added to a clean purge and trap vial. Internal standards are added, either manually or automatically by the purge and trap system. Sample vials are sealed with a cap and Teflon-lined septum and are loaded onto the autosampler. VOCs are purged from the samples with an inert gas and are trapped on a solid sorbent trap. The trap is rapidly heated and the contents are transferred to the GC column via a heated transfer line.

GC/MS: Initial calibrations must be five points or more (no more than one point may be excluded). At least one Internal Standard is required for BTEX/Styrene/MTBE analysis. At least two Internal Standards must be used for the analysis of other multicomponent VOC lists. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual QC samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g., 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80–120%, except 75–125% for the asterisked VOCs (refer to MDL column in analyte table), and any other VOC analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Internal Standard Area Checks	All samples and QC	Area counts must be 50–200% of the initial calibration CVS
Surrogate Compounds	All samples and QC	70–130% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80–120% recovery
Field Blank or Trip Blank	Strongly Recommended (1 per sampling event)	Less than reported DL
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	1 per batch (max 20 samples)	70–130% recovery (60–140% for asterisked and non-listed analytes — see analyte table)
Matrix Spike (MS) or Reference Material (RM)	1 per batch (max 20 samples)	70–130% recovery (60–140% for asterisked and non-listed analytes — see analyte table)
Lab Duplicates (DUP)	1 per batch (max 20 samples)	≤ 30% RPD (≤ 50% RPD for gasses)
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch	80–120% recovery for mid-level standards (70–130% for asterisked and non-listed analytes — see analyte table)
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to RM DQOs if targets are < 10x MDL (derive lab-specific DQOs in this case) or to MS results where sample background exceeds spike amount.		

Internal Standards: Recommended internal standards include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs.

Surrogates: Appropriate Surrogate Compounds must be added to each sample prior to extraction. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs (must differ from internal standards).

Calibration Verification Standard (CVS): Analysis of a second source VOC standard to ensure validity (accuracy) of the calibration. All calibrated and reported parameters must be included.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the instrument run to monitor calibration drift.

Prescribed Elements

The following components of this method are mandatory:

Preservation as per the Sample Handling and Preservation section is mandatory.

Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

When using GC/MS, at least two surrogates are required to be added to all samples prior to analysis. Stated calibration and internal standard requirements must be met.

Wherever possible, the same sample must be used for the analysis of both $VH_{W_{6-10}}$ and targeted VOC compounds, so that sub-sampling variability does not affect the calculated VPH result.

All target compound analysis must be conducted by GC/MS, except that BTEX, Styrene, and MTBE analysis may alternatively be conducted by GC-PID (Photoionization Detection). GC-PID is less selective than GC/MS, and is much more subject to false positives and false negatives than GC/MS.

Samples that exceed the calibration range must be diluted and re-analyzed or reported as estimated or minimum values.

All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

Test Methods for Evaluating Solid Wastes — Physical / Chemical Methods, SW-846, 3rd Edition, Method 8260D, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Revision 4, February 2017. United States Environmental Protection Agency, Washington, D.C.

Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003. United States Environmental Protection Agency, Washington, D.C.

Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 2, July 2014. United States Environmental Protection Agency, Washington, D.C.

Test Methods for Evaluating Solid Wastes — Physical/Chemical Methods, SW-846, Method 8021B, Aromatic and Halogenated Volatiles by Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors, Revision 3, July 2014. United States Environmental Protection Agency, Washington, D.C.

American Public Health Association, 1998. Standard Methods for the Examination of Water and Wastewater (20th Edition), Introduction Section 6010 B, Sample Collection and Preservation, Volatile Organic Compounds.

Ontario MOE. Practices for the Collection and Handling of Drinking Water Samples, version 1.0. June 2003. Reference for preservation of chlorinated water samples with sodium thiosulfate alone.

Revision History

July 10, 2017	Updated to current method format. Updated reference methods. Where applicable, aligned with VOC in solids method, including use of headspace GC/MS and PID for selected analytes. Expanded list of analytes to cover additional volatile substances in 2017 CSR. Included additional information in the interferences and precautions section. Deleted copper sulfate preservation option. Updated QC and internal standard acceptance criteria.
Jun 10, 2007	Preservation options modified to use sodium thiosulfate for chlorinated samples, and sodium bisulfate for non-chlorinated samples.
Apr 5, 2006	Additional analytes added to method as required for Hazardous Waste Leachate Quality Standards.
May 7, 2004	Revised. Additional analytes added. Updated to PBM format. Preservation options modified.
Dec 31, 2000	SEAM codes replaced by EMS codes.
Feb 14, 1994	Publication in 1994 Laboratory Manual.

Volatile Petroleum Hydrocarbons (VPH) in Solids, Waters, or Air (Vapour) — Calculation

Parameters

Volatile Petroleum Hydrocarbons in water — VPH_W

Volatile Petroleum Hydrocarbons in solids — VPH_S

Volatile Petroleum Hydrocarbons in air (vapour) — VPH_V

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Code
VPH_W	100 µg/L	VPH-F099
VPH_S	10 µg/g	VPH-F100
VPH_V	100 µg/m^3 *	code pending.

*MDL for VPH_V varies with analytical technique and with air volume sampled.

Note that the above EMS codes are for results corrected for BTEX, styrene, n-hexane, and n-decane (as defined below for each parameter).

Analytical Method

Refer to the following VH precursor methods:

Volatile Hydrocarbons in Water by GC/FID

Volatile Hydrocarbons in Solids by GC/FID

Volatile Hydrocarbons in Air-Vapour by GC-FID / GC-MS

Units

Waters: µg/L

Soils: µg/g (dry weight)

Air: µg/m^3

Method Summary

Volatile Petroleum Hydrocarbons (VPH) is a calculated parameter. VPH is determined by subtracting analytical results for specified discrete parameters (which are regulated separately under the BC CSR) from Volatile Hydrocarbons (VH) results.

VH and all subtracted discrete parameter results must be analyzed using applicable Director-approved methods from the BC Environmental Laboratory Manual.

The Procedure section lists the different discrete compounds which are excluded from waters, solids, and air (vapour) matrices.

Procedure

Calculate VPH as follows:

$VPH_S = VH_{S_{6-10}} - \Sigma$ [BTEX, styrene]

$VPH_W = VH_{W_{6-10}} - \Sigma$ [BTEX, styrene]

$VPH_V = VH_{V_{6-13}} - \Sigma$ [BTEX, styrene, n-hexane, n-decane]

where BTEX = benzene, toluene, ethylbenzene, *o*-Xylene, *m*-Xylene, *p*-Xylene

Where practical, laboratories should use the same sample extract or aliquot to determine both VH and BTEX. This minimizes the potential error in the final VPH result that could otherwise occur due to the normal variability of sub-sampling.

It is strongly recommended that all BTEX, styrene, n-hexane, and n-decane results be determined by GC/MS. Less selective detectors like Photo-Ionization Detectors (PIDs) or Flame Ionization Detectors (FIDs) are far more susceptible to interferences, but may be used where appropriate, for example:

a) field testing (see below).
b) for samples where no significant interferences are apparent.

For the calculation of VPH, treat as zero any discrete substance results that are reported as less than detection limit (no subtraction).

When the sum of parameters to be subtracted from VH is small compared to the magnitude of VH (e.g., <⅓ VH), use the reported detection limit for VH as the detection limit for VPH.

When the sum of parameters to be subtracted from VH is large (e.g., >⅓ VH), the measurement uncertainties of the component parameters can influence the resulting detection limit. Consult the QA/QC section of the BC Lab Manual for guidance on when and how to increase reporting limits (Guidelines for Analytical Parameters Determined by Calculation — Parameters Determined by Subtraction).

Co-Reporting Requirements

Designated regulated substances, as defined below, are allowed (and required) to be subtracted from VH concentrations to arrive at VPH concentrations, because these substances are regulated independently. Consequently, it is required that the subtracted substances must be co-reported where VPH results are reported. Laboratories are not permitted to remove test results for co-reported parameters after initial reporting.

BC MOE Co-Reporting Requirements for VPH parameters are as follows:

VPH_S	benzene ethylbenzene styrene toluene xylenes (m-, p-, & o-)	VPH_V	benzene ethylbenzene n-decane n-hexane styrene toluene xylenes (m-, p-, & o-)
VPH_W	benzene ethylbenzene styrene toluene xylenes (m-, p-, & o-)		

Revision History

Nov 6, 2015:	Revised to include subtraction of styrene for VPHv and VPHw. Added and defined new co-reporting requirements. Aligned preferred units with CSR standards. Effective Date: Jan 4, 2016.
June 19, 2009:	VPHv added. Text simplified. Additional detection limit guidance added (reference to QA/QC section, calculated parameters).
Dec 31, 2000:	Incorporated into main BC Laboratory Manual, EMS codes added, former methods superceded.
July 1999:	Finalization of method based on results of a vetting round robin.
1998-1999:	Revision of historical hydrocarbon methods by ASL (now ALS) under contract to BC MELP and with guidance from the BCLQAAC Technical Committee (now BCELTAC).
March 1997:	Initial publication of version 1.0 of VPH in water method.