Section D

ORGANIC CONSTITUENTS AND COMPOUNDS

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SECTION D Organic Constituents and Compounds

Acid Extractable Herbicides in Water

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 x 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.
    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 the 1 mg/L intermediate herbicide standard to give a concentration of 0.0004 mg/L.
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 dichloromethane each time.
d) Filter the dichloromethane extracts through anhydrous sodium sulfate, supported in a glass funnel by glass wool, into a 250 mL round bottom flask.
d) 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 definite 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 dichloromethane 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 One method blank 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:	Publication in 1994 Laboratory Manual.
December 31, 2000:	EAM codes replaced by EMS codes. Out of print reference deleted.

Adsorbable Organic Halides in Water

Parameter Adsorbable Organic Halides.

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_2SO_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 $HN0_3$ 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

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

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

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

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

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

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

g) Sodium sulfite (Na_2SO_3) 0.1M: Dissolve 12.5 g Na_2SO_3, A.R. grade, in 1.0 L deionized water.

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

i) 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.

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

k) Starch indicator solution: 1% aqueous.

l) 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_2SO_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.

Base-Neutral and Acid Semi-Volatile Extractables in Water

Parameter Base-neutral and acid extractables

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 dichloromethane 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	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 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.

Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) in Water

Parameter

Benzene
Ethylbenzene
Toluene
Xylenes

Analytical Method

Purge and Trap/GCMS

EMS Code

Benzene	**B020 X384**
Toluene	**T001 X384**
Ethylbenzene	**B021 X384**
Xylene	**X001 X384**
O-Xylene	**X002 X384**
m-Xylene plus p-Xylene	**X003 X384**

Introduction

This method is applicable to the qualitative and quantitative determination of BTEX, a subset of volatile organic compounds (VOCs), in water samples.

Summary

The sample is analyzed by purge and trap gas chromatography with detection by mass spectrometry. The procedure involves purging the volatile compounds from the sample with an inert gas, and trapping them on a solid sorbent. When purging of the sample is complete, the trap is heated and the compounds are transferred to the gas chromatographic column. Analysis is then accomplished by separation of the components by gas chromatography with detection by mass spectrometry.

MDL

Benzene	0.5 µg/L
Toluene	0.5 µg/L
Ethylbenzene	0.5 µg/L
Xylenes	0.5 µg/L

Matrix

Fresh Water
Wastewater
Marine Water
Sludge

Interferences and Precautions

Proper sample containers should be used at all times to reduce loss of components by evaporation. Samples can be contaminated by diffusion of some volatile organic compounds through the septum. Samples should be stored to reduce the possibility of contamination. A transportation blank, prepared from reagent water and carried through the sampling and handling protocol, serves as a check on contamination from external sources. Contamination of the analytical system can occur if low level samples are analyzed after high level samples. Frequent bakeout of the analytical system and analysis of reagent water should be performed in these circumstances to ensure a contamination-free system.

Sample Handling and Preservation

Container - volatile vial with Teflon-lined septum
Preservation - HCl to pH < 2 or 0.1% Cu SO_4

Do not rinse the vial with sample. Collect the sample with as little aeration as possible, filling the vial to just overflowing. Cap the vial and ensure no

bubbles are present. Samples should be collected in duplicate to allow for a second analysis if dilution is required.

Stability

Holding Time - analyze within 14 days of sampling
Storage - store at 4°C until analyzed

Principle or Procedure

See Method 624, Purgeables, EPA 40 CFR Ch. 1 (7-1-90 Edition), SW 846, EPA 5030/8240 or 8260 or 8021, EPA 524.

Precision

None listed.

Accuracy

None listed.

Quality Control

A transportation blank may be carried along with the samples to check for contamination during handling.

If a second analysis is required for dilution purposes, a second sample container which has not been opened should be used.
One method Blank and Spike should be performed per analytical batch or 1 in 14.

References

a) Code of Federal Regulations, Title 40, Chapter 1 (Environmental Protection Agency), Part 136, App. A, Method 624 - Purgeables, July 1, 1990.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Biochemical Oxygen Demand (BOD), Performance Based Format (PBM)

Parameter: **Biochemical Oxygen Demand - PBM**

Method Codes And EMS Codes

Parameter	Seed Added	Nitrogen Inhibitor	EMS Code
Total BOD	No	No	0115 X482
Total BOD, Seeded	Yes	No	0115 X483
Carbonaceous BOD	No	Yes	0115 X410
Carbonaceous BOD, Seeded	Yes	Yes	0115 X013

Analytical Method 5-day BOD, 20°C

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 waste waters. 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 sulphides and ferrous iron.

Method Summary The biochemical oxygen demand (BOD) is an empirical bioassay-type procedure that measures the dissolved oxygen (DO) consumed by microbial life while it assimilates and oxidises 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 calibrated in water saturated air or calibrated against a sample of known dissolved oxygen (DO) determined by the Winkler method is used to acquire all dissolved oxygen measurements. Alternatively DO may be measured by a modified winkler titration). 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. The method used to determine BOD depends upon the nature of the sample.

Note: The mandatory elements are specified in bold text.

Definitions

Biochemical Oxygen Demand (BOD) is primarily a measure of the amount of oxygen used by micro-organisms during the aerobic decomposition of organic material. However, it also includes chemical oxidation of inorganics such as sulphides and ferrous iron. It is an index of the biodegradable organic substances present.

Unseeded Biochemical Oxygen Demand: A sample of water is incubated in the dark for 5 days at 20°C ± 1°C without seeding applied. Measurement includes both carbonaceous and nitrogenous oxygen demand.

Seeded BOD: A sample of water is incubated in the dark for 5 days at 20°C ± 1°C with seeding applied. Measurement includes both carbonaceous and nitrogenous oxygen demand.

Carbonaceous Biochemical Oxygen Demand is a measure of the amount of oxygen used by micro-organism during the aerobic decomposition of organic material when a chemical nitrogen inhibitor is used to eliminate the nitrogenous demand. Sample is not seeded in this test.

Seeded Carbonaceous Biochemical Oxygen Demand with nitrogen inhibitor and seed applications.

Nitrogenous Oxygen Demand: is a measure of the amount of oxygen used to oxidize reduced forms of nitrogen unless their oxidation is prevented by an inhibitor.

MDL

A nominal detection limit of 5 mg/L reflects the requirement for a minimum Dissolved Oxygen (DO) depletion of 2 mg/L to ensure reliable results. A suitable dilution factor establishes the working range (e.g., 5 - 120 mg/L BOD is a typical working range for sewage effluents).

Matrix

Municipal and Industrial Wastewaters

Sample handling and Preservation

a) **Sampling must be done by qualified personnel, experienced in sampling procedures and working under standard documented operating conditions**. It is important that the sample be properly taken in a quality-controlled manner for submission to a laboratory and that the sample be representative of the area being sampled.

b) **Samples must be collected and stored such that degradation or alteration of the sample is minimized**. Collect the sample in a clean, polyethylene or glass bottle, taking care to fill it completely to exclude any air and tightly cap immediately. **The samples must be unpreserved and cooled at 4°C**. The sample should be examined as soon as possible, as any delay could cause a BOD changes due to ongoing chemical reactions in the water system. The recommended holding time not greater than 24 hours, **and it is mandatory that the holding time not exceed the 72 hours from the time of sampling**. **Results reported beyond holding times must be flagged as not reliable.**

c) It is generally acceptable to use high-density polyethylene (HDPE) containers as they are less expensive than glass and are less likely to break, especially if samples are inadvertently frozen. Glass bottles are also acceptable. Sample bottles should preferably be new and unused and should be purchased as certified clean. **Both new and washed reused bottles must be proofed by a documented cleaning procedure with a bottle lot number control system**. If bottles are reused, **cleanliness must be demonstrated by the use of blanks. Frequency of field blanks must be increased to at least 5% of all samples if cleaned reused bottles are utilized.**

d) **Samples must be clearly labelled with the date and time of sampling, location or source of the sample, whether the sample is a grab or composite, analysis required and the identity of the individual who collected the sample. Labels must be filled out in indelible ink and fixed to the sample container such that they will not fall off when wet or during transport.**

e) When a sample could be considered as evidence in an investigation, chain of custody procedures are required to demonstrate that samples have not been tampered with at any point in handling or shipping and that the individuals in charge of the samples can be identified at every stage in the sampling and analysis.

Interferences

a) Oil and grease interfere with DO measurements if they are present in sufficient quantity to coat the probe's Teflon membrane. Pre-diluting the sample and replacing the membrane should improve performance.

b) Chemical reducing agents such as ferrous iron (II), sulphite, and sulphide can exert an immediate DO demand that is not biological in nature; wait 15 minutes before acquiring the initial DO reading.

c) 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 0.2 mg O_2/L [a].

d) **Pre-dilute samples containing appreciable quantity of suspended solids to ensure that the final concentration of solids in the BOD bottle is less than 10 mg/L if necessary**.

e) **The absence of toxic materials must be established before BOD results can be considered valid. This is accomplished by comparing BOD values for several dilutions – if toxins are present then the BOD value tends to increase with dilution until the toxic effect is diluted out.**

f) **Residual chlorine is an example of a toxic substance which must be removed prior to the test (Procedure d)3 & d)3)i).**

g) Samples taken from waste streams at chemical pulping plants may contain high concentration of sulphite ion. This is a reducing agent and will scavenge for oxygen. The sample will have an immediate oxygen demand, **therefore, samples must be tested for the presence of reducing agent (procedure d)3 & d)3)ii)).**

h) **Samples will have to be also tested for the presence of reducing agents**, such as sulphide ions.

i) Many synthetic organic components in industrial waste waters are not bio-degradable without the seeding procedure because of either a toxic effect or a deficiency or absence of appropriate micro-organisms.

j) **The contribution of the seed culture to the measured oxygen uptake must be removed to obtain the sample BOD**; this seed correction can introduce error when the oxygen uptake reaction for micro-organisms in the seed controls differs from that in the seeded sample (this may occur when the chemical characteristics of the

sample do not match those of the seed stock). Seed correction should be carefully applied only after considering its potential effect on data interpretation [c].

k) Certain organic substances, for example, cellulose, are difficult for bacteria to break down. Hence, cellulose may exert a low BOD for a long period, i.e., 5 days.

l) Oxygen super-saturation will cause oxygen loss during incubation. Shake a ½ full bottle of the sample to achieve an oxygen saturation (around 9.17 mg/L at 20 °C).

m) The temperature of the dilution water should be 20 °C ± 1 °C. Aeration rate should be slow at room temperature. Water should not supersaturate if left standing 30 minutes after aeration to reach equilibrium.

n) **Samples which have an extreme pH must be neutralised**. The pH of the sample should be adjusted to between 6.5 and 7.5 with 1 N H_2SO_4 or 1 N NaOH.

o) An incubator should be thermostatically controlled at 20 ± 1 °C. All light should be excluded to prevent formation of DO by algae in the sample.

p) A number of factors, for example, soluble versus particulate organics, settleable and floatable solids, oxidation of reduced iron and sulphur compounds, or lack of mixing may affect the accuracy and precision of BOD measurements. Presently, there is no way to include adjustments or corrections to account for the effect of these factors.

q) Sample properties, dilution water quality, seed characteristics, and dilution technique can introduce considerable variation in BOD test measurements. Several factors must be closely controlled to eliminate any extraneous variation. In general, test variation is smallest for unseeded samples and sample aliquot ≥ 15 mL (15 mL in a 300 mL BOD bottle, i.e., 5% dilution). As sample volume becomes smaller, test variation is usually greater, because of the greater errors associated with measuring and transferring small volumes and the improbabilityof obtaining representative samples with each transfer.

Method Performance

The following method performance criteria are mandatory and must be demonstrated before and during analysis.

a) The Method Detection Limit (MDL) is set at the 95% confidence level above zero (or the blank) is 5.0 mg/L.

$$\mathbf{MDL = 2 * t_{.95} * Std.\ Dev._{near\ zero}}$$

where, t = Student's t value for a 95% confidence level and a standard deviation estimate with n-1 degrees of freedom.

$\mathbf{Std.\ Dev._{near\ zero}}$ **= Standard deviation of the replicate analyses.**

b) **Method Blanks: Analyse two aliquots of dilution water as a rough check on quality of unseeded dilution water and cleanliness of**

incubation bottles. If the oxygen depletion of a candidate water exceeds 0.2 mg/L obtain a satisfactory water by improving purification or check glassware cleaning procedure. Typical values obtained are listed in Table 1.

Table 1 Method Blank

	N	Acceptable BOD mg/L	Mean Measured BOD mg/L	Std. Dev.	Control Limits
Blank	24	< 10.0	0.17	0.11	± 0.33

c) Glucose-Glutamic Acid Check: Because the BOD test is a bioassay its results can be influenced greatly by the presence of toxicants or by use of a poor seeding material. Some sewage seeds are relatively inactive. Low results are always obtained with such seeds and waters**. Routinely, it is necessary to check dilution water quality, seed effectiveness, and analytical technique by making BOD measurements on pure organic compounds and samples with known additions.** Thus, the purpose of the glucose-glutamic acid check is not intended to serve as a measure of the accuracy of the BOD test. For BOD determinations, in general, use a mixture of 150 mg glucose/L and 150 mg glutamic acid/L as a "standard" check solution (BOD 300 mg/L). Glucose has an exceptionally high and variable oxidation rate but when it is used with glutamic acid, the oxidation rate is stabilised and is similar to that obtained with many municipal wastes.

For the 300-mg/L mixed primary standard, the average 5 day BOD would be 198 mg/L with a standard deviation of 30.5 mg/L [a]. Typical values obtained are listed in Table 3.

Table 3 Glucose-Glutamic Acid Check

Organic Compound	N	Mean mg/L	Std. Dev.	Control Limits
Glucose-Glutamic Acid	56	184	26.30	± 78.89

Most data from the Glucose Glutamic Acid tests run at Env. Canada prior to June 1999.

d) Method Bias: The results of regular interlaboratory studies and certified reference solutions provide an indication of method bias at 95% confidence level; typical results obtained using seeded samples appears in Table 4 and Table 5.

Table 4 Single Analyst Method Bias

Reference Value (mg/L)	N	Measured BOD Mean	Measured BOD Std Dev	% Bias	Significant (95% CL)
12 ± 6	4	14	0.8	+ 16.7	Yes
29 ± 10	4	37	2.6	+27.6	Yes
54 ± 17	4	61	2.6	+13.0	No

Most data from the interlaboratory studies run at Env. Canada Lab prior to June 1999.

Table 5 Single Analyst Method Bias

Reference Samples	Certified Value mg/L	Performance Acceptance Limits	N	Mean	Std Dev.	Within Advisory Range	Control Limits
ERA 9972 {a}	94.0	63.0 - 114	12	87.3	4.9	Yes	± 15
ERA 9975 {b}	58.6	39.3 - 70.9	8	55.1	4.6	Yes	± 13.8
ERA 9976 {c}	31.1	20.8 - 37.6	8	29.0	1.5	Yes	± 4.4

Most data from the reference materials run at Env Canada Lab prior to June 1999.

{a} BOD standard by Environmental Resource Associates. Lot # 9972.
{b} BOD standard by Environmental Resource Associates. Lot # 9975.
{c} BOD standard by Environmental Resource Associates. Lot # 9976.

e) Method Precision: Reproducibility data obtained from duplicate measurements of unseeded samples have been used to set control limits (3 SD) in order to monitor procedure variability for unseeded samples. Typical values obtained are listed in Table 5.

Table 6 Single Analyst (Within-Run) Precision - Data current to July 1998

BOD Analytical Range (mg/L)	Number of Duplicate Pairs	Mean Normalised Range	Std Dev	Control Limit for Normalised Duplicate Range
5 - 6,200+	102	0.146	0.129	0.387

Most data from duplicates run at Env. Canada lab prior to 1999.

f) Mandatory Method Data Quality Objectives (DQO's) are listed in Table 7

Table 7 Mandatory Method DQO's

Sample Type	MDL (mg/L)	Bias	Precision
Effluent	**10**	**15%**	**± 15%**
Freshwater	**10**	**15%**	**± 15%**
Marine	**10**	**15%**	**± 15%**

***Bias and precision will increase as you approach the MDL.**
***Tabulated DQO's do not apply for samples where results are less than three times the MDL (i.e., <30mg/L).**

Reagents

a) Record all the weights and volumes of chemicals used in preparation of reagent or standard on "Reagent / Standard Preparation Log."

b) Type 1 Water - reagent grade water that has <10 coliform unit/mL of bacteria, Resistance >10 megaohm-cm at 25 °C, Conductance < 0.1 µmhos/cm at 25 °C and SiO_2 <0.05 mg/L, particulate matter filtered using 0.22 µm filters and organic contaminants removed using activated carbon.

c) Phosphate Buffer Solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$, and 1.7 g NH_4Cl in about 500 mL of Type 1 water and dilute to one litre. The pH should be 7.2**. Discard reagent if there is sign of biological growth in the stock bottle.**

d) Magnesium Sulphate Solution: Dissolve 22.5 g $MgSO_4.7H_2O$ in Type 1 water and dilute to one litre. **Discard reagent if there is sign of biological growth in the stock bottle.**

e) Calcium Chloride Solution: Dissolve 27.5 g anhydrous $CaCl_2$ in Type 1 water and dilute to one litre. **Discard reagent if there is sign of biological growth in the stock bottle.**

f) Ferric Chloride Solution: Dissolve 0.25 g $FeCl_3 . 6H_2O$ in Type 1 water and dilute to one litre. **Discard reagent if there is sign of biological growth in the stock bottle.**

g) Dilution water: To 5 gallon carboy of Type 1 water, add one mL each of the phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions for each litre of water used. Aerate the water so as to saturate it with oxygen. Prepare this solution fresh daily. Alternatively one can use HACH BOD nutrient buffer pillows instead.

h) HACH BOD nutrient buffer pillows (cat. # 14863-98 & # 14862-98). Each big pillow prepares 19 litres and small pillow prepares 6 litres of dilution water that consist of a phosphate buffer plus mineral nutrients. **Prepare fresh daily.**

i) Seeding Materials:

1) Seeding material is routinely obtained by using the supernatant liquor from domestic sewage which has been stored at 20 °C for 24 to 36 hours.

2) In special cases (e.g. Industrial wastewater), acclimatised seed may be necessary.

3) Polyseed® BOD Inoculum (by Polybac Corporation; EPA accepted), containing a dry blend of microbial cultures free of nitrifying organisms. Upon re-hydration each capsule provides 500 mL of seed material. **Prepare fresh daily.**

4) Bioseed™ BOD_5 Seed Inoculum (by International Chemicals Ltd., EPR approved). Re-hydration of one Bioseed capsule provides a 1000 mL seed material. **Prepare fresh daily.**

j) HACH Nitrogen Inhibitor, Formula 2533 ™ - Contains 2-chloro-6 (trichloromethyl) pyridine(N-Serve), coated on an inert substrate. “Two shots” or 0.16 gm per 300 mL sample (use the dispenser cap) inhibits nitrogenous oxygen demand in the BOD test. **Do not use past expiry date on the bottle.**

k) Glucose-Glutamic Acid (G+Gac, 300 mg/L) Solution: Dry reagent-grade glucose and glutamic acid at 103 °C for one hour and cool for one hour. Add 150 mg of glucose and 150 mg of glutamic acid to Type 1 water, adjust pH to around 7 and dilute to 1 litre; this solution serves as a check standard to verify seed effectiveness and measurement technique. Based upon interlaboratory studies the solution should provide a mean BOD_5 value of 180 mg/L [b] to 198 mg/L [a]. When the colour of glucose powder turns off white, replace the glucose. **Prepare solution fresh weekly**.

Note: If pH of Glucose-Glutamic Acid Solution is not adjusted to neutral pH, the recovery would be low.

l) Standard BOD check solution: Dissolve 0.18 g anhydrous potassium biphthalate $KHC_8H_4O_4$ to one litre of deionized water and adjust to about pH 7.0. Determine the 5 day BOD of this seeded solution. If the BOD value of the check is outside the range of 150 ± 10 mg/L, reject any determinations made with the seed and dilution water and seek the cause of the problem. **Prepare this check solution daily.**

m) Sulphuric Acid, 1 N: Slowly and while stirring, add 28 mL conc. sulphuric acid to Type 1 water. Dilute to 1 litre. Prepare solution as required.

n) Sodium Hydroxide, 1 N: Dissolve 40 g sodium hydroxide in Type 1 water. Dilute to 1 litre. Prepare solution as required.

o) Sodium Sulphite Solution, 0.025 N: Dissolve 1.575 g Na_2SO_3 in 1000 mL Type 1 water. **This solution is not stable; prepare fresh daily.**

p) Sodium Hypochlorite, 1%: Dilute 4-6 % NaOCl 5 times.

q) Commercial Starch Indicator Solution.

Procedure

a) Preparation of Dilution Water and Seed Material

1) Dilution water: To 5 gallon carboy of Type 1 water, add one mL each of the phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions for each litre of water used. Aerate the water so as to saturate it with oxygen**. Prepare this solution fresh daily**. Alternatively one can use HACH BOD nutrient buffer pillows instead.

2) Estimate the amount of dilution water need for blanks, seeds, control QCs and samples. Add one HACH BOD nutrient buffer big pillow to 19 litres or one small pillow to 6 litres of Type 1 water**. Prepare fresh daily.**

3) Aerate the dilution water with organic-free air until the solution is saturated at room temperature (about half an hour). The dilution water can be stored for 24 hours at room temperature. **Let water stand for 30 minutes before use after aeration.**

4) Seeding material is routinely obtained by using the supernatant liquor from domestic sewage which has been stored at 20 °C for 24 to 36 hours.

5) In special cases (e.g. Industrial wastewater), acclimatised seed may be necessary or,

6) To prepare the seed material add the contents of one Polyseed® capsule to 500 mL or one Bioseed™ capsule to 1 litre of aerated dilution water. Stir and aerate the solution for two hours before use, and continue to do so while withdrawing seed aliquot**. Prepare fresh daily**.

b) Calibration of Membrane Electrode

1) calibrate the oxygen probe as per the manufacturer's standard operating procedure and recalibrate every two hours during use.

c) Measurements

1) The dilution water blanks, seed controls, and each sample must first be measured for Initial dissolved oxygen

2) Prepare Blanks, Seed Control and QC check bottles: 2 dilution water blanks without seeding (300mL), 2-3 Polyseed/domestic sewage at 10 ml, 15 & 25 Mls, 1 Reference Material – ERA seeded and 2 Glucose-Glutamic acid (300mg) seeded.

d) Sample Pre-treatment

1) Sample temperature adjustment: Allow samples to warm at ambient room temperature to 20 $\pm$ 1 °C before making dilutions to ensure that the test sample is not supersaturated with Dissolved Oxygen (DO) at 20 °C.

2) **Sample pH adjustment: Measure pH of samples. Neutralise samples containing acidity or caustic alkalinity to approximately pH 7 with H_2SO_4 (1 N) or NaOH (1 N) using a pH meter. Do not dilute the sample by more than 0.5%.**

3) **Samples containing residual chlorine compounds or reducing substances: Test for presence of residual chlorine. Take 100 mL portion of neutralised sample. Add 2 mL of 1+1 acetic acid, 2 mL 10% potassium iodide (KI) , 1 mL of starch. If the sample turns blue, it indicates the presence of oxidising agent (like chlorine). If the sample remains clear, it indicates the presence of reducing agent. See Figure 1 on the following page.**

i) Removal of residual chlorine. If residual chlorine is present, de-chlorinate sample and seed the dilution water. Destroy chlorine residual by adding 0.025 N sodium thiosulphite ($Na_2S_2O_3$) solution. Determine required volume of $Na_2S_2O_3$ solution on the 100 mL portion of sample (in Section 4.3) by titrating with $Na_2S_2O_3$ solution to the starch-iodine end point (colourless) for residual chlorine. Add to the neutralized sample the relative volume of $Na_2S_2O_3$ solution determined by the above test, mix. Allow 10 to 20 minutes for reaction time and then check the sample for residual chlorine again.

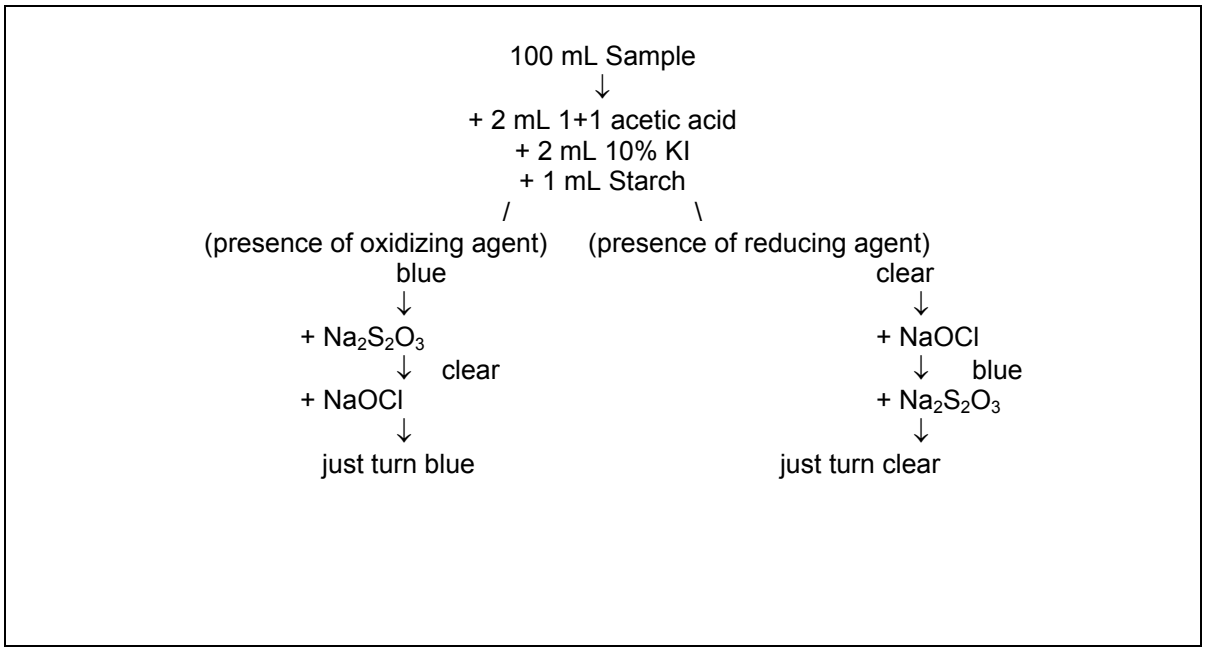
Note: Excess $Na_2S_2O_3$ exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples.

ii) Removal of reducing agent. If sample contains reducing agent, it will exert an oxygen demand. Determine

required volume of bleach solution on the 100 mL portion of sample by titrating with 1% Sodium Hypochlorite solution just to turn blue. Add a drop of $Na_2S_2O_3$ to make the solution to turn clear again. Add to the neutralised sample the relative volume of NaOCl solution determined by the above test, mix, and after 10 to 20 minutes, check sample for presence of reducing agent again.

Note: Always seed chlorinate/dechlorinated samples.

FIGURE 1 - Sample Pre-treatment Flow Chart For Chlorine Residuals



4) Samples supersaturated with oxygen: This situation may occur during winter or during algae blooms. **The dissolved oxygen content must be reduced to saturation (9.17 mg/L at 20 °C) by vigorous shaking of partly filled sample container.**

e) Pre-dilution is recommended if the waste is strong enough that a 5% dilution (i.e., 15 mL in a 300 mL BOD bottle) will yield a residual DO < 1 mg/L. This step can also ensure that the final concentration of total solids in the BOD bottle does not exceed 10 mg/L.

1) Dilution Technique:

i) Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 day incubation produce the most reliable results. Make at least three different dilutions of a prepared sample in duplicate or preferably in triplicate with dilution water to obtain DO uptake within range. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilution (always, COD > BOD). In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for

strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

ii) Prepare dilutions either in volumetric flasks, and then transfer to BOD bottles, or prepare directly in BOD bottles. For dilutions greater than 5:300 make a primary dilution in appropriate volumetric flasks before making final dilution in the bottle. For dilution prepared directly in BOD bottles: Use a wide-tip volumetric pipette or a graduated measuring cylinder, add the desired sample volume to individual BOD bottles of known capacity (300 mL).

iii) **Seed all samples that are chlorinated (d)3)i) or dechlorinated (d)3)ii). Also seed samples that lack the micro-organisms necessary for oxidation of organic materials, samples that contain very few micro-organisms, and samples containing other toxic substances (e.g. plating waste).** If a substance in the original sample is toxic, dilution may reduce its concentration to below the toxic level. Apply pre-dilution and seed the samples, 5 mL of Polyseed or 3 mL of Bioseed material is usually adequate per bottle. **The DO uptake due to the seed material is subtracted from the total DO uptake to obtain the sample BOD.**

iv) **Samples that call for nitrification add 0.16 g or 2 shots of Nitrification Inhibitor Formula 2533 ™ into the bottle. Alternatively, add the nitrogen inhibitor to the dilution water in the carboy.**

v) Fill bottles by siphoning with enough dilution water so that insertion of stoppers will displace all air leaving no bubbles, avoid entrainment of air while filling up the bottles, and overflow so that water seal is maintained. Use polyethylene caps to reduce evaporation of the water seal during incubation.

f) The Determination of initial DO Values

1) **Determine initial DO** on the bottles; with stirring the reading should stabilise within 60 seconds. Stopper tightly, water-seal. Place plastic cap over flare mouth of bottle and incubate for 5 days at 20°C in the dark.

2) Rinse DO electrode with Type 1 water between determinations to prevent cross-contamination of samples.

3) For those using Winkler method, titrate one of the bottles to determine initial DO value.

g) Determination of Final DO Values (5 Days after measurement of Initial DO)

1) **After five days measure the DO** remaining in the dilution water blanks, the check standards, and the sample dilutions.

2) The DO depletion, the final Total BOD_5/Total Seeded BOD_5S/Total Carbonaceous BOD_5/Total Seeded Carbonaceous BOD_5, and the average are calculated as the measurements proceed; various flags may appear to indicate an error or to give more information about the sample bottle the program documentation explains the flags that may occur.

3) When all DO measurements are completed, a daily batch report may be generated.

Calculations

The sample BOD is calculated as follows:

$$BOD_5 = \frac{Depletion_5 - Seedcomp_{avg}}{Dilution/100}$$

where: $Depletion_5$ = initial DO - final DO at 5 days
Dilution = % aliquot in bottle
$Seedcomp_{avg}$ = average seed correction

The seed correction based on anyone dilution is given by:

$$Seedcomp_{dil} = seed\ depl_5 - R$$

where: Seed $depl_5$ = initial DO - final DO for the seed dilution

$$R = \frac{\text{Quantity of seed material added to diluted sample}}{\text{Quantity of innoculant in seed control dilution}}$$

The results are entered into the lab database and rounded off to a maximum of 3 significant figures above the detection limit.

Quality Control

a) **Before analyzing any samples, the laboratory must demonstrate that the selected analytical methods can provide valid data under practical conditions in the laboratory. The laboratory should have in place a method validation process and data to demonstrate that validation has occurred and that the methods chosen can meet the data quality objectives.**

b) **Include two dilution water blanks in each batch. The blanks should show an average depletion ≤ 0.2 mg/L; if they do not, this may be due to either a probe calibration problem or poor-quality dilution water. Re-calibrate and/or identify the contamination problem - repeat the batch if necessary. Document any corrective action taken.**

c) **Include at least one check standard (Glucose+Glutamic acid or Potassium Biphthalate) and a certified reference material) in each batch; the measured BOD should lie within the advisory range (usually ± 3σ) or control limits. If they do not, this may be due to either a probe calibration problem or poor-quality dilution water. Re-calibrate and/or identify the contamination problem - repeat the batch if necessary. Document any corrective action taken.**

d) **At minimum, for each batch of 10 samples, randomly select one sample to be analysed in duplicate; also include a pH reference solution / standard and blank for every 20 samples (that lies**

within the calibration range) as a check standard. If the range of the duplicate samples exceeds the warning limits, the results are rejected and the analysis should be repeated. Document any corrective action taken.

e) The uncertainty of the results, detection limits, selectivity of the analysis, and its robustness in the hands of different staff should be tested and documented. Techniques used for validation include results obtained on certified or other reference materials, comparison of results with data obtained using other methods, interlaboratory comparison data, systematic assessment of factors which could influence the results, and assessment of uncertainty based on accuracy and precision. The influence of instrumental, human and environmental factors should be considered.

f) **Assess whether the method shows statistical control by considering:**

- **the range of duplicate results, to monitor precision**
- **the measured BOD of the check standards, to monitor accuracy**

If any parameter lies outside of the established (3σ) *control limits* OR if two consecutive parameters lie outside of the (2σ) *warning limits*, then re-calibration and/or an instrument check may be necessary. Document any non-conformance and the action taken.

References

a) American Public Health Association (APHA). 1999 *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Washington, DC: APHA, AWWA, WPCF.

b) U.S. Environmental Protection Agency (USEPA). 1986. *Method-by-Method Statistics from Water Pollution Laboratory Performance Evaluation Studies*. Cincinnati: Office of Research and Development, Quality Assurance Branch.

c) Young, J.C. 1984. Waste Strength and Water Pollution Parameters. In *Water Analysis: Volume III, Organic Species* (R.A. Minear and L.H. Keith, ed.), pp. 1- 39. Orlando: Academic Press.

d) BC Environmental Laboratory Manual.

Revision History

February 2000	Method Introduction
November 2002	Method Incorporated into main Laboratory Manual; reformatting to match style of Lab Manual, EMS codes and units added

Chlorinated Phenols in Water

Parameter Chlorinated Phenol Package

Analytical Method Acid extraction, methylation, GC/ECD.

Introduction The chlorinated phenols are a group of compounds which include pentachlorophenol, tetrachlorophenols and trichlorophenols.

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

MDL & EMS Codes

Parameter	EMS Code	MDL(mg/L)
Pentachlorophenol	**P022 P008**	0.0001
Tetrachlorophenols*	**T020 P008**	0.0002
Trichlorophenols†	**T021 P008**	0.0002

* including 2,3,4,5-, 2,3,4,6- and 2,3,5,6- tetrachlorophenol
† including 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trichlorophenols.

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 method. If interfering co-extractives are present or likely, then a Florisil clean-up step is incorporated into the procedure. The presence of a target compound may be confirmed by analysis on a dissimilar column.

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_2SO_4/L in field.

Stability
Holding time - extract sample within 14 days of sampling, analyze within 40 days.
Storage - 4°C until analyzed.

Procedure: None listed.

Apparatus
a) Separatory funnels, 500 mL.
b) Graduated cylinders, 12 mL.
c) Round bottom flasks, 250 mL.
d) Glass chromatography columns, 9 mm ID x 300 mm with a 200 mL reservoir.
e) Diazomethane generator (or alternate derivatizing device).

f) Glass filtering funnels, 75 mm diameter.

Reagents

a) Solvents, glass distilled, pesticide grade.
   1) Dichloromethane.
   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 (other derivatizing reagents are available).
d) Sodium hydroxide, 10% weight to volume, aqueous solution.
e) Sodium sulfate, anhydrous, heat treated.
f) Florisil, PR grade, heat treated at 650°C and deactivated with 1% (weight to weight) deionized water.
g) 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 the 1 mg/L intermediate phenol solution to give a concentration of 0.0004 mg/L.
b) For samples that have not been treated with an acid, add 1 mL of 36N sulfuric acid to a 250 mL sample.
c) Extract a 250 mL sample three times with 60 mL of dichloromethane each time.
d) Filter the dichloromethane 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 definite 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 dichloromethane 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.
   1) Fraction 1: 150 mL of petroleum ether. This fraction contains the methylated chlorophenols.
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

Blanks: One method blank per batch or 1 in 14.
Replicates: Duplicate one sample per batch or 1 in 14.
Recovery Control: A 250 mL water sample is spiked with 0.100 mL of the 1.00 mg/L intermediate standard solution containing all target compounds.

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.

Chlorophenols in Water by GC/MS/SIM

Parameter

Trichlorophenol, 2,4,6-
Trichlorophenol, 2,3,6-
Trichlorophenol, 2,4,5-
Trichlorophenol, 2,3,5-
Trichlorophenol, 3,4,5-
Trichlorophenol, 2,3,4-
Total Trichlorophenols
Tetrachlorophenol, 2,3,4,5-
Tetrachlorophenol, 2,3,4,6-
Total Tetrachlorophenols
Pentachlorophenol

EMS Codes

Analytical Method

Acid extraction, methylation, GC/MS/SIM

Introduction

This method is applicable to the quantitative determination of chlorophenols in water.

Summary

An acidified water sample is extracted with dichloromethane. The raw extract is concentrated and the phenols are reacted with diazomethane to produce corresponding methylated derivatives. The derivatives are analyzed by capillary gas liquid chromatography with a mass selective detector. If required, the extracts are cleaned by Florisil column chromatography prior to gas liquid chromatography.

MDL

Chlorophenols	mg/L
Trichlorophenol, 2,4,6-	0.0001
Trichlorophenol, 2,3,6-	0.0001
Trichlorophenol, 2,4,5-	0.0001
Trichlorophenol, 2,3,5-	0.0001
Trichlorophenol, 3,4,5-	0.0001
Trichlorophenol, 2,3,4-	0.0001
Total Trichlorophenols	0.0001
Tetrachlorophenol, 2,3,4,5-	0.0001
Tetrachlorophenol, 2,3,4,6-	0.0001
Total Tetrachlorophenol	0.0001
Pentachlorophenol	0.0001

Matrix

Fresh Water
Wastewater
Saline 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 conditions of the analysis.

b) Matrix interferences by contaminants that could be co-extracted from the sample are minimized with the GC/MS approach. The extent of the matrix interferences will vary from source to source.

Sample Handling and Preservation

Water samples should be collected in hydrocarbon clean 500 mL amber glass bottles and stored at 4°C. Minimum required volume is 500 mL.
Preservation: 2 mL/L conc. HCl.

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, 500 mL
b) Round bottom flasks, 250 mL, 500 mL
c) Glass filter funnels
d) Glass columns 1.4 cm x 30 cm with 150 mL reservoir
e) Pipettes, 2 mL
f) Rotary evaporator
g) Graduated centrifuge tubes with ground glass stoppers, 15 mL
h) Polytron homogeniser
i) Waring blender, stainless steel
j) Diazomethane generator
k) Erlenmeyer flasks, 250 mL
l) Apparatus for agitating 250 mL erlenmeyer flasks
m) Buchner funnels
n) Whatman #41 filter paper

Reagents

a) Solvents, distilled in glass or Pesticide grade
   1) Dichloromethane
   2) Acetone
   3) Isooctane
   4) Hexane
   5) Petroleum Ether
   6) Ethyl Acetate
   7) Diethyl Ether
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% water.
d) Glass wool, heat treated at 300° C.
e) Sulfuric acid, 36N.
f) N-Nitrosomethylurea for diazomethane generation
g) Sodium hydroxide, 10% weight to volume, aqueous solution
h) Extracting solvent: dichloromethane: methanol (2:1) v/v containing 1% sulfuric acid
i) Acidic sodium sulfate.
j) Dibromophenol, tribromophenol, and pentabromoanisole.

Procedure

a) Pour 250 mL of sample into a 500 mL separatory funnel. Add 50 µL of 20 ppm surrogate (Dibromophenol) and 1.0 mL of 36N sulfuric acid.
b) Extract the sample three times with 60 mL of dichloromethane each time.

c) Filter the dichloromethane extracts through anhydrous acidic sodium sulfate supported in a glass funnel by glass wool into a 250 mL round bottom flask.
d) Add about 23 mL of isooctane and concentrate the combined extracts to about 5.0 mL on a rotary evaporator
e) Spike extract with 50 µL of 10 ppm surrogate (Tribromophenol).

WARNING: Methylation work must be carried out in a fumehood with proper ventilation

f) Methylate with diazomethane as follows:
   1) In the bottom of a glass impinger place 10 mL of 10% sodium hydroxide
   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 pipette attached. The end of the pipette is submerged under the solvent.
   4) Continue bubbling until the extract turns a dark yellow(about three minutes). Remove from the generator and allow to sit in a fume hood for a minimum of thirty minutes.
g) Remove excess diazomethane by bubbling a gentle stream of nitrogen through the extract.
h) Add 2-3 mL of isooctane to the round bottom flask and evaporate the dichloromethane using a rotary evaporator.
i) Place glass wool at the outlet of a glass column (1.4 x 30 cm) and add about 1 cm of heat treated sodium sulfate.
j) 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 4-5 cm above the Florisil add 1 cm of heat treated sodium sulfate.

Note: Maintain the solvent level above the sodium sulfate.

k) Pipette 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.
l) Add 200 mL of petroleum ether to the column and collect the eluate in a 250 mL round bottom flask.
m) Add 2 mL of isooctane and concentrate to 23 mL on a rotary evaporator. Do not allow the solution to go to dryness.
n) Transfer to a 15 mL graduated centrifuge tubes and blow down to 1mL with prepurified nitrogen.
o) Spike with 50 µL of 20 ppm anthracened10 and analyze by GC/MS.

Instrument Conditions

Instrument	HP 5890 gas chromatograph with HP 5970 mass selective detector
Column	DB1701, 30 m x 0.25 mm i.d., 0.025 µm film thickness
Carrier gas	Helium
Scan mode	Selected ion monitoring (SIM)
Scan rate	1 scan/sec (minimum)
Head pressure	25 psi
Injector temperature	250°C
Injection volume	1 µL
Injection mode	Splitless, 1 minute

Initial temperature	70°C
Initial time	2 min
Temperature program	25°C/min to 130°C, then 2°C/min to 220°C, then 10°C/min to 280°C
Final Hold	10 min

GC/MS Calibration

a) To each prepared calibration standard mixture add a known constant amount of the internal standard (anthracene-d10) to yield a resulting concentration of 1 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 pesticide and internal standard, and calculate the relative response factor (RRF) for each using the following equation:

$$RRF = (A_x C_{is}) / (A_{is} C_x)$$

where:

A_x = Area of the chlorophenol to be measured
C_x = Concentration of the chlorophenol, (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 original 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 0.1 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 mid-scale calibration standard and obtain the RRF. Calculate the percent difference between the current RRF and average RRF using the following equation:

% Difference = (RRF_c RRF_i) / RRF_i x 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 pesticides 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 three-point curve **MUST** be generated.

Calculations:

Concentration of chlorophenol$_x$ = (A_x/A_{is}) x (W_{is}/RRF_x) / Wt

where:

A_x = Area of chlorophenol$_x$, of the chlorophenol to be measured.
A_{is} = Area of internal standard
W_{is} = Amount of internal standard added to the final extract
RRF_x = Relative response factor of chlorophenol$_x$ from a calibration run
Wt = Initial sample weight or volume

Precision

RSD 38% at 0.4 µg/L and 5% at 0.002 µg/L

Accuracy

95% at 0.4 µg/L

Quality Control
Method Blank Analysis:

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 sample is spiked with a known concentration of chlorophenol. 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:

$$\% \text{ recovery} = \frac{[(\text{sample + spike}) - (\text{sample only})]}{[\text{spiked amount}]} \times 100$$

Allowed recoveries are: 40-130%. Samples for which the spike is outside the limit are to be reinjected. If it fails again, repeat the batch.

Laboratory 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: < 30% (if both samples are greater than 5 times the MDC).
Replicates outside the limits are required to be repeated.

Surrogates:
Acceptable surrogate recoveries:
40-130% for dibromophenol
65-130% for tribromophenol

References Not available

Revision Dates November 2002 Method adopted from Supplement Manual #1, EMS Codes assigned

Chlorinated Phenols in Solids by GC/ECD

Parameter

Chlorinated Phenols
Pentachlorophenol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,3,5,6-Tetrachlorophenol
2,3,4-Trichlorophenol
2,3,5-Trichlorophenol
2,3,6-Trichlorophenol
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
3,4,5-Trichlorophenol

EMS Codes

Analytical Method

Solvent Extraction, Acetylation, GC/ECD

Introduction

This procedure is suitable for the qualitative and quantitative determination of tri-, tetra, and penta-chlorinated phenols in solid matrices. Tetra- and penta-chlorophenol were commonly used as wood preservatives until the late 1970's. They are still in limited use today. Chlorophenols may also be formed as a by-product of the chlorine bleaching of wood pulp.

Summary

The samples are extracted with acidified acetone. This extract is cleaned up using an acid-base partition technique. The final hexane extract is reduced in volume and the phenolic compounds are derivatized prior to analysis. The final extracts are analysed using capillary column gas chromatography with electron capture detection (GC/ECD).

MDL

The following detection limits are based on the analysis of samples containing low levels of interferences. Actual detection limits will vary depending on instrument sensitivity and matrix effects.

Analyte	Detection Limit (ug/g)
Pentachlorophenol	0.02
2,3,4,5-Tetrachlorophenol	0.02
2,3,4,6-Tetrachlorophenol	0.02
2,3,5,6-Tetrachlorophenol	0.02
2,3,4-Trichlorophenol	0.02
2,3,5-Trichlorophenol	0.02
2,3,6-Trichlorophenol	0.02
2,4,5-Trichlorophenol	0.02
2,4,6-Trichlorophenol	0.02
3,4,5-Trichlorophenol	0.02

Matrix

Soil (Marine)
Sediment Solids (Concrete, Wood Chips, etc.)

Interferences and Precautions

Any co-extracted compound that produces a response on an electron capture detector is a potential interference. Samples that contain naturally occurring polar compounds may produce emulsions during any of the extraction or back extraction steps. The acetates formed during the derivatization step are not stable. Derivatized extracts must be analysed within 24 hours of preparation.

Sample Handling and Preservation

Container: wide mouth glass jar
Preservation: 4 degrees Celsius

Stability

Holding time: extract sample within 14 days of collection. Underivatized extracts must be analysed within 40 days. Derivatized extracts must be analysed within 24 hours.

Principal or Procedure

a) Extraction (Adapted from EPA SW-846, Method 3500)
   1) Weigh a representative sub-sample into a clean, solvent rinsed extraction tube.
   2) Using a mechanical shaker, extract the sample three times with acetone that has been acidified to pH <2 with phosphoric acid. Collect extracts in a separatory funnel.
   3) To the acetone extract add an excess of contaminant free water.
   4) Extract the aqueous solution with hexane. Discard the aqueous layer.

b) Clean-up (Adapted from EPA SW-846, Method 3650)
   1) Back-extract the hexane extract with water that has been made alkaline to pH >12 with sodium or potassium hydroxide. Discard the hexane layer.
   2) Acidify the aqueous extract to pH <2 with phosphoric acid.
   3) Extract the acidified water once again with hexane.

c) Derivatization: Derivatizing phenolic compounds significantly improves their chromatography. A number of different derivatization techniques may be used. The procedure below describes acetylation.
   1) Reduce the final hexane extract in volume to 1 or 2 millilitres.
   2) Treat a portion of the final extract with acetic anhydride and trimethylamine to acetylate the chlorinated phenols.
   3) Remove residual acetylation reagents from the extract using 1M potassium dihydrogen phosphate buffer solution.

d) Analysis (Adapted from EPA SW-846, method 8000A)
   1) Analyse the derivatized extracts using a capillary column gas chromatograph equipped with an electron capture detector.
   2) Confirmation of the target compounds may be required if the sample extract contains interferences. Confirmation may be carried out by chromatographing the extract on a column containing a different stationary phase.

Precision

Not available

Accuracy

Not available

Quality Control

a) Tribromophenol is added to the samples prior to extraction as a surrogate standard.
b) One method blank per analytical batch (10-20 samples).
c) One method spike or reference material per analytical batch (10-20 samples).
d) One laboratory replicate per every 10 samples.

References

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

Revision Dates:

November 2002	Method adopted from Manual Supplement #1, EMS Codes Assigned

Chlorophenols in Solids by GC/MSD/SIM

Parameter

2,4,6-Trichlorophenol
2,3,6-Trichlorophenol
2,4,5-Trichlorophenol
2,3,5-Trichlorophenol
3,4,5-Trichlorophenol
2,3,4-Trichlorophenol
Total Trichlorophenols
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
Total Tetrachlorophenols
Pentachlorophenol

EMS Codes

Analytical Method

Acid soil extraction, methylation, florisil, GC/MSD/SIM

Introduction

This method is applicable to the quantitative determination of chlorophenols in soil.

Summary

The sample is extracted with a mixture of dichloromethane, methanol and sulfuric acid. The acidic components are then reextracted into dichloromethane under acidic conditions. The raw extract is cleaned up by Florisil column chromatography, concentrated and treated with diazomethane. The corresponding derivatives are analyzed by GC/MS.

MDL

Chlorophenols	µg/g
2,4,6-Trichlorophenol	0.005
2,3,6-Trichlorophenol	0.005
2,4,5-Trichlorophenol	0.005
2,3,5-Trichlorophenol	0.005
3,4,5-Trichlorophenol	0.005
2,3,4-Trichlorophenol	0.005
Total Trichlorophenols	0.005
2,3,4,5-Tetrachlorophenol	0.005
2,3,4,6-Tetrachlorophenol	0.005
Total Tetrachlorophenol	0.005
Pentachlorophenol	0.005

Matrix

Soil (Marine)
Sediment Solids (Concrete, Wood chips, 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.

Matrix interferences by contaminants that could be coextracted from the sample are minimized with the GC/MS approach. The extent of the matrix interferences will vary from source to source.

Sample Handling and Preservation

Soil samples should be collected in hydrocarbon clean 0.5 litre wide mouth amber glass jars and stored in a freezer at -10° C. Minimum required sample size is 10 g however, preferred sample size is 50 g.

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, 500 mL
b) Round bottom flasks, 250 mL, 500 mL
c) Glass filter funnels
d) Glass columns 1.4 cm x 30 cm with 150 mL reservoir
e) Pipettes, 2 mL
f) Rotary evaporator
g) Graduated centrifuge tubes with ground grass stoppers, 15 mL
h) Polytron homogenizer
i) Waring blender, stainless steel
j) Diazomethane generator
k) Erlenmeyer flasks, 250 mL
l) Apparatus for agitating 250 mL erlenmeyer flasks
m) Buchner funnels
n) Whatman #41 filter paper

Reagents

a) An automated system consisting of:
   1) Dichloromethane
   2) Acetone
   3) Isooctane
   4) Hexane
   5) Petroleum Ether
   6) Ethyl Acetate
   7) Diethyl Etherdata collection

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% water.

d) Glass wool, heat treated at 300 °C.

e) Sulfuric acid, 36N, ACS grade.

f) N-Nitrosomethylurea for diazomethane generation

g) Sodium hydroxide, 10% weight to volume, aqueous solution

h) Extracting solvent: dichloromethane: methanol (2:1) v/v containing 1% sulfuric acid

i) Acidic sodium sulfate: Prepared by placing about 1 litre of sodium sulfate granules in 1 litre of acetone to which 7 mL of concentrated sulfuric acid has been added. Mix and let stand for 1 hour. Filter and dry for 2 hours in fume hood.

j) Dibromophenol, tribromophenol, and pentabromoanisole.

Procedure

a) Weigh 10.0 g of sample into a 250 mL erlenmeyer flask.

b) Add 50 µL of 20 ppm surrogate (Dibromophenol) and 150 mL of extracting solvent. Let soak with agitation for one hour.

c) Filter through a Buchner funnel with Whatman #41 filter paper.

d) Wash sample with 2 x 50 mL of extracting solvent.

e) Transfer the filtrate and washings to a 500 mL separatory funnel containing 100 mL deionized water.

f) Shake the separatory funnel well and drain the organic layer through acidic sodium sulfate into a 500 mL round bottomed flask.

g) Re-extract the aqueous layer with 2 x 50 mL of dichloromethane. Add the dichloromethane to the round bottomed flask.

h) Add about 2-3 mL of isooctane and concentrate the combined extracts to 5.0 mL on a rotary evaporator

i) Spike extract with 50 µL of 10 ppm surrogate (Tribromophenol)

Note: perform following methylation in fume hood.

j) Methylate with diazomethane as follows:
   1) In the bottom of a glass impinger place 10 mL of 10% sodium hydroxide
   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 pipette attached. The end of the pipette is submerged under the solvent.
   4) Continue bubbling until the extract turns a dark yellow (about three minutes). Remove from the generator and allow to sit in a fume hood for a minimum of thirty minutes.

k) Remove excess diazomethane by bubbling a gentle stream of nitrogen through the extract.

l) Add 23 mL of isooctane to the round bottom flask and evaporate the dichloromethane using a rotary evaporator.

m) Place glass wool at the outlet of a glass column (1.4 x 30 cm) and add about 1 cm of heat treated sodium sulfate.

n) 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.

o) Pipette 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.

p) Add 200 mL of petroleum ether to the column and collect the eluate in a 250 mL round bottom flask.

q) Add 2 mL of isooctane and concentrate to 23 mL on a rotary evaporator. Do not allow the solution to go to dryness.

r) Transfer to a 15 mL graduated centrifuge tubes and blow down to 1 mL with prepurified nitrogen.

s) Spike with 50 µL of 20 ppm anthracene-d10 and analyze by GC/MS.

Instrument Conditions

Instrument	HP 5890 gas chromatograph with HP 5970 mass selective detector
Column	DB1701, 30 m x 0.25 mm i.d., 0.025 µm film thickness
Carrier gas	Helium
Scan mode	Selected ion monitoring (SIM)
Scan rate	1 scan/sec (minimum)
Head pressure	25 psi
Injector temperature	250°C
Injection volume	1 µL
Injection mode	Splitless, 1 minute
Initial temperature	70°C
Initial time	2 min
Temperature program	25°C/min to 130°C, then 2°C/min to 220°C, then 10°C/min to 280°C
Final Hold	10 min

GC/MS Calibration

a) To each prepared calibration standard mixture add a known constant amount of the internal standard (anthracene-d10) to yield a resulting concentration of 1 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 chlorophenol and internal standard, and

calculate the relative response factor (RRF) for each using the following equation:

$RRF = (A_x - C_{is}) / (A_{is} - C_x)$

where:

A_x = Area of the chlorophenol to be measured
C_x = Concentration of the chlorophenol, (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 initial calibration 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 0.1 relative retention time units of the nearest internal standard.

Daily One Point Calibration Check

At the beginning of each work day, a daily onepoint 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:

$\% \text{ Difference} = (RRF_c - RRF_i) / RRF_i \times 100$

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 chlorophenols 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

Concentration of chlorophenol$_x$ = (A_x/A_{is}) x (W_{is}/RRF_x) / Wt

where:

A_x = Area of chlorophenol$_x$, the chlorophenol to be measured.
A_{is} = Area of internal standard
W_{is} = Amount of internal standard added to the final extract
RRF_x = Relative response factor of chlorophenol$_x$ from a calibration run
Wt = Initial sample weight or volume

Precision

To be determined

Accuracy

To be determined

Quality Control
Method Blank Analysis

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. 10 g of sample is spiked with a known concentration of chlorophenol. 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 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: 40-130%. Samples for which the spike is outside the limit are to be reinjected. If it fails again, repeat the batch.

Laboratory 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: < 30% (if both samples are greater than 5 times the MDL).
Replicates outside the limits are required to be repeated.

	Surrogates: Acceptable surrogate recoveries: 40 - 130% for dibromophenol 65 - 130% for tribromophenol	
References	Not Available	
Revision Dates	November 2002.	Method adopted from Manual Supplement #1. EMS Codes assigned.

Chlorinated and Non-Chlorinated Phenols in Solids by Soxhlet, Acetylation, GC/MS

Parameter Chlorinated and Non-Chlorinated Phenols.

EMS Codes

Analytical Method Soxhlet Extraction, Acetylation, GC/MS

Introduction This procedure is suitable for the qualitative and quantitative determination of a selected group of phenolic compounds. The complete list can be found in the MDL section. The soxhlet procedure provides a more rigorous extraction than conventional mechanical shaking procedures.

Summary The samples are extracted with dichloromethane on a soxhlet apparatus. The dichloromethane extract is reduced in volume and the phenolic compounds are derivatized prior to analysis. The final extracts are analysed using capillary column gas chromatography with mass spectrometric detection (GC/MS).

MDL The following detection limits are based on the analysis of samples containing low levels of interferences. Actual detection limits will vary depending on instrument sensitivity and matrix effects.

Analyte	Detection Limit (ug/g)
Pentachlorophenol	0.02
2,3,4,5-tetrachlorophenol	0.02
2,3,4,6-tetrachlorophenol	0.02
2,3,5,6-tetrachlorophenol	0.02
2,3,4-trichlorophenol	0.02
2,3,5-trichlorophenol	0.02
2,3,6-trichlorophenol	0.02
2,4,5-trichlorophenol	0.02
2,4,6-trichlorophenol	0.02
3,4,5-trichlorophenol	0.02
2,3-dichlorophenol	0.02
2,4-dichlorophenol	0.02
2,5-dichlorophenol	0.02
2,6-dichlorophenol	0.02
3,4-dichlorophenol	0.02

3,5-dichlorophenol	0.02
2-chlorophenol	0.02
3-chlorophenol	0.02
4-chlorophenol	0.02
2,4-dimethylphenol	0.05
ortho-cresol	0.05
meta-cresol	0.05
para-cresol	0.05
phenol	0.05

Matrix

Soil (Marine)
Sediment Solids (Concrete, Wood Chips, etc.)

Interferences and Precautions

The phenol, cresols, and mono-substituted phenolic compounds are volatile. Losses of these analytes may occur during the solvent reduction step. The acetates of 2,4-dichlorophenol and 2,5-dichlorophenol may co-elute depending on the analytical system being used. The acetates formed during the derivatization step are not stable. Derivatized extracts must be analysed within 24 hours of preparation.

Sample Handling and Preservation

Container: wide mouth glass jar
Preservation: 4 degrees celsius

Stability

Holding time: extract sample within 14 days of collection. Underivatized extracts must be analysed within 40 days. Derivatized extracts must be analysed within 24 hours.

Principal or Procedure

a) Extraction (Adapted from EPA SW-846, Method 3500)
   1) Mix a representative sub-sample with anhydrous sodium sulfate. Place the mixture into an extraction thimble.
   2) Soxhlet extract the sample with dichloromethane for at least 12 hours.
   3) Reduce the dichloromethane extract in volume to 1 or 2 millilitres.

b) Derivatization: The derivatization of phenolic compound significantly improves their chromatography. A number of derivatization techniques may be used. The procedure below describes actylation.
   1) Treat a portion of the final extract with acetic anhydride and trimethylamine to acetylate the chlorinated phenols.
   2) Remove residual acetylation reagents from the extract using 1M potassium dihydrogen phosphate buffer solution.

c) Analysis (Adapted from EPA SW-846, method 8270B)
   1) Analyse the derivatized extracts using a capillary column gas chromatograph equipped with an mass spectrometric detector.

Precision	Not available	
Accuracy	Not available	
Quality Control	a) Tribromophenol is added to the samples prior to extraction as a surrogate standard. b) One method blank per analytical batch (10-20 samples). c) One method spike or reference material per analytical batch (10-20 samples). d) One laboratory replicate per every 10 samples.	
References	a) EPA (1986) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, SW-846, 3rd Ed., November 1986.	
Revision Dates:	November 2002.	Method adopted from Manual Supplement #1. EMS Codes assigned.

Chlorinated Phenols in Solids by Soxhlet, Methylation, GC/ECD

Parameter Trichlorophenols, Tetrachlorophenols and Pentachlorophenol

Analytical Method

US EPA Method 3540	Soxhlet Extraction
US EPA Method 3620	Florisil Cleanup
US EPA Method 8040	Phenols by Gas Chromatography

EMS Codes:

Introduction This analysis is applicable to chlorinated phenols. While pentachlorophenol is of primary interest for its use as a wood preservative, the total trichlorophenols and tetrachlorophenols are also reported.

Method Summary The soil or sediment is initially homogenized, and a sub-sample taken for the determination for the moisture content. A known amount of soil is mixed with a drying agent and soxhlet extracted with dichloromethane for 16 hours. The extract is concentrated and the phenols derivatized to their respective methyl anisoles. The extract is then submitted to florisil cleanup. Final extracts are analysed by GC/ECD. Final results are calculated using the internal standard method.

MDL

Target Compound	Detection Limit (ug/g)
Trichlorophenols*	0.01
2,3,4-trichlorophenol	0.02
2,3,5-trichlorophenol	0.02
2,3,6-trichlorophenol	0.02
2,4,5-trichlorophenol	0.02
2,4,6-trichlorophenol	0.02
3,4,5-trichlorophenol	0.02
Tetrachlorophenols†	0.005
2,3,4,5-tetrachlorophenol	0.02
2,3,4,6-tetrachlorophenol	0.02
2,3,5,6-tetrachlorophenol	0.02
Pentachlorophenol	0.005

Matrix Soil (Marine)
Sediment Solids (concrete, wood chips, etc.)

Interferences and Precautions Interfering co-extractive compounds will vary with sample matrix. While the cleanup step eliminates many interferences, certain compounds such as PCBs and phthalate esters may interfere if present in the sample. Molecular sulfur will also interfere. Certain tetrachlorophenol isomers co-elute on the columns listed in this procedure (2,3,4,5 & 2,3,4,6).

Sample Handling and Preservation

Container - pre-cleaned glass jar, Teflon or foil-lined cap.
Samples should be stored in the dark at 4°C and care should be taken during extract concentration to avoid losses of trichlorophenols.

Stability

Holding time - extract within seven days of sampling and analyse within 40 days after extraction.

Procedure

Appartus

a) Mixing Bowls (glass or aluminum foil)
b) Analytical and Top-Loading Balance
c) Drying Oven: use at 105°C
d) Soxhlet Extraction Apparatus
e) Flat Bed Shaker
f) Rotary Evaporator
g) Kuderna-Danish (KD) apparatus
h) N-Evap Apparatus
i) GC Vials
j) Chromatography Columns
k) Graduated Test Tubes
l) GC/ECD System

Reagents

a) Solvents: distilled in glass grade
   - Dichloromethane (DCM)
   - Hexane
   - Diethyl Ether
b) Sodium Sulfate, Anhydrous
c) Concentrated Sulfuric Acid
d) Florisil: 2% (wt/wt) deactivated

Procedure

a) Rinse glassware with DCM prior to use (acid washing is also advised).
b) Transfer the entire sample into a mixing bowl and homogenize the soil sample well.
c) Determine the moisture content by adding 5-10 grams of sample into a pre-weighed dish. Dry overnight at 105°C. Reweigh the dried soil and calculate the moisture.
d) Recovery Control:
   For each set of samples, prepare the following:
   - one Method Blank (use a chlorophenol free soil)
   - one Duplicate Sample
   - one Spike (add known amount of chlorophenols to a chlorophenol free soil)
e) Using a top-loading balance, weigh 10-30 g of sample. Add a small amount (0.5 mL) of concentrated sulfuric acid. Mix sample with enough anhydrous sodium sulfate to create a free flowing mixture. Some samples may require grinding with a mortar and pestle. Add sample to a soxhlet thimble, and place thimble in the soxhlet extractor (or place sample in extractor on a plug of sodium sulfate and glass wool).
f) Add appropriate amount of surrogate (2,4,6-tribromophenol) solution to each sample.
g) Add 250-300 mL of DCM to a 500 mL boiling flask and add boiling chips. Connect the flask, soxhlet and condenser.
f) Ensure the cooling water is running through the condenser. Turn the heaters on. Extract samples for 16 hours.
   Note: alternate methods of extraction include:
   - Flat-bed Shaker Table
   - Microwave Assisted Extraction
   - Ultrasonic Probe Extraction

Internal laboratory validation of these methods should be performed before use.

g) Allow extracts to cool to room temperature. Rinse soxhlet apparatus with DCM.

h) Concentrate the extract to 5-10 mL using KD apparatus or rotary evaporation, and to 1 mL using gentle stream of nitrogen or air, exchanging the solvent to hexane.

i) Derivatize the phenols by adding 1 mL of diazomethane in diethyl ether (add additional amount if yellow color does not persist). Refer to the following diazomethane preparation method and safety notes. Allow the extracts to stand at room temperature for 30 minutes.

j) Using gentle stream of nitrogen or air, concentrate the derivatized extract to 1 mL, exchanging the solvent to hexane.

k) Prepare a florisil (2% deactivated) mini-column by adding florisil to a height of seven centimeters in a pasteur pipette plugged with glass wool, and top with about 0.5 cm of anhydrous sodium sulfate. Rinse the column with 5 mL hexane and discard. Quantitatively transfer the extract to the florisil column. Elute with 9 mL of 6% DCM, collecting the eluant in a graduated test tube.

l) Using a gentle stream of nitrogen or air, evaporate the extract to 1.0 mL, exchanging solvent to hexane.

m) Add appropriate amount of internal standard solution, make up to 2.0 mL with hexane, transfer to GC vial and proceed with instrumental analysis.

n) Analyse extracts using GC/ECD. Use dual capillary columns which exhibit different retention characteristics (eg. J&W DB-5 & DB-1701) to confirm all peaks.

o) Calculate final results on a dry weight basis, using the internal standard method. All isomers listed above are determined in the test, and the trichlorophenol and tetrachlorophenol isomers summed to obtain the totals. Results are usually not adjusted for surrogate recovery.

Diazomethane Safety Notes

a) Diazomethane is a known carcinogen, and can be explosive under certain conditions (high concentrations in the gaseous form). Although diazomethane is a gas at room temperature, it is soluble in diethyl ether and can be handled safely when dissolved in an ether solution. When preparing diazomethane, wear solvent resistant gloves, and prepare in a fume hood with most of the doors closed to ensure adequate flow. Alert other lab staff to the preparation of diazomethane.

b) Check the diethyl ether for peroxides before use by adding 4 mL diethyl ether to 4 mL 10% potassium iodide and mixing well. Wait for 3-5 minutes and observe the ether layer. If the ether turns cloudy, peroxides are present and they must be destroyed before use.

c) Diethyl ether is extremely flammable. Use only in a fume hood and keep away from any sources of ignition.
Note that the generation apparatus is a closed system and if used properly, poses no threat of exposure.

Diazomethane Generation From Diazald

a) Start the water bath to reach a temperature of 65 °C. Fill the double walled condenser with dry ice, then add acetone slowly until the coldfinger is about 3/4 full. Add additional dry ice if needed. Stir to form a slushy mixture.

b) Add 10 mL ethyl alcohol (95% min. purity) and a solution of potassium hydroxide (5 g) dissolved in water (8 mL), to the lower reaction vessel.

c) Attach the round bottom flask below the condenser. Cool the flask in a salt/ice bath (33g NaCl/100g ice).
d) Fill the vapour trap with diethyl ether and place the hose into it.
e) Fill the separatory funnel with a solution of Diazald (5.0 g) dissolved in diethyl ether (45 mL).
f) Install the separatory funnel and warm the lower reaction flask in the hot water bath.
g) Add the Diazald/diethyl ether mixture slowly over the period of about 20 minutes. The rate of addition should not exceed the capacity of distillation, ensuring full condensing of the diazomethane produced.
h) When all the Diazald solution has been added, wait for the reaction to subside. Place about 10 mL of diethyl ether in the separatory funnel, and drain slowly, continuing the distillation until the distillate is colourless.
i) The above reaction will produce about 40 mL of diazomethane in diethyl ether solution. Additional amounts can be produced by using multiples of the quantities described, and increasing the amounts of solvents employed accordingly.
j) Use silica gel or acetic acid for disposal and/or spill clean up, as it rapidly reacts with diazomethane.

Precision

Refer to EPA Method 8040

Accuracy

Refer to EPA Method 8040

Quality Control

For each analytical batch (not greater than 14 samples) include the following:
a) one method blank
b) one duplicate
c) one spike

Add to each sample:
a) Surrogate Compounds
   - 2,4,6-tribromophenol
b) Internal Standard Compounds
   - tetrabromobenzene

Safety Notes

a) Diazomethane is a carcinogen. Use caution at all times when generating and handling diazomethane. See additional safety notes with the diazomethane generation procedure.
b) Use caution when handling solvents. Some are flammable and others are suspect carcinogens. Read material safety data sheets (MSDS) before using solvents.
c) While the toxicity of the analytes may not be known, each compound should be treated as potentially hazardous.

References and Method Sources

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

Revision Dates

November 2002. Method adopted from Manual Supplement #1. EMS Codes assigned.

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 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.

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

Parameter (3-Iodo-2-propenyl-n-butylcarbamate)

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.

2-(Thiocyanomethylthio)-benzothiazole (TCMTB) 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.

Glyphosate and AMPA

Parameter	Glyphosate AMPA
Analytical Method	Derivatization, extraction, HPLC/UV-VIS
EMS Code	Glyphosate **G001 X365** AMPA **A001 X365**
Introduction	This method is for the determination of the herbicide glyphosate and its derivative, aminomethylphosphonic acid (AMPA).
Summary	An aliquot of the water sample is reacted with dinitrofluoro-benzene (DNFB) to form derivatives of glyphosate and AMPA. Interferences are removed from the reaction mixture by extraction with dichloromethane. A subsequent extraction with iso-butanol removes the derivatives. The derivatives are then back-extracted into a borax solution in preparation for analysis by high performance liquid chromatography.
MDL	Glyphosate - 0.005 mg/L AMPA - 0.005 mg/L
Matrix	Fresh water Wastewater
Interferences and Precautions	No known interferences for water samples.
Sample Handling and Preservation	Bottle: 0.5 L amber glass, narrow mouth, Teflon-lined cap Preservation: none required
Stability	Holding time: analyze within 30 days Storage: store at 4°C until analyzed
Principle or Procedure	See Reference 1, p. 188-190
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. Recovery control: 1 spike 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.

Lipid Content

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.

Monocyclic Aromatic Hydrocarbons (BETX) in Water by Dynamic Headspace and GC/PID/FID

Parameter

BETX-
Benzene
Ethylbenzene
Toluene
m+p-Xylene
o-Xylene

EMS Code

Analytical Method

Dynamic Headspace - GC/PID/FID.

Introduction

This method is applicable to the quantitative and qualitative analysis of BETX in water. BETX are prominent components of gasoline and their presence in water is usually an indication of gasoline contamination.

Summary

An aliquot of a water sample is sealed in an airtight vial. The vial is then heated to a predetermined temperature for a given period of time. After the sample has equilibrated, a portion of the headspace vapour above the sample is introduced onto a gas chromatograph equipped a suitable capillary column and photoionization (PID) and flame ionization detectors (FID) placed in series.

MDL

The following detection limits are based on analysis of water samples containing low levels of interfering hydrocarbons.

Analyte	Detection Limit (ug/L)
Benzene	0.5
Toluene	0.5
Ethylbenzene	0.5
m+p-Xylenes	0.5
o-Xylenes	0.5

Matrix

Fresh Water (FW)
Waste Water (WW)
Marine Water (MW)
Sludge

Interferences and Precautions

The presence of co-eluting aliphatic hydrocarbons may interfere with the quantification of BETX. It may be necessary to increase the detection limit for the individual analytes to avoid reporting false positive results in these cases. The analytical system may become contaminated by high level samples. Carry-over may produce false positive results. Photoionization detectors have a limited linear range. Samples may require dilution prior to analysis to bring them into the linear working range of the detector. Because of the volatility of the BETX components, care must be taken to ensure minimal exposure of the samples to open air.

Sample Handling and Preservation

Container: 40 ml water sampling (purge and trap) vial with teflon lined cap. Samples should always be collected in duplicate.
Preservation: Hydrochloric Acid to pH < 2 ; or 0.1% Copper Sulphate. Collect the sample so that absolutely no bubbles or headspace are present in the sample container.
Samples must be stored at 4 degrees celsius at all times during transport and storage.
Samples may become contaminated if stored in the presence of gasoline, gasoline vapour, or automotive exhaust.

Stability

Samples must be analysed within 7 days of collection. BETX are extremely volatile. The sample must remain tightly sealed and at 4 degrees celsius at all times prior to analysis. Once a vial has been opened for analysis, the sample in that vial should not be analysed again. Samples should therefore be collected in duplicate.

Principal or Procedure

a) Preparation of Calibration Standards.
   1) Prepare a number of clean headspace vials by filling each to approximately half full with identical measured amounts of contaminant free water. Seal the headspace vials using septa lined with teflon.
   2) Prepare a concentrated solution of BETX in Methanol. The concentration of this solution should be chosen so that the final concentration of methanol in the most concentrated working standard does not exceed 2%.
   3) Prepare a reies of calibration standards by adding appropriate amounts of the concentrated BETX solution prepared in (a)2) to each of the headspace vials prepared in (a)1). The range of concentrations prepared will depend on the linearity of the analytical system being used. The most concentrated calibration standard should not exceed the linear working range of the analytical system.

b) Preparation of Samples.
   1) Transfer a measured amount of water sample to a clean headspace vial. The amount of sample used should be identical to the final volume of the calibration standards.
   2) For samples containing concentrations of BETX that exceed the linear range of the analytical system, transfer a smaller aliquot of sample to the headspace vial and dilute to volume with contaminant free water. The final volume in the headspace vials must be identical for all samples analysed.

c) Analysis of Samples.
   1) Allow samples and calibration standards to equilibrate at 85 degrees celsius for at least 45 minutes.
   2) Transfer between 0.5 and 2.0 cubic centimetres of the headspace above the sample onto a gas chromatograph equipped with an appropriate capillary column and photoionization and flame ionization detectors placed in series. The headspace may be transferred using a gas tight syringe, or using an automated headspace sampling system.

3) Photoionization detectors are selective for aromatic compounds. Flame ionization detectors are non selective. BETX are quantified from the PID signal. The FID signal can be used for confirmation by differentiating aliphatic hydrocarbons from aromatic hydrocarbons.

Precision Not available

Accuracy Not available

Quality Control

a) Surrogate Standards (3-Fluorotoluene and 1,4 Difluorobenzene) are added to all samples, standards, and quality control samples prior to the equilibration step.
b) One method blank is analysed for every analytical batch (12-24 samples).
c) One laboratory replicate is analysed for every 12 samples.
d) One method spike or standard reference material is analysed for every analytical batch (12-24 samples).

References

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

Revision Dates: November 2002. Method adopted from Manual Supplement #1. EMS Codes assigned.

Monocyclic Aromatic Hydrocarbons (BETX) in Solids by Dynamic Headspace and GC/PID/FID

Parameter

BETX -
Benzene,
Ethylbenzene,
Toluene, and
m+p-Xylene
o-Xylene

EMS Code

Analytical Method

Dynamic Headspace - GC/PID/FID.

Introduction

This method is applicable to the quantitative and qualitative analysis of BETX in solids. BETX are prominent components of gasoline and their presence is usually an indication of gasoline contamination.

Summary

Samples are extracted with methanol. A portion of the extract is transferred to a headspace vial. Water is added to the vial and the vial is sealed. The vial is then heated to a predetermined temperature for a given period of time. After the sample has equilibrated, a portion of the headspace vapour above the sample is introduced onto a gas chromatograph equipped a suitable capillary column and photoionization (PID) and flame ionization detectors (FID) placed in series.

MDL

The following detection limits are based on analysis of samples containing low levels of interfering hydrocarbons.

Analyte	Detection Limit (µg/g)
Benzene	0.5
Toluene	0.5
Ethylbenzene	0.5
m+p-Xylene	0.5
o-Xylene	0.5

Matrix

Soil (Marine)
Sediment Solids (concrete, wood chips, etc.)

Interferences and Precautions

The presence of co-eluting aliphatic hydrocarbons may interfere with the quantification of BETX. It may be necessary to increase the detection limit for the individual analytes to avoid reporting false positive results in these cases. The analytical system may become contaminated by high level samples. Carry-over may produce false positive results. Photoionization detectors have a limited linear range. Samples may require dilution prior to analysis to bring them into the linear working range of the detector. Because of the volatility of the BETX components, care must be taken to ensure minimal exposure of the samples to open air.

Sample Handling and Preservation

Container: wide mouth glass jar with teflon lined lid.
Preservation: 4 degrees celsius.
Collect the sample so that minimal headspace is present in the sample container.
Samples must be stored at 4 degrees celsius at all times during transport and storage.
Samples may become contaminated if stored in the presence of gasoline, gasoline vapour, or automotive exhaust.

Stability

Samples must be analysed within 7 days of collection. BETX are extremely volatile. The sample must remain tightly sealed and at 4 degrees celsius at all times prior to analysis. Once a sub-sample has been removed from a container, losses of volatiles will occur due to the headspace in that container.

Principle Procedure

a) Preparation of Calibration Standards.
   1) Prepare a number of clean headspace vials by filling each to approximately half full with identical measured amounts of contaminant free water. Seal the headspace vials using septa lined with teflon.
   2) Prepare a concentrated solution of BETX in Methanol. The concentration of this solution should be chosen so that the final concentration of methanol in the most concentrated working standard does not exceed 20%.
   3) Prepare a series of calibration standards by adding appropriate amounts of the concentrated BETX solution prepared in (a)2) to each of the headspace vials prepared in (a)1). The range of concentrations prepared will depend on the linearity of the analytical system being used. The most concentrated calibration standard should not exceed the linear working range of the analytical system.
   4) Add pure methanol to each of the calibration standards so that the final concentration of methanol in the standards is 20%.

b) Extraction.
   1) Weigh a representative sub-sample into a 40 millilitre (purge and trap) vial. Add a measured amount of methanol to the vial and seal it.
   2) Vortex the contents of the vial for one minute.
   3) Leave the sample to extract for two hours.
   4) Decant a portion of the methanol extract into a scintillation vial.

c) Preparation of samples.
   1) Prepare a number of headspace vials as described in (a)1).
   2) Add a portion of the methanol extract prepared in (b) to the headspace vials prepared in (c)1) so that the final concentration of methanol in solution is 20%.
   3) For samples containing concentrations of BETX that exceed the linear range of the analytical system, transfer a smaller aliquot of methanol extract to the headspace vial. Add pure methanol to all of the sample vials so that the total concentration of methanol in solution is 20% for all of the samples. The total volume in the headspace vials must be identical for all samples analysed.

d) Analysis
   1) Allow samples and calibration standards to equilibrate at 85 degrees celsius for at least 45 minutes.
   2) Transfer between 0.5 and 2.0 cubic centimetres of the headspace above the sample onto a gas chromatograph equipped with an appropriate capillary column and photoionization and flame ionization detectors placed in series. The headspace may be transferred using a gas tight syringe, or using an automated headspace sampling system.
   3) Photoionization detectors are selective for aromatic compounds. Flame ionization detectors are non selective. BETX are quantified from the PID signal. The FID signal can be used for confirmation by differentiating aliphatic hydrocarbons from aromatic hydrocarbons.

Precision Not Available

Accuracy Not Available

Quality Control

a) Surrogate Standards (3-Fluorotoluene and 1,4 Difluorobenzene) are added to all samples, standards, and quality control samples prior to extraction.
b) One method blank is analysed for every analytical batch (12-24 samples).
c) One laboratory replicate is analysed for every 12 samples.
d) One method spike or standard reference material is analysed for every analytical batch (12-24 samples).

References

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

Revision Date November 2002. Method adopted from Manual Supplement #1. EMS Code assigned**.**

Monocyclic Aromatic Hydrocarbons (BETX) in Water by Purge and Trap GC/MS or GC/PID

Parameter

BETX -
Benzene,
Ethylbenzene,
Toluene, and
m+p-Xylene
o-Xylene

EMS Codes

Analytical Method

Purge & Trap GC/MS Purge & Trap GC/PID

Introduction

This method is applicable to the quantitative determination of benzene, toluene, ethylbenzene and xylenes in water.

Summary

An inert gas is bubbled through a 5 mL water sample contained in a specially-designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapour phase. The vapour is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and volatiles are transferred to a second narrow-bore trap. The second trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer or photoionisation detector.

MDL

Parameter - GC/MS	mg/L
Benzene	0.0003
Ethylbenzene	0.0002
Toluene	0.0003
m+p-Xylene	0.0006
o-Xylene	0.0003

Parameter - PID	mg/L
Benzene	0.0005
Ethylbenzene	0.0005
Toluene	0.0005
m+p-Xylene	0.0005
o-Xylene	0.0005

Matrix

Fresh water
Wastewater

Saline Water

Interferences and Precautions

The presence of co-eluting aliphatic hydorcarbons may interfere with the quantification of BETX. It may be necessary to increase the detection limit for the individual analytes to avoid reporting false positive results in these cases. The analytical system may become contaminated by high level samples. Carry-over may produce false positive results. Because of the volatility of the BETX components, care must be taken to ensure minimal exposure of the samples to open air.

Sample Handling and Preservation

Water samples should be received in a 43 mL amber glass vials with a teflon lined septum cap. Sample bottles should be filled to overflowing so that when capped, no headspace is trapped. Samples should be submitted in duplicate. The samples are stored at 4° C.

Stability

Samples must be analysed within 7 days of collection. BETX are extremely volatile. The sample must remain tightly sealed and at 4 degrees celsius at all times prior to analysis. Once a sub-sample has been removed from a container, losses of volatiles will occur due to the headspace in that container.

Procedure

Instrument Tuning - GC/MS:

a) Inject 50 ng of BFB (bromofluorobenzene) into every sample.
b) Check the abundance criteria of the BFB in the midrange standard at the beginning and as part of each calibration.

m/z	Ion Abundance Criteria
50	8-40% of base peak
75	30-60% of base peak
95	base peak
96	5-9% of base peak
173	<2% of mass 174
174	50%-120% of base peak
175	4-9% of mass 174
176	93%-101% of mass 174
177	5-9% of mass 176

c) The tune must meet abundance criteria before proceeding to samples.
d) Criteria must be met once every twelve hours of continuous operation.

GC Conditions:
Column: Rtx-Volatiles, 30m x 0.32 mm i.d., 1.5 µm film thickness
(Restek Corp.) or
DB624 or
HP-VOC

MSD Conditions:
Source: 70 eV

Scan Mode: Full scan, 35-260 amu

Scan Rate: >1 scan/second

Initial Calibration:
A three point calibration (10, 20, 40 ug/L or 50, 100, 200 total ng) or a five point (10, 15, 20, 30, 40 ug/L or 50, 75, 100, 150, 200 total ng) is performed.

a) Calculate the %RSD (Relative Standard Deviation) for the list of target compounds. They must be less than ±30%.
b) Calculate the Relative Response Factors (RRF) for the list of target compounds. They must all be > 0.30.

RRF =

$$\frac{\text{area of the analyte standard}}{\text{area of the internal standard}} \times \frac{\text{conc. of the internal std.}}{\text{conc. of the analyte standard}}$$

c) Repeat the injection if any criteria is not met.

Continuing Calibration:
A single point calibration at 20 µg/L is performed if the condition described above is met. It must be performed at least every 12 hours, if the 20 µg/L standard has drifted more than 25%.

a) Calculate the RRF for the list of target compounds. They must all be > 0.30.
b) Calculate % difference of RRF of the list of target compounds between single & multipoint (mean value) calibration. They must be <25%. If >25% repeat injection. If fails again, do full calibration.

% Difference =

$$\frac{\text{average RRF (initial calibration) - RRF (current calibration)}}{\text{average RRF (initial calibration)}} \times 100$$

Precision

Relative standard deviation was 5% at a concentration of 2.9 ug/L using PID detector.

Accuracy

Not available

Quality Control

Method Blank Analysis:
Analyzed 1 every 12 hours or 1 per sample batch. Blanks should not contain >MDL of any compound, except benzene and toluene, are acceptable up to 5 x MDL. Results are tabulated and control charts of absolute area counts are plotted for toluene and benzene. All sample data are reported corrected for blanks.

Internal Standards:
The internal standard (IS) is 1,4-Difluorobenzene. Every sample, standard, method blank and matrix spike sample is spiked with 50 ng of IS before injection. Check retention time (RT) of each compound; must be within ±30 seconds between runs. If >30 seconds the system has to be inspected for malfunction and correction made as required.

Surrogate Standards:
Surrogate volatiles are d8-toluene, BFB and d4-1,2-dichloroethane. For PID analysis, only BFB is used. Every sample, standard, method blank and matrix spike sample is spiked with 50 ng of each compound. NO DEVIATION OF CONCENTRATION IS ALLOWED.

Calculate the recovery of each surrogate:

$$\% \text{ Surrogate Recovery} = \frac{\text{quantity determined by analysis}}{\text{quantity added to sample}} \times 100$$

Acceptable % surrogate recoveries for water are:

compound	acceptable limits
d8-toluene	88-110
BFB	86-115
d4-DCA	76-114

Check calculations and reanalyse if recoveries are outside these limits. Surrogate recoveries are reported with sample results.

Matrix Spike:
Analyse on a frequency of 1 in 20 or 1 per sample batch. Spike a duplicate sample with 16 µL of the 50 µg/L working standard (800 ng of each compound). If insufficient sample remains, spike blank DI water. Calculate matrix spike % recoveries for each compound.

$$\text{matrix spike \% recovery} = \frac{\text{spike sample result - sample result}}{\text{spike added from spiking mix}} \times 100\%$$

Acceptable % surrogate recoveries for water are:

Compound	% recovery
toluene	76 - 125
benzene	76 - 127
ethylbenzene	70 - 130
xylenes	70 - 130

Duplicates:
For duplicate analyses, calculate Relative % Difference (RPD)

$$RPD = \frac{\text{first sample value - duplicate sample value}}{\text{(first sample value + duplicate sample value)/2}} \times 100$$

$$RPD = \frac{\text{difference of duplicate sample values}}{\text{average of duplicate sample values}} \times 100$$

Acceptable RPDs for water are:

Compound	% recovery
toluene	±25
benzene	±25
ethylbenzene	±30
xylenes	±30

Data outside these limits DO NOT require reanalysis, but should be noted as part of a QA report.

References

a) EPA SW846, Method 8260A, EPA SW846, Method 8020A

Revision Date

November 2002. Method adopted from Manual Supplement #1. EMS Codes assigned.

Monocyclic Aromatic Hydrocarbons (BETX) in Solids by Purge and Trap GC/MS

Parameter

BETX -
Benzene,
Ethylbenzene,
Toluene, and
m+p-Xylene
o-Xylene

EMS Code

Analytical Method

Methanol extraction - Purge and Trap - GC/MS.

Introduction

This method is applicable to the quantitative and qualitative analysis of BETX in solids. BETX are prominent components of gasoline and their presence is usually an indication of gasoline contamination. This procedure may also be used to determine halogenated volatile organic compounds (VOC) in solids.

Summary

BETX are extracted from the sample using a purge and trap technique. Samples with difficult matrices, or samples with elevated levels of BETX are first extracted with methanol. The methanol extract is extracted using a purge and trap technique, or injected directly onto a gas chromatograph. Purge and trap involves purging the volatile BETX from the sample with an inert gas, and trapping them on a solid sorbent trap. The trap is then heated and the BETX are directed onto a gas chromatograph equpped with a suitable capillary column and a mass spectrometric detector (GC/MS). Results are determined using internal standard calibration.

MDL

The following detection limits are based on analysis of samples containing low levels of interfering hydrocarbons.

Analyte	Direct Purge & Trap Detection Limit (µg/g)	Methanol Extraction Detection Limit (µg/g)
Benzene	0.01	0.1
Toluene	0.01	0.1
Ethylbenzene	0.01	0.1
m+p-Xylene	0.01	0.1
o-Xylene	0.01	0.1

Matrix

Soil (Marine)
Sediment Solids (concrete, wood chips, etc.)

Interferences and Precautions

The presence of co-eluting aliphatic hydrocarbons may interfere with the quantification of BETX. It may be necessary to increase the detection limit for the individual analytes to avoid reporting false positive results in these cases. The analytical system may become contaminated by high level samples. Carry-over may produce false positive results. Because of the volatility of the

BETX components, care must be taken to ensure minimal exposure of the samples to open air.

Sample Handling and Preservation

Container : wide mouth glass jar with teflon lined lid.
Preservation : 4 degrees celsius.
Collect the sample so that minimal headspace is present in the sample container. Samples must be stored at 4 degrees celsius at all times during transport and storage. Samples may become contaminated if stored in the presence of gasoline, gasoline vapour, or automotive exhaust.

Stability

Samples must be analysed within 7 days of collection.
BETX are extremely volatile. The sample must remain tightly sealed and at 4 degrees celsius at all times prior to analysis. Once a sub-sample has been removed from a container, losses of volatiles will occur due to the headspace in that container.

Principle or Procedure

a) Methanol Extraction.
   1) Weigh a representative sub-sample into a 40 millilitre (purge and trap) vial. Add a measured amount of methanol to the vial and seal it.
   2) Vortex the contents of the vial for one minute.
   3) Leave the sample to extract for two hours.
   4) Decant a portion of the methanol extract into a scintillation vial.

b) Purge and Trap Procedure.
   1) This procedure is described in detail in EPA SW-846 [a] Method 5030A.

c) Analysis.
   1) This procedure is described in detail in EPA, 40 CFR Part 136 [b] Method 624.

Precision

Not Available

Accuracy

Not Available

Quality Control

a) Surrogate standards (4-bromofluorobenzene, d5-chlorobenzene, fluorobenzene) are added to the samples prior to the purge and trap procedure.
b) Internal standards (bromochloromethane, 1,4-difluorobenzene, d6benzene, d8-toluene, d10-ethylbenzene, d4-1,2-dichlorobenzene) are added to the samples prior to the purge and trap procedure.
c) One method blank is analysed per analytical batch (10-20 samples).
d) One method spike or reference material is analysed per analytical batch (10-20 samples).
e) One laboratory replicate is analysed per every 10 samples.

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).

Revision Date: November 2002. Method adopted from Manual Supplement #1. EMS Codes assigned.

Hydrocarbons, Total Extractable (Dichloromethane), in Water, by Gas Chromatography (GC)

Parameter

Total extractable hydrocarbons.

Analytical Method

Dichloromethane extraction, GC/FID.

EMS Code

H-TE X366

Introduction

This method detects extractable hydrocarbon material in the n-C_{10} to n-C_{30} range in water. The method provides several advantages over "Total Extractable Hydrocarbons by Infrared Detection" and "Oil and Grease in Water" in that: i) volatile hydrocarbons are included; ii) the chromatographic procedure can be used to fingerprint the type of contamination; iii) the detector response is linear over the hydrocarbon range being tested. There are some disadvantages: i) compounds with low volatility will not be detected; ii) loss of volatile components is possible if solvent reduction is required.

Summary

The sample is extracted with dichloromethane in a separatory funnel. The extract is dried, then reduced to a known volume. The final extract is then analyzed with capillary column gas chromatography with flame ionization detection. The results are determined by obtaining the total area under the chromato-graphic curve between n-C_{10} and n-C_{30}, then quantifying by external calibration.

MDL

The detection limit is dependent upon the final volume. A one litre sample extracted to 2.0 mL final volume provides a detection limit of 1.0 mg/L .

Matrix

Fresh water
Wastewater
Marine water

Interferences and Precautions

Loss of the light fraction may occur during the extraction or solvent reduction steps. Compounds in the n-C_{28} to n-C_{40}+ range will give corresponding low recoveries, especially branched chain compounds. Naturally occurring organic material will give elevated results. A solvent instrumental blank should be run after high samples to reduce carry over. The choice of the reference standard e.g., (gasoline, diesel, or motor oil) will cause variance in the calculated data. The test is not suited for the quantification of gasoline-contaminated waters.

Sample Handling and Preservation

Container - 1 or 0.5 litre glass bottle
Preservation - 3 mL/L of conc. HCl to pH <2 (to inhibit bacterial degradation)

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 sample is needed. It is reScommended that the entire sample be extracted, with rinsing of container, to ensure that material adhering to the sample container is included.

Stability

Holding Time - extract within seven days of collection, analyze within 30 days
Storage - store at 4°C until analyzed.

Principle or Procedure

See Reference [a], method 3510A and 8100

Precision

None listed.

Accuracy

None listed.

Quality Control

Samples: batch size 1 to 15 samples.
Blanks: 1 method blank per analytical batch.
Replication: 1 sample duplicate if available; if not, an instrument duplicate per analytical batch.
Recovery control: 1 reagent spike per analytical batch.

Note: solvent or instrument blanks should be run following samples containing high concentrations of hydrocarbons

Initial Instrument Set-Up

The following procedure should be followed to ensure optimum chromatography performance.

- An instrument check standard of equal portions of decane, eicosane, and triacontane (n-C_{10}, n-C_{20}, and n-C_{30} respectively) should be prepared at a concentration of 10 to 100 µg/mL.
- The mixture should be analyzed 10 times using the appropriate GC conditions. The average area ratio of the three compounds should meet the following criteria:

  n-C_{10} peak area should be greater than 80% of n-C_{20}
  n-C_{30} peak area should be greater than 60% of n-C_{20}

Note: Insertion of silanized glass wool into the injection port liner will greatly increase response of the heavier molecular weight hydrocarbons.

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) State of Oregon, Department of Environmental Quality, Laboratories and Applied Research , Organic Section ,"Total Petroleum Hydrocarbons Analytical Methods", OAR 340-122-350, 11 December 90.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Note that Freon extraction methods now deleted.

Volatile Hydrocarbons in Water by GC/FID

Parameters

Volatile Hydrocarbons$_{(nC6-nC10)}$ in water

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
VH_{W6-10}	VHC- F083

Analytical Method

Purge and Trap - Gas Chromatography with Flame Ionization Detection (GC/FID).

Units

mg/L

Introduction

This method measures the collective concentration of Volatile Hydrocarbons (VH_W) in water. Volatile Hydrocarbons (VH) are quantitated against m-xylene and 1,2,4-trimethylbenzene. 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, Lands and Parks (BCMELP) method “Calculation of Volatile Petroleum Hydrocarbons in Solids and Waters”.

The Volatile Hydrocarbons (VH) method is normally used in conjunction with the BCMELP Extractable Petroleum Hydrocarbons (EPH) method. Together, these methods can generate quantitative values for the concentration of most petroleum products. Note that the correlation of these results with the actual concentration of petroleum product in a sample (i.e. accuracy) may be less than would be achieved for single compound analyses.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC6 through nC10 (e.g. VH captures the majority of most unweathered gasolines, mineral spirits, and paint thinners). Petroleum products that are predominantly captured with the EPH parameters are those whose primary components are within the boiling point range of nC10 through nC32 (e.g. EPH captures the majority of most diesel fuels, lubricating oils, greases, hydraulic oils, waxes). Many petroleum products contain components within both the VH and EPH parameter ranges (e.g. kerosenes, jet fuel, and weathered gasolines). Petroleum products that contain a substantial proportion of hydrocarbons with boiling points greater than nC32 will not be accurately quantitated by either of the VH or EPH methods.

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 VH results among

laboratories. British Columbia Ministry of the Water, Land and Air Protection encourages method innovations and supports the performance based methods approach, but recognizes that the application of performance based methods to method-defined aggregate parameters like Volatile Hydrocarbons is somewhat limited.

Every laboratory that uses this method, or a modified version of this method, to report VH_{W6-10} or VPH data to BCWLAP must perform an in-house validation of the method as described in the Method Validation section.

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 compounds, although FID may be more appropriate in cases where sample concentrations exceed the GC/MS calibration range *and* where interferences are not evident.

A dual column GC system with both FID and MS detectors is strongly recommended for this method, so that VH can be determined simultaneously along with targeted MAH parameters like BTEX, styrene, and naphthalene. Analyzing VH and MAHs from the same sample aliquot reduces the impact of sub-sampling variability on the final VPH result.

A slightly higher degree of relative response bias is normally experienced with Purge and Trap than with Direct Injection (the VH solids analytical technique). Purge and Trap was selected over Direct Injection for water samples to achieve the sensitivity needed to meet BCMELP criteria.

Method Summary

Volatile organic compounds are purged from water samples with helium, adsorbed onto a sorbent trap, and then thermally desorbed to a capillary column gas chromatograph equipped with a flame ionization detector.

Matrix

Fresh Water
Waste Water
Marine Water

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 (where possible) any hydrocarbons which may be present as solids or adsorbed to solids within the sample container, but excluding any hydrocarbons which may be adsorbed to the surface of the sample container.

Contamination by carryover from the GC or the Purge and Trap system 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 is suspected.

Any component of the purge gas flow path within the Purge and Trap system can be subject to contamination, and may sometimes require bake-out and/or replacement.

Excessive methanol decreases purge efficiency, can prevent resolution of hexane from the solvent peak, and may cause difficulties with the adsorptive trap and with chromatography. Do not add more than a total of 100 uL of methanol to any sample or calibration standard, and ensure that all samples and calibration standards are closely matrix matched with respect to methanol concentration.

The purging efficiency of aqueous solutions is influenced by pH and ionic strength. Therefore, all samples and calibration standards must be matrix matched with respect to preservatives.

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

Collect samples in 40 mL glass screw-cap vials with Teflon-lined silicone septa. To prevent cross-contamination, it is recommended that only new septa be used. Collect samples with zero headspace.

Preserve all samples using one of the following procedures:

a) Add 2 drops of 50% HCl or 50% H_2SO_4 to each 40mL vial (to a pH of ~ 2), or

b) Add 0.5 mL of 10% by weight $Cu_2SO_4.5H_2O_{(aq)}$ to each 40 mL vial.

The acid preservation technique is referenced to US EPA (1) and (3). The Copper Sulfate preservation technique is referenced to CPPI (2). For samples that will also be analyzed for chlorinated volatile organic compounds, additional preservation with ascorbic acid or sodium thiosulphate may be necessary if residual chlorine is likely to be present. For further details, refer to US EPA (3) Method 524.2.

Store samples away from direct sunlight at (4 $\pm$ 2)°C in an area free from organic solvent vapors.

Maximum holding time prior to analysis is 7 days after sampling. Where holding times are exceeded, data must be qualified.

At least two replicate samples should be taken for each sample location. This allows the laboratory to analyze Field Replicates as desired, and/or to re-analyze any sample if confirmation is required.

Sampling staff are referred to the British Columbia Field Sampling Manual (4) for additional sample collection guidelines.

Apparatus

Glassware and Support Equipment

Glass sparge vessels (5 mL fritted spargers recommended)
Micro-syringes
5 mL glass syringe with wide-bore entry port (not a syringe with a needle)

Purge and Trap Device
The purge and trap device consists of a sample purging chamber, an adsorbent trap, and a mechanism for thermal desorption. Several complete systems are commercially available. Recommended specifications for the components of the system are outlined below. Alterations from these recommendations are permitted, but can influence the relative responses of VH components, and may cause a failure of the Instrument Performance Check acceptance criteria.

Purging Chamber
The purging chamber should be designed to accept 5-20 mL samples with a water column at least 3 cm deep. Helium purge gas should pass through the water column as finely divided bubbles with a diameter of less than 3 mm at their origin. Fritted glass sparge cells are recommended. Needle spargers are permitted if an acceptable relative response of nC10 is achieved in Instrument Performance Checks. Increasing the purge flow and/or purge time will increase the nC10 relative response.

Adsorbent Trap
The recommended adsorbent trap contains 10 cm of Carbopack B, 6 cm of Carboxen 1,000 and 1 cm of Carboxen 1001, packed in 1/8" outside diameter stainless steel tubing (e.g. Supelco VOCARB 3000 K trap). The Carboxen molecular sieve material contained in this trap is not necessary for the analysis of VH components, but permits the simultaneous analysis of gaseous VOCs. This trap may be baked at temperatures up to 270°C, and is relatively hydrophobic. Condition the trap prior to use as recommended by the manufacturer.

Purge and Trap - GC Interface
A direct-split interface between the purge and trap device and the GC is recommended. This permits adequate gas flows (15-20 mL) for thermal desorption of the trap, and dramatically reduces chromatographic interferences caused by trapped water. Sharp chromatographic peaks for all VOC components may be achieved without cryogenic focusing.

Gas Chromatograph (GC)
A temperature programmable capillary gas chromatograph is required. A heated split inlet is recommended for the GC - Purge and Trap interface.

It is strongly recommended that the GC be configured as a single inlet, dual detector, dual column system, with FID and MS as the detectors. This configuration permits the simultaneous analysis of VH by FID, and of BTEX and other VOCs by GC/MS. See the Purge and Trap Conditions section and the Gas Chromatograph Conditions section for further details.

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}. FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

Use of a dual column GC system equipped with both Mass Spectrometric and Flame Ionization Detectors is strongly recommended, as described in

the Purge and Trap Conditions section and the Gas Chromatograph Conditions section.

Chromatographic Column
The reference column for this method is a 30 meter, 0.53mm internal diameter capillary column with a 1.5 um coating of 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified.

With a dual column GC/MS-FID configuration, any appropriate GC column may be used for the simultaneous analysis of target analytes by GC/MS, but a column of 30 meters in length and 0.25 mm internal diameter is recommended to achieve a reasonable division of flow between the two columns using a single GC head pressure. Refer to the Gas Chromatograph Conditions section for further details.

Reagents and Standards

Reagents
Acetone (2-propanone)
Methanol - Purge and Trap grade
Organic-free reagent water - Refer to US EPA (3) Method 524.2, section 7.2.2.
Preservatives – one of the following is required:
- Hydrochloric acid (HCl), diluted 1:1 with reagent water
- Sulfuric acid (H_2SO_4), diluted 1:1 with reagent water
- 10% Copper Sulfate ($CuSO_4.5H_2O$) by weight in reagent water

Calibration Standard Stock Solution
Prepare a Calibration Standard Stock Solution in methanol containing 5,000 µg/mL of each of hexane (nC6), octane (nC8), decane (nC10), benzene, toluene, ethylbenzene, meta-xylene, ortho-xylene, and 1,2,4-trimethylbenzene. This mixture may be purchased commercially or prepared from neat standards. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Calibration Standard
Prepare a 50 µg/mL Calibration Standard in methanol by diluting the 5,000 µg/mL stock standard. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Add 10 uL of this solution to 5 mL of reagent water to create a 0.100 µg/mL Calibration Standard.

Note: The concentration and/or amounts above may not be applicable if sample volumes or GC split ratios are varied from those specified in this method.

Control Standard Stock Solution
Prepare a Control Standard Stock Solution containing 5,000 µg/mL meta-xylene and 5,000 µg/mL 1,2,4-trimethylbenzene in methanol. This solution may also contain other target analytes, and may be purchased commercially or prepared from neat compounds. It must be prepared from a different source than the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions). Store refrigerated at (4 ± 4)°C.

Control Standard
Prepare a 250 µg/mL Control Standard by diluting the 5,000 µg/mL Control Standard Stock Solution in methanol. Add 10 uL of this solution to 5 mL of reagent water to create a 0.500 µg/mL Control Standard.

Note: The concentration and/or amounts above may not be applicable if sample volumes or GC split ratios are varied from those specified in this method.

Gasoline Stock Solution
Prepare a 50,000 µg/mL stock solution of unleaded gasoline in methanol. Prepare the solution by weight (e.g. weigh 0.250g gasoline into a 5.00 mL volumetric flask, or use a syringe to dispense an appropriate volume of gasoline with consideration of its density). Any unweathered, fresh source of gasoline is acceptable. Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Note: The 50,000 µg/mL concentration above can be referred to as the "product concentration" of the solution, where the product is in this case gasoline. It is important to note that the product concentration of the solution is not equivalent to its VH_{W6-10} concentration.

Detection Limit Check Standard Solution
Dilute the 50,000 µg/mL Gasoline Stock Solution to prepare a Detection Limit (DL) Check Standard Solution in methanol. Prepare the solution at a concentration that permits addition of 10 – 20 uL of solution to an aqueous sample to achieve an aqueous concentration that is approximately equal to the Reporting Detection Limit for VH_{W6-10}. This standard is required for Initial Calibration QC (Detection Limit Check section). Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Refer to the Determination of DL Check Standrad Concentration and VH_{W6-10} Target section under Method Validation for the procedure to determine an appropriate concentration for this solution.

Gasoline Method Spike Solution
If Gasoline Method Spikes will be analyzed (see the Gasoline Method Spike section), prepare a Gasoline Method Spike Solution at a suitable concentration by diluting the Gasoline Stock Solution into methanol. Concentrations ranging from 50 - 5,000 µg/mL of gasoline may be appropriate, depending on the desired Method Spike concentrations. Select a spike solution concentration such that 10uL of the Gasoline Method Spike Solution can be added directly to the sparge vessel. Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Quality Control (QC)

Table I-21 summarizes all the required and recommended calibration and QC components of this method. Each of these components is described in detail in this section.

Table I-21: Summary of VH_W QC and Calibration Requirements and Recommendations		
QC Component	**Minimum Frequency**	**Minimum Acceptance Criterion**
Instrument Performance QC		
Instrument Performance Check	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Relative response ratios must be 0.6-1.4 for all components
Calibration QC and Verification		
Control Standard	1/analysis batch	Within 15% of expected concentration
Detection Limit Check Standard	1/analysis batch	50 – 150% of VH target
Ongoing Verification of Calibration	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Within 25% of previous std & Within 35% of initial calibration (in continuing calibration mode).
Method QC		
Method Blank	1/preparation batch	< reported detection limit
Gasoline Method Spike	Not required	None
Laboratory and Field Sample Replicates	Not required	None
Surrogate Compounds	Not required	None

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 (5). 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 Purge and Trap - GC in a set that is referred to as an analysis batch. In many cases preparation and analysis are conducted together as a single operation, in which case both batches will be identical.

If any of the specified acceptance criteria for Instrument Performance QC, Initial Calibration QC, or Method QC cannot be met for the analysis of a given sample, then the data reported for that sample must be appropriately qualified.

Instrument Performance QC

Instrument 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.

The Calibration Standard is used for initial calibration (see Initial Calibration section) and for ongoing verification of calibration (see the Ongoing Verification of Calibration (Verification Standards) section). In addition, it is used for the Instrument Performance Check to do the following:

a) Measure and control relative response ratios of specified VH components,
b) Determine retention time windows for VH integration ranges,
c) Confirm resolution of hexane (nC6) from the solvent peak.

One 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 (nC6), octane (nC8), benzene, toluene, and ethylbenzene against meta-xylene. Compare the peak areas of decane (nC10) and o-xylene against 1,2,4-trimethylbenzene. For all compounds within the mixture, these ratios should normally fall between 0.70 and 1.30. Acceptance criteria for relative response ratios are 0.6 – 1.4 for all components of the Instrument Performance Check. 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
Not applicable. See Method Blank.

Control Standard
REQUIRED - minimum 1 per analysis batch of no more than 100 samples.

Analyze a Control Standard (see the Control Standards 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, and to verify calibration linearity if single-point calibration is used. Where possible, the Control Standard should be traceable to national chemical metrology standards.

If single-point calibration is used, the concentration of the Control Standard must differ from the concentration of the Calibration Standard by at least a factor of five.

Note: At concentrations above ~50-100 ng on-column, chromatographic peak shapes may be distorted due to column phase overload, but FID responses are not normally affected.

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 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 analysis batch of no more than 100 samples. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low level gasoline solution.

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 Solution section).

The procedure for determining the target concentration for this standard is described under Method Validation in the Determination of DL Check Standrad Concentration and VH_{W6-10} Target section. Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the VH_{W6-10} target (calculated as described in the Determination of DL Check Standrad Concentration and VH_{W6-10} Target section). Data reports must be qualified if this acceptance criterion is not met for the analysis batch in which the samples were run.

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 50 samples. Prepare a Method Blank using reagent water. Extract and analyze as described in the Sample Preparation Procedure section and the GC Analysis-Purge and Trap section.

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 (increasing the Reported Detection Limit of affected sample results to a level above that of the Method Blank result(s) is acceptable).

Method Performance Check Spike
Not applicable. A Method Performance Check Spike for water samples by purge and trap would be prepared, analyzed, and interpreted exactly as an Instrument Performance Check (see the Instrument Performance Check section).

Gasoline Method Spike
OPTIONAL. Prepare a Gasoline Method Spike by fortifying reagent water with an accurate volume of a Gasoline Method Spike Solution in methanol (see the Gasoline Method Spike Solution section). Spikes may be prepared at any reasonable concentration, depending on the objective.

Determine the target for VH_{W6-10} by analyzing several replicates of the Gasoline Method Spike Solution prepared in water at the selected spike concentration.

A Gasoline Method Spike prepared in this way normally provides information about method precision, but not about method bias (accuracy). This is partly because the purge and trap process *defines* the VH_{W6-10} parameter for water samples, and partly because any losses incurred during the purge and trap process will also affect the measurement of “targets” (i.e. it is normal to achieve 100% recovery, on average, for Gasoline Method Spikes where the

targets are determined experimentally). Acceptance criteria are at the discretion of the laboratory.

Laboratory Sample Replicates and 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 (4), 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*
OPTIONAL. The use of one or more Surrogate Compounds for VH is at the discretion of the laboratory. 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.

Note that sample interferences will often preclude the accurate measurement of any surrogate by FID. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

*Surrogate Compounds have chemical characteristics similar to those of analytes, but provide analytical response that is distinct from analytes. They are added to samples prior to sample preparation. Surrogate percent recovery measurements are used as Method QC to estimate sample preparation losses and matrix effects. They are only useful when not subject to measurement interferences.

Sample Preparation Procedure

All field samples, calibration standards, and QC samples must be matrix matched (including preservatives).

Prepare calibration standards directly in the sparge vessels. To 5 mL of reagent water, add the same amount and type of preservative as was added to samples. Then add 10.0 uL of the 50 µg/mL calibration standard in methanol using a 10 uL syringe, with the tip of the syringe needle below the surface of the water.

Use a 5 mL syringe with wide-bore entry port to measure (5.0 $\pm$ 0.1) mL of sample into a sparge vessel (ensure the sample is not exposed to strong vacuum in the syringe). If the sample is suspected to contain high levels of volatile organics, less sample may be used, with the total volume made to 5 mL with reagent water.

Dispense all samples as quickly as possible, without allowing them to warm to room temperature (**Note**: the density of water changes by only 0.16% between 0 and 20°C).

Prepare appropriate and required Method QC samples in sparge vessels as described in the Method QC section. Use 5 mL of reagent water for the Method Blank, Calibration Standards, and Gasoline Method Spike samples.

If desired, add an appropriate amount of Surrogate Compound solution in methanol directly to each sparge vessel (refer to the Surrogate Compound section).

The total volume of added methanol must be the same for all samples and standards, to within ± 20 uL, and the total amount of methanol in any sample or calibration standard must not exceed 100 uL.

GC Analysis Procedure

Purge and Trap

Place the sparge vessel with prepared sample onto the autosampler or purging device and initiate the purge and trap process. The sample is purged with helium and volatile compounds are trapped on a sorbent trap. When purging is complete, the sorbent trap is heated and the compounds are thermally desorbed to the gas chromatograph.

Purge and Trap Conditions

Sparge vessel type:	5 mL fritted glass (recommended)
Trap type:	Supelco VOCARB 3000 K trap (recommended)
Purge gas:	helium (ultra high purity)
Purge gas flow rate:	40 mL / minute
Trap temp at purge:	40°C
Purge time:	11 minutes
Dry purge time:	5 minutes
Desorb temperature:	250°C
Desorb time:	6 minutes
Bake temperature:	260°C
Bake time:	4 minutes
Valve & Line temps:	150-200°C

Gas Chromatograph Conditions

GC conditions are described for a single inlet, dual column GC-MS/FID system, as recommended in the Purge and Trap Device section:

Carrier Gas:	Helium (from Purge & Trap desorb output)
Head pressure:	9.0 psi @ 40°C (with column dimensions as specified)
FID column:	DB-1, 30 m, 0.53 mm id, 1.5 um phase
FID column flow:	15 mL/minute @ 9.0 psi & 40°C (88 cm/sec linear velocity)
MS column:	DB-1, 30m, 0.25 mm, 1.5 um phase (suggested)
MS column flow:	1.2 mL/minute @ 9.0 psi & 40°C (39 cm/sec linear velocity)
Constant flow:	recommended (set to be constant for FID column)
Injector temp:	200°C
Injection mode:	split (connect P&T desorb exit to GC injection port inlet)
GC liner type:	2 mm id splitless liner, no glass wool
Initial inlet purge:	ON
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)
FID gas flows:	as recommended by manufacturer

Note: Split ratio is defined as [(total desorb flow):(column flow)] for each column that is configured as described. On a Hewlett Packard 5890 or 6890 GC, total desorb flow equals the combined column flows plus any flows out the injection port split vent and septum purge vent. Total purge and trap desorb flow must be greater than the combined column flows (as determined

by head pressure and GC temperature set-points), or the GC will not maintain head pressure.

Initial Calibration
Analyze a 0.100 µg/mL Calibration Standard at the beginning of each new analytical batch (see the Calibration Standards section).

Note: This concentration may not be applicable if sample volumes or GC split ratios are varied significantly from those specified in this method.

Calibration is by single or multi-point external standard technique, using meta-xylene and 1,2,4-trimethylbenzene.

A continuing calibration is recommended (i.e. reslope the calibration with each Verification Standard). Changes in response between standards must be monitored and controlled (see the Ongoing Verification of Calibration (Verification Standards) section).

Linear calibration must be used for this method. Either single or multi-point calibrations are acceptable, due to the linear response of GC/FID systems. If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control Standard section).

For each analysis batch, verify that the GC – Purge and Trap system is performing adequately by conducting all checks specified in the Instrument Performance QC section (see the Instrument Performance QC section), ensuring that all specified acceptance criteria are met.

For each analysis batch, verify that the initial calibration is adequate by performing all tests specified in the Initial Calibration QC section, ensuring that all specified acceptance criteria are met.

Calculate the Calibration Factors (CFs) for meta-xylene and 1,2,4-trimethylbenzene in the Calibration Standard using the equation below. The Calibration Factors are based on the total weight of analyte in the sparge vessel:

$$CF_{m\text{-}Xylene} \text{ in } \mu g^{-1} = \frac{\text{Area of meta-xylene peak}}{\text{meta-xylene amount (µg in sparge vessel)}}$$

$$CF_{1,2,4\text{-}Trimethylbenzene} \text{ in } \mu g^{-1} = \frac{\text{Area of 1,2,4-trimethylbenzene peak}}{\text{1,2,4-trimethylbenzene amount (µg in sparge vessel)}}$$

Ongoing Verification of Calibration (Verification Standards)
After initial calibration, the Calibration Factors ($CF_{m\text{-}Xylene}$ and $CF_{1,2,4\text{-}Trimethylbenznene}$) must be verified, at minimum, after every 12 hours of continuous operation. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

Use a Calibration Standard as a Verification Standard (see the Calibration Standards section).

Under a continuing calibration mode, if either Calibration Factor changes by more than 25% from the previous standard, or by more than 35% from the

initial calibration standard, then corrective action must be taken, and samples analyzed after the last acceptable standard must be re-run.

Alternatively, an initial calibration may be used for as long as both Calibration Factors remain within 15% of their initial values. If this criterion is exceeded, the calibration may be updated using the Verification Standard Calibration Factors, but only if the continuing calibration acceptance criteria specified above are satisfied.

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_{W6-10}

The Volatile Hydrocarbons parameter is defined to include all GC/FID peaks eluting between hexane (nC6) and decane (nC10). VH_{W6-10} is quantitated by summing the results for two sub-ranges within the nC6-nC10 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 the calculated by summing the two results.

Note: Calculating VH using two sub-ranges reduces the impact of relative response biases which exist between higher and lower volatility VH components in most purge and trap systems.

Determine the total integrated peak area of each VH sub-range, where:

a) The $VH_{W(6-oX)}$ range begins at the apex of the nC6 peak and ends at the apex of the o-xylene peak.
b) The $VH_{W(oX-10)}$ range begins at the apex of the o-xylene peak and ends at the apex of the nC10 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch, and should be established using marker compound concentrations that do not overload the liquid phase of the GC column.

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 potential error may exceed 1-2%.

Calculations

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 calibration standard. $VH_{W(oX-10)}$ is quantitated against the 1,2,4-trimethylbenzene calibration standard.

If any VH-range Surrogate Compounds are added to samples, the contribution to VH of those Surrogates must be subtracted from calculated VH results. Because Surrogate Compounds frequently experience FID interference, it is most practical to subtract the actual spiked concentrations of Surrogate Compounds from calculated VH concentrations. No Surrogate Compounds within the VH-range should be added such that their concentration exceeds the Reporting Detection Limit for $VH_{W6-10.}$

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 Surrogate Conc* (µg/mL)

* Only Surrogates (if any) that elute within the VH_{W6-10} range are subtracted.

$VH_{W(6-oX)}$ (µg/mL) = $A_{(6-oX)}$ / ($CF_{m\text{-}Xylene}$ x Vol)

$VH_{W(oX-10)}$ (µg/mL) = $A_{(oX-10)}$ / ($CF_{1,2,4\text{-}Trimethylbenzene}$ x Vol)

where:

$A_{(6-oX)}$ = Total area between nC6 and ortho-xylene for the sample chromatogram.
$A_{(oX-10)}$ = Total area between ortho-xylene and nC10 for the sample chromatogram.
$CF_{m\text{-}Xylene}$ = Calibration Factor for meta-xylene standard (μg^{-1})
$CF_{1,2,4\text{-}Trimethylbenzene}$ = Calibration Factor for 1,2,4-trimethylbenzene standard (μg^{-1})
Vol = Volume of sample purged (mL)

When reporting to BCMELP, report VH_{W6-10} results for water samples in units of µg/L (ppb). Multiply µg/mL (ppm) results (as calculated above) by 1,000 to convert results to units of µg/L.

Diluting High Level Samples
Where sample results exceed the linear working range of the GC-FID system, they must be diluted and re-analyzed at a more appropriate concentration. Note that over-dilution of samples can introduce significant error to VH results. Diluted samples should be prepared such that their VH_{W6-10} areas fall within the linear working range of the GC-FID system, as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section.

Where samples are diluted prior to analysis, Reporting Detection Limits must be increased accordingly.

Method Validation

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 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_W Concentrations of a Petroleum 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 $VH_{W6\text{-}10}$ Concentrations are required within this method for the following purposes:

a) determination of GC/FID linear range for VH_W (i.e. calibration range),
b) determination of VH_W Instrument Detection Limits (IDLs),
c) preparation of Detection Limit Check Standards and Method Spike Solutions,
d) calculation of VH_W targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual $VH_{W6\text{-}10}$ Concentration* of an aqueous petroleum product solution:

a) Prepare the petroleum product in aqueous solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for $VH_{W6\text{-}10}$ (see the Establishing Instrument Calibration Working Range and Estimated IDLs section). A petroleum product concentration of at least 5 µg/mL in water is recommended for this purpose.

b) Perform replicate analyses of the aqueous petroleum product solution prepared in (i) using the instrumental conditions specified within this method. A minimum of 7 replicates is recommended. Do not dilute the solution prior to analysis. Determine the average measured concentration of $VH_{W6\text{-}10}$ using the calculations specified in the Calculations section. In the example below, the measured $VH_{W6\text{-}10}$ concentration is denoted as $[VH_{W6\text{-}10,measured}]$, where the square brackets denote concentration. Percent Relative Standard Deviations (%RSDs) of these values may also be determined, and may be useful to set statistical warning and control limits for some applications.

c) Calculate the percentage that the $VH_{W6\text{-}10}$ range represents of the total petroleum product concentration. Example (for a given source of gasoline):

$$\%VH_{W6\text{-}10} \text{ in gasoline} = 100\% \times [VH_{W6\text{-}10,measured}] \ / \ [Gasoline_{grav}]$$

where:

[ ]	=	symbol for concentration
$[VH_{W6\text{-}10}$, measured]	=	measured $[VH_{W6\text{-}10}]$ of a solution of gasoline in water.
$[Gasoline_{grav}]$	=	actual [Gasoline] in weight of gasoline / volume water for the same solution.
Units	=	same for both concentrations (e.g. µg/mL).

Note: The percentage of $VH_{W6\text{-}10}$ in gasoline is considerably less than 100% (typically about 50%) because not all components of gasoline fall within the nC6 - nC10 boiling point range.

d) To calculate the *Actual $VH_{W6\text{-}10}$ Concentrations* of other concentrations of the same product, use the $VH_{W6\text{-}10}$ percentage relative to the total petroleum product concentration as follows (the gasoline example is continued):

Actual $VH_{W6\text{-}10}$ conc. in gasoline = (%$VH_{W6\text{-}10}$ in gasoline) / 100% x *[$Gasoline_{grav}$]*

where:
[$Gasoline_{grav}$] = the conc. of gasoline (in wt. gasoline / volume water) of any solution.

Establishing Instrument Calibration Working Range and Estimated IDLs
Establish the linear working range of the GC/FID system for $VH_{W6\text{-}10}$ 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 $VH_{W6\text{-}10}$ results for each solution using the procedure described in the Calculations section. These are referred to below as *Calculated $VH_{W6\text{-}10}$ Results*.

Follow the procedure in the Calculation of Actual VH_W Concentrations of a Petroleum Reference Solution section to calculate the *Actual $VH_{W6\text{-}10}$ Concentrations* for all of the above solutions.

Make a plot of *Calculated $VH_{W6\text{-}10}$ Results* (y-axis) versus *Actual $VH_{W6\text{-}10}$ Concentrations* (x-axis), and determine the linear working range of $VH_{W6\text{-}10}$.

Instrument accuracy for $VH_{W6\text{-}10}$ is measured as *Calculated $VH_{W6\text{-}10}$ Results* / *Actual $VH_{W6\text{-}10}$ Concentrations.* As $VH_{W6\text{-}10}$ concentration approaches the Instrument Detection Limit (IDL), instrument accuracy decreases because the less abundant components of the petroleum hydrocarbon blend (e.g. gasoline) cease to be detected. For the purposes of this method, the Instrument Detection Limit for the $VH_{W6\text{-}10}$ parameter is defined as the lowest $VH_{W6\text{-}10}$ concentration at which instrument accuracy consistently falls within the range of 70-130%. However, a gasoline chromatogram at the IDL must still resemble chromatograms of higher concentrations. At the IDL, any chromatographic peak that normally comprises more than 5% of total $VH_{W6\text{-}10}$ area must still be visible as a distinct peak; this requirement takes precedence over the 70-130% accuracy requirement.

The IDL is expressed in units of *Actual $VH_{W6\text{-}10}$ Concentration*.

Establishing Method Detection Limits
Determine the Method Detection Limits (MDLs) at the 95% confidence level for $VH_{W6\text{-}10}$, using the procedure outlined in the British Columbia Environmental Laboratory Manual (7). This method requires the use of the procedure described below, which is one of several generic approaches described in the BC Environmental Laboratory Manual.

Select a concentration for method spikes of gasoline into water of between one and three times the estimated IDL for $VH_{W6\text{-}10}$ (as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section). Prepare and analyze at least 7 method spikes at this concentration. Use a Gasoline Method Spike Solution to prepare these method spikes (see the Gasoline Method Spike Solution section).

Calculate the Method Detection Limit (MDL) at the 95% confidence level for VH_{W6-10} using the calculations described in the BC Environmental Laboratory Manual (7).

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 Concentrations of a Petroleum Reference Solution section. If this condition is not met, repeat the MDL determination at a higher spike level.

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. Reporting Detection Limits for VH_{W6-10} must be greater than or equal to the Method Detection Limits (at the 95% confidence level) that were experimentally determined in-house using the procedure described in the Establishing Method Detection Limits section.

Ensure that calculated Method Detection Limits and Reporting Detection Limits are below any regulatory criteria values or regulatory standards specified by BCMELP or other applicable regulatory body. For BC requirements, refer to BCMELP method "Calculation of Volatile Petroleum Hydrocarbons in Solids or Water" (July, 99).

Determination of DL Check Standard Concentration and VH_{W6-10} Target

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 product concentration units to (and from) VH_{W6-10} concentration units (in aqueous solution).

Results from the Calculation of Actual VH_W Concentrations 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:

a) Calculate the percentage of the total gasoline concentration that VH_{W6-10} represents, using the procedure described in the Calculation of Actual VH_W Concentrations of a Petroleum Reference Solution section. Typically, VH_{W6-10} represents about 50% of the total gasoline concentration. This percentage is less than 100% because not all components of gasoline fall within the nC6 - nC10 boiling point range.

b) Determine the concentration of gasoline in water that corresponds to the VH_{W6-10} Reporting Detection Limit. Use the calculated percentage from (a) to calculate this gasoline concentration:

   [Gasoline in water] equiv. to VH_{W6-10} DL =

   100 x (Reporting DL for VH_{W6-10}) / (%VH_{W6-10} 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. Prepare a Detection Limit Standard Solution (see the Gasoline Method Spike Solution section) at a concentration such that adding 10 – 20 uL of it to a reagent water sample will produce a Detection Limit Standard at the selected concentration. The DL Check Standard can then be used to verify that the Reporting Detection Limit for $VH_{W6\text{-}10}$ remains valid.

Example: For a Reporting Detection Limit of 100 µg/L $VH_{W6\text{-}10}$ with a sample size of 5 mL, add 10 uL 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 $VH_{W6\text{-}10}$ in the gasoline is 50%, then the aqueous concentration of $VH_{W6\text{-}10}$ in the Detection Limit Check Standard will be 100 µg/mL.

c) Calculate the target for $VH_{W6\text{-}10}$ in the Detection Limit Check Standard by multiplying the concentration selected in (b) by the $VH_{W6\text{-}10}$ percentage from (a).

Target for $VH_{W6\text{-}10}$ =

(DL Std. gasoline concentration in water) x (%$VH_{W6\text{-}10}$ in gasoline)

Accuracy and Precision

For a limited period of time, individual laboratories may assess their accuracy and/or precision for this method by analyzing replicates of the 1998 BCMELP Hydrocarbon Round Robin samples, and comparing results against single laboratory and interlaboratory consensus values. This is not a formal requirement for the validation of this method, but is strongly recommended.

Alternatively, multiple method spikes of an appropriate petroleum product (unweathered gasoline is recommended) may be used to assess the method, although less information can be derived about accuracy without interlaboratory consensus data. Better measures of overall method bias and accuracy are obtained from analysis of BCMELP Interlaboratory Study samples, and from Instrument Performance Checks.

Determine Method Spike targets using *Actual VH_W Concentrations* of the spike solution by following the procedure outlined in the Calculation of Actual VH_W Concentrations of a Petroleum Reference Solution section.

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 a needle sparger with 20 mL sample volumes, and using a purge flow of 60 mL / minute. Otherwise, all instrument conditions were as described in the Sample Preparation Procedure section and the GC Analysis-Purge and Trap section.

VH_W Instrument Performance Check Data

Multiple laboratory (Round Robin) data and single laboratory data for Instrument Performance Checks are presented in Table I-22. These

samples were analyzed as described in the Instrument Performance Check section. Note that for purge and trap, instrument performance is equivalent to method performance.

Table I-22: VHw Instrument / Method Performance Check Data						
	Round Robin Results			Single Lab Results		
Relative Response	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Hexane (nC6)[1]	5	0.96	25.8%	7	0.98	0.3%
Benzene[1]	5	1.09	9.4%	7	1.09	0.1%
Toluene[1]	5	1.04	4.9%	7	1.05	0.1%
Octane (nC8)[1]	5	0.90	25.1%	7	0.98	0.0%
Ethylbenzene[1]	5	0.99	4.1%	7	1.01	0.0%
m,p-Xylene[1]	5	1.00	n/a	7	1.00	n/a
o-Xylene[2]	4	1.08	6.4%	7	0.96	0.0%
1,2,4-Trimethylbenzene[2]	5	1.00	n/a	7	1.00	n/a
Decane (nC10)[2]	4	0.76	24.0%	7	0.86	0.3%

Method Detection Limit Data

The Method Detection Limit data reported in Table I-23 was obtained from the 1998 Single Laboratory Validation Study, and was generated as described in the Establishing Method Detection Limits section. The VH_W *target* was determined by analysis of a higher concentration of the same spike solution. Please note that the data presented demonstrates an achievable MDL; each laboratory must determine the MDL that applies to their individual circumstances.

Table I-23: VH_W Method Detection Limits (Single Laboratory Data)													
Units = µg/L	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**Mean**	**Std. Dev.**	**Target**	**Mean**	**MDL**
VH_{W6-10}	24	36	29	31	31	32	29	30	**30.3**	**3.4**	**25.0**	**121%**	**13**

VH_W Gasoline Method Spike Data

Multiple laboratory (Round Robin) data and single laboratory data for Gasoline Method Spikes are presented in Tables I-24 and I-25. These samples were analyzed as described in the Gasoline Method Spike section. Two different concentrations of gasoline spikes were performed, at 2,000 µg/L and 10,000 µg/L of gasoline in reagent water. MAH and calculated VPH_W results are also presented for the same samples.

1 Relative response calculated against m,p-Xylene.

2 Relative response calculated against 1,2,4-Trimethybenzene.

Table I-24: VHw Low Level Method Spike Data

	Round Robin Results			Single Lab Results		
VH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
$VH_{W6\text{-}oXylene}$	5	892	27.3%	8	864	5.0%
$VH_{WoXylene\text{-}10}$	5	117	42.9%	8	169	4.7%
$VH_{W6\text{-}10}$	5	1010	25.6%	8	1033	4.7%
VPHw	4	880	26.7%	8	806	6.0%
MAH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Benzene	6	17.1	13.5%	8	15.4	0.8%
Toluene	6	90.0	19.6%	8	107	3.0%
Octane (nC8)	6	21.4	18.7%	8	20.5	1.6%
Ethylbenzene	6	72.9	37.6%	8	60.2	2.3%
m,p-Xylene	6	25.4	15.7%	8	23.7	1.7%
o-Xylene	4	1.08	6.4%	7	0.96	0.0%

Table I-25: VHw High Level Method Spike Data

	Round Robin Results			Single Lab Results		
VH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
$VH_{W6\text{-}oXylene}$	5	4688	29.2%	8	4259	2.2%
$VH_{WoXylene\text{-}10}$	5	725	39.9%	8	1072	1.0%
$VH_{W6\text{-}10}$	5	5412	25.4%	8	5330	1.8%
VPHw	3	3817	16.1%	8	4195	2.1%
MAH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Benzene	4	84.6	18.4%	8	76.8	0.8%
Toluene	4	466	17.5%	8	536	3.0%
Ethylbenzene	4	103	27.9%	8	102	1.6%
m,p-Xylene	4	323	27.7%	8	301	2.3%
o-Xylene	4	121	24.8%	8	119	1.7%

Use of Alternative Methods

This method contains several 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 $VH_{W6\text{-}10}$ 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 BCMELP:

a) 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.

b) "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.

c) All samples must be preserved using one of the preservation techniques specified in the Sample Collection and Preservation section. All field samples, calibration standards, and QC samples must be matrix matched prior to analysis.

d) Maximum holding time prior to Purge & Trap analysis is 7 days after sampling. Where holding times are exceeded, data must be qualified.

e) Purge and Trap is the required sample extraction / introduction mechanism.

f) The amount of methanol must be equivalent among samples and calibration standards, to within 20 uL. The total amount of methanol in any sample or calibration standard must not exceed 100 uL.

g) If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control Standard section).

h) Gas Chromatography with Flame Ionization Detection is required for measurement of VH_W.

i) GC column must be a capillary column.

j) GC column stationary phase must be 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent).

k) Meta-xylene (or meta and para-xylenes) and 1,2,4,-trimethylbenzene must be used as the calibration standards for $VH_{W6-10.}$

l) Calibration stability must be monitored as described in the Ongoing Verification of Calibration (Verification Standards) section.

m) VH_{W6-10} 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 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 BCMELP. This information must be available in the event of audit by BCMELP.

Pay particular attention to the results of Instrument Performance Checks (see the Instrument Performance Check section), since these checks are designed to identify potential sources of instrument and method biases. 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 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:

a) Apparatus
b) Reagents and Standards
c) Sample Preparation Procedure
d) Purge and Trap Conditions
e) Gas Chromatograph Conditions

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

Modifications Where Equivalence Testing is Required
None. Substantial modifications to this method are not permitted. Minor modifications to the method are permitted, and are covered under the Modifications Where Equivalence Testing is Not Required section.

References

a) US EPA, Test Methods For Evaluating Solid Waste (SW-846), Chapter 2, Table 2-36, Containers, Preservations Techniques, and Holding Times for Aqueous Matrices, Revision 3, December 1996.
b) CPPI (Canadian Petroleum Products Institute), Inter-Laboratory Study #3 to Evaluate the Analytical Variability of Volatile Organics, Phenol, and Sulfide Procedures, CPPI Report No. 92-1, March 1992.
c) J.W. Eichelberger et al., Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1992, Method 524.2 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography / Mass Spectrometry, Revision 4.0.
e) 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 E.
f) Canadian Standards Association, January 1995, Requirements for the Competence of Environmental Laboratories, CAN/CSA-Z753.
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) 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, section 3 (Protocol for Setting Method Detection Limits).

i) Massachusetts Department of Environmental Protection, January 1998, Method for the Determination of Volatile Petroleum Hydrocarbons (VPH).

Disclaimer

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

Acknowledgments

Mark Hugdahl and Scott Hannam of ASL Analytical Service Laboratories developed and wrote this method. ASL Analytical Service Laboratories analyzed and compiled the Single Laboratory Data.

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BCMELP 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.

Revision History

March 1997:	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Water.
1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
July 1999:	Finalization of present method based on results of a vetting round robin.
December 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.

Volatile Hydrocarbons in Solids by GC/FID

Parameters

Volatile Hydrocarbons$_{(nC6-nC10)}$ in solids

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
VH_{S6-10}	VHC- F084

Analytical Method

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

Units

µg/g

Introduction

This method measures the collective concentration of Volatile Hydrocarbons in solids (VH_S). Volatile Hydrocarbons (VH) are quantitated against meta-xylene and 1,2,4-trimethybenzene. 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 Ministry of Environment, Lands and Parks (BCMELP) method “Calculation of Volatile Petroleum Hydrocarbons in Solids and Waters”.

The Volatile Hydrocarbons (VH) method is normally used in conjunction with the BCMELP Extractable Petroleum Hydrocarbons (EPH) method. Together, these methods can generate quantitative values for the concentration of most petroleum products. Note that the correlation of these results with the actual concentration of petroleum product in a sample (i.e. accuracy) may be less than would be achieved for single compound analyses.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC6 through nC10 (e.g. VH captures the majority of most unweathered gasolines, mineral spirits, and paint thinners). Petroleum products that are predominantly captured with the EPH parameters are those whose primary components are within the boiling point range of nC10 through nC32 (e.g. EPH captures the majority of most diesel fuels, lubricating oils, greases, hydraulic oils, waxes). Many petroleum products contain components within both the VH and EPH parameter ranges (e.g. kerosenes, jet fuel, and weathered gasolines). Petroleum products that contain a substantial proportion of hydrocarbons with boiling points greater than nC32 will not be accurately quantitated by either of the VH or EPH methods.
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 VH results among laboratories. British Columbia Ministry of the 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 Volatile Hydrocarbons is somewhat limited.

Every laboratory that uses this method, or a modified version of this method, to report VH_{S6-10} or VPH data to BCMELP must perform an in-house validation of the method as described in the Method Validation section.

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e. MAHs). However, the methanol extract produced by this method can and should be used for the analysis of targeted MAHs by selective detector (GC/MS is strongly recommended).

Method Summary

Wet solids samples are extracted with methanol using a mechanical shaker. Extracts are directly analyzed by capillary column gas chromatography with flame ionization detection.

Matrix

Soil
Sediment
Marine Sediment

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 diminished (especially when refrigerated). Therefore, use a 2:1 ratio of methanol : wet solids for samples with moisture contents of less than approximately 50%, and use a 3:1 ratio of methanol : wet solids for samples with moisture contents of greater than approximately 50% (see the Sample Preparation section).

Detection limits may be elevated for samples with moisture contents exceeding approximately 50%.

Some highly contaminated samples do not mix well with methanol, and would therefore be poorly extracted by methanol (e.g. oil soaked soils/sediments). For such samples, acetone must be substituted as the extraction solvent (see the Sample Preparation section – Solvent Substitution Requirement).

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 Reporting Detection Limits is suspected.

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

Collect samples with minimal headspace in glass wide-mouth jars with Teflon-lined lids. No chemical preservation is recommended. Store samples away from direct sunlight at (4 ± 2)°C in an area free from organic solvent vapors.

Maximum holding time prior to extraction is 7 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

Sampling staff are referred to the British Columbia Field Sampling Manual (1) for additional sample collection guidelines.

Apparatus

Glassware and Support Equipment
Extraction tubes (e.g. 50 mL centrifuge tubes with caps and Teflon-lined lids)

Mechanical shaker device
Micro-syringes
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 VH_{S6-10}. FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

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

Chromatographic Column
The reference column for this method is a 30 meter, 0.53 mm internal diameter capillary column with a 1.5 um coating of 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type must not be modified.

Reagents and Standards

Reagents
Acetone (2-propanone)
Methanol - Purge and Trap grade
Organic-free reagent water – Refer to US EPA (2) Method 524.2, section 7.2.2.
Clean soil/sediment matrix (e.g. Ocean Construction Sakrete “Play Sand”)*.

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

Calibration Standard Stock Solution
Prepare a Calibration Standard Stock Solution in methanol containing 5,000 µg/mL of each of hexane (nC6), octane (nC8), decane (nC10), benzene, toluene, ethylbenzene, meta-xylene, ortho-xylene, and 1,2,4-trimethylbenzene. This mixture may be purchased commercially or prepared from neat standards. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Calibration Standard
Prepare a 50 µg/mL Calibration Standard in methanol by diluting the 5,000 µg/mL stock standard. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Control Standard Stock Solution
Prepare a Control Standard Stock Solution containing 5,000 µg/mL meta-xylene and 5,000 µg/mL 1,2,4-trimethylbenzene in methanol. This solution may also contain other target analytes, and may be purchased commercially or prepared from neat compounds. It must be prepared from a different source than the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions). Store refrigerated at (4 ± 4)°C.

Control Standard
Prepare a 250 µg/mL Control Standard by diluting the 5,000 µg/mL Control Standard Stock Solution in methanol.

Gasoline Stock Solution
Prepare a 50,000 µg/mL stock solution of unleaded gasoline in methanol. Prepare the solution by weight (e.g. weigh 0.250g gasoline into a 5.00 mL volumetric flask, or use a syringe to dispense an appropriate volume of gasoline with consideration of its density). Any unweathered, fresh source of gasoline is acceptable. Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Note: The 50,000 µg/mL concentration above can be referred to as the "product concentration" of the solution, where the product is in this case gasoline. It is important to note that the product concentration of the solution is not equivalent to its VH_{S6-10} concentration.

Detection Limit Check Standard
Dilute the 50,000 µg/mL 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 (see the Detection Limit Check section). Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Refer to the Determination of DL Check Standard Concentration and VH_{S6-10} Target section under Method Validation for the procedure to determine an appropriate concentration for this solution.

Gasoline Method Spike Solution
If Gasoline Method Spikes will be analyzed (see the Gasoline Method Spike section), it will normally be appropriate to use the 50,000 µg/mL Gasoline Stock Solution in methanol as the spiking solution. If necessary, dilutions of this solution may be prepared in methanol or acetone. Warm the solution and mix well prior to use to ensure complete dissolution of all components. Store refrigerated at (4 ± 4)°C.

Quality Control (QC)

Table I-14 summarizes all the required and recommended 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 and Recommendations

QC Component	Minimum Frequency	Minimum Acceptance Criterion
Instrument Performance QC		
Instrument Performance Check	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Relative response ratios must be: 0.6-1.4 for nC6 and nC10, 0.7-1.3 for all other components
Calibration QC and Verification		
Instrument blank	1/analysis batch	None
Control Standard	1/analysis batch	Within 15% of expected concentration
Detection Limit Check Standard	1/analysis batch	50 – 150% of VH target
Ongoing Verification of Calibration	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Within 25% of previous std & Within 35% of initial calibration, (in continuing calibration mode).
Method QC		
Method Blank	1/preparation batch	< reported detection limit
Method Performance Check Spike	1/preparation batch	*Average* recovery for each component must be 80-120%
Gasoline Method Spike	Not required	None
Laboratory and Field Sample Replicates	Not required	None
Surrogate Compounds	Not required	None

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

Samples are prepared in a set that is referred to as a preparation batch, and are analyzed by GC in a set that is referred to as an analysis batch.

If any of the specified acceptance criteria for Instrument Performance QC, Initial Calibration QC, or Method QC cannot be met for the analysis of a given sample, then the data reported for that sample must be appropriately qualified.

Instrument Performance QC

Instrument 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.

The 50 µg/mL Calibration Standard is used for initial calibration (see the Initial Calibration section) and for ongoing verification of calibration (section the Ongoing Verification of Calibration (Verification Standards) section). In addition, it is used for the Instrument Performance Check to do the following:

a) Measure and control relative response ratios of specified VH components,
b) Determine retention time windows for VH integration ranges,
c) Confirm resolution of hexane (nC6) from the solvent peak.

One 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 (nC6), octane (nC8), benzene, toluene, and ethylbenzene against meta-xylene. Compare the peak areas of decane (nC10) and o-xylene against 1,2,4-trimethylbenzene. For all compounds within the mixture, these ratios should normally fall between 0.80 and 1.20. Acceptance criteria for relative response ratios are 0.6 – 1.4 for nC6 and nC10, and 0.7 – 1.3 for all other components of the Instrument Performance Check. 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 analysis batch of no more than 100 samples. Inject a methanol solvent blank to the GC system to establish the chromatographic baseline. All GC parameters must be identical to those of samples run in the same analysis batch.

Control Standard

REQUIRED - minimum 1 per analysis batch of no more than 100 samples.

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, and to verify calibration

linearity if single-point calibration is used. Where possible, the Control Standard should be traceable to national chemical metrology standards.

If single-point calibration is used, the concentration of the Control Standard must differ from the concentration of the Calibration Standard by at least a factor of five.

Note: At concentrations above ~ 50-100 µg/mL, chromatographic peak shapes may be distorted due to column phase overload, but FID responses are not normally affected.

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 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 analysis batch of no more than 100 samples. 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 $VH_{S6\text{-}10}$ at a concentration that is approximately equivalent to the $VH_{S6\text{-}10}$ Reporting Detection Limit for the method (see the Detection Limit Check Standard section).

The procedure for determining the target concentration for this standard is described under Method Validation in the Determination of DL Check Standard Concentration and $VH_{S6\text{-}10}$ Target section. Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the $VH_{S6\text{-}10}$ target (calculated as described in the Determination of DL Check Standard Concentration and $VH_{S6\text{-}10}$ Target section). Data reports must be qualified if this acceptance criterion is not met for the analysis batch in which the samples were run.

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 50 samples. Prepare a Method Blank using a clean soil/sediment matrix. Extract and analyze as described in sections 12 and the GC Analysis Procedure section.

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).

Method Performance Check Spike
REQUIRED - minimum 1 per preparation batch of no more than 50 samples. Prepare a Method Performance Check Spike by fortifying a clean soil/sediment matrix (containing 20% moisture) with the Calibration Standard Stock Solution at a concentration of 100 µg/g.

Spike 160 uL of the 5,000 µg/mL Calibration Standard Stock Solution into 8.0g of clean sand and 2.0 mL of reagent water. Extract and analyze as described in sections 12 and the GC Analysis Procedure section.

Calculate the spike recovery of each component of the mixture by quantitation against the appropriate component of the Calibration Standard (i.e. calculate benzene against benzene). Spike recoveries must normally be between 80% and 120% for all components. Where recoveries fall significantly outside this range with unknown cause, or with known cause that may impact samples, then samples from the same preparation batch must be repeated, or their data reports must be qualified.

Gasoline Method Spike
OPTIONAL. Prepare a Gasoline Method Spike by fortifying a clean sediment/soil matrix (containing approximately 20% water) with an accurate volume of the Gasoline Method Spike Solution (see the Gasoline Method Spike Solution section). Extract and analyze as described in sections 12 and the GC Analysis Procedure section. Spikes may be prepared at any reasonable concentration, depending on the objective.

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).

A Gasoline Method Spike prepared in this way provides information about method precision and about method bias (accuracy), where bias is in this case a measure of losses associated with the extraction process. Acceptance criteria are at the discretion of the laboratory.

Laboratory Sample Replicates and 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 (4), 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*
OPTIONAL. The use of one or more Surrogate Compounds for VH is at the discretion of the laboratory. 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.

Note that sample interferences will often preclude the accurate measurement of any surrogate by FID. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

*Surrogate Compounds have chemical characteristics similar to those of analytes, but provide analytical response that is distinct from analytes. They are added to samples prior to sample preparation. Surrogate percent recovery measurements are used as Method QC to estimate sample preparation losses and matrix effects. They are only useful when not subject to measurement interferences.

Sample Preparation Procedure

This extraction procedure is required for the analysis of both VH_{S6-10} and targeted MAH parameters (i.e. BTEX). The same extract must normally be used to analyze all of these parameters.

Where possible, mix sediment samples in their sample containers prior to sub-sampling. For samples that cannot be easily mixed, take a representative sub-sample by combining portions of sample taken from top to bottom at several locations in the container. To prevent losses of volatiles, sub-sampling must be done quickly, and samples must not be allowed to warm to room temperature (do not leave any sample un-refrigerated for more than 10 minutes).

Accurately weigh an appropriate amount of wet solids sample into an extraction tube. For samples with less than approximately 50% moisture, use approximately 10 g of wet sample. To reduce sub-sampling variability, no less than 5 grams (wet weight) may be used, except where limited by available sample.

Note: If the moisture determination has not been completed in advance of the VH extraction process, estimate the moisture content for the purpose of determining the amount of sediment to extract.

For samples with less than approximately 50% moisture, use a 2:1 ratio of methanol volume (in mL) to wet weight of solids (in grams). For samples with moisture contents of greater than approximately 50% (e.g. sludge samples), use a 3:1 ratio of methanol to wet solids.

Once a sub-sample is taken, add methanol to the sample as quickly as possible to prevent evaporative losses. It is strongly recommended that this process be performed serially, so that methanol is added to one sample before the next is sub-sampled and weighed.

Take an aliquot of each sample to perform an accurate moisture determination on the sample. Prepare appropriate and required Method QC samples as described in the Method QC section. Use 10 g of a clean, dry soil/sediment matrix for the Method Blank. Use 8.0 g of a clean soil/sediment matrix plus 2.0 mL of reagent water for the Method Performance Check Spike and Gasoline Method Spike samples (this simulates samples of 20% moisture).

Surrogates may be required for MAH analyses, and are recommended for the analysis of VH_S (see the Surrogate Compound section). Where applicable, add an appropriate amount of Surrogate Compound solution in methanol directly to the sample in the extraction tube.

Immediately after the Surrogate Compound solution is dispensed, add the appropriate amount of methanol to the extraction tube. For 10 gram samples with less than approximately 50% moisture, add exactly 20.0 mL of purge and trap grade methanol.

Solvent Substitution Requirement: Some highly contaminated samples do not mix well with methanol, and would therefore be poorly extracted by methanol (e.g. oil soaked soils/sediments). Such samples result in a 2-phase methanol extract, with distinct oil droplets sticking to the walls of the extraction vessel. Use acetone as the extraction solvent for samples where this occurs. Acetone extracts may be diluted in methanol and analyzed against a methanol Calibration Standard, or may be analyzed without dilution using a Calibration Standard prepared in acetone.

Cap the extraction tube and shake for 1 hour on a mechanical shaker.

Let suspended solids settle by gravity or use a centrifuge. Transfer all or a portion of the extract to a vial for refrigerated storage. Store remaining extract at (4 ± 4)°C for at least 40 days in case re-analysis is required.

Caution: Refrigerated extracts must be warmed to room temperature and mixed gently before use or before sub-sampling (non-polar aliphatic sample components may be insoluble in methanol at cold temperatures).

Dispense aliquots of sample extract into GC autosampler vials for both MAH and VH analyses.

Analyze target MAH compounds using a method approved by BCMELP (e.g. GC/MS). The analysis procedure for VH_{S6-10} is described in the GC Analysis Procedure section.

GC Analysis Procedure

Gas Chromatograph Conditions

Column:	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 uL (higher volumes tend to cause GC backflash)
Injection mode:	splitless or on-column
GC liner type:	4mm id splitless liner with silanized glass wool
Initial inlet purge:	OFF
Inlet purge on time:	0.3 minutes
FID temperature:	250°C
Oven program:	Initial Temp 36°C (hold 3.0 minutes) 5°C /min to 150°C (no hold) 15°C/min to 240°C (hold 6.0 minutes)
FID gas flows:	as recommended by manufacturer

Initial Calibration
Analyze a 50 µg/mL Calibration Standard at the beginning of each new analytical batch (see the Calibration Standard section).

Calibration is by single or multi-point external standard technique, using meta-xylene and 1,2,4-trimethylbenzene.

A continuing calibration is recommended (i.e. reslope the calibration with each Verification Standard). Changes in response between standards must be monitored and controlled (see the Ongoing Verification of Calibration (Verification Standards) section).

Linear calibration must be used for this method. Either single or multi-point calibrations are acceptable, due to the linear response of GC/FID systems. If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control 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), ensuring that all specified acceptance criteria are met.

For each analysis batch, verify that the initial calibration is adequate by performing all tests specified in the Initial Calibration QC section (see the Initial Calibration QC section), ensuring that all specified acceptance criteria are met.

Calculate the Calibration Factors (CFs) for meta-xylene and 1,2,4-trimethylbenzene in the Calibration Standard using the equation below. The Calibration Factors are based on the concentration of analyte in the solution that is injected onto the GC:

$$CF_{m\text{-}Xylene} \text{ in mL/µg} = \frac{\text{Area of meta-xylene peak}}{\text{meta-xylene concentration (µg/mL in methanol)}}$$

$$CF_{1,2,4\text{-}Trimethylbenzene} \text{ in mL/µg} = \frac{\text{Area of 1,2,4-trimethylbenzene peak}}{\text{1,2,4-trimethylbenzene concentration (µg/mL in methanol)}}$$

Ongoing Verification of Calibration (Verification Standards)
After initial calibration, the Calibration Factors ($CF_{m\text{-}Xylene}$ and $CF_{1,2,4\text{-}Trimethylbenznene}$) must be verified, at minimum, after every 12 hours of continuous operation. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

Use a Calibration Standard as a Verification Standard (see the Calibration Standard section).

Under a continuing calibration mode, if either Calibration Factor changes by more than 25% from the previous standard, or by more than 35% from the initial calibration standard, then corrective action must be taken, and samples analyzed after the last acceptable standard must be re-run.

Alternatively, an initial calibration may be used for as long as both Calibration Factors remain within 15% of their initial values. If this criterion is exceeded, the calibration may be updated using the Verification Standard Calibration Factors, but only if the continuing calibration acceptance criteria specified above are satisfied.

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}

The Volatile Hydrocarbons parameter is defined to include all GC/FID peaks eluting between hexane (nC6) and decane (nC10). VH_{S6-10} is quantitated by summing the results for two sub-ranges within the nC6-nC10 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 the 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 in some instrument systems. 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:

a) The $VH_{S(6-oX)}$ range begins at the apex of the nC6 peak and ends at the apex of the o-xylene peak.
b) The $VH_{S(oX-10)}$ range begins at the apex of the o-xylene peak and ends at the apex of the nC10 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch, and should be established using marker compound concentrations that do not overload the liquid phase of the GC column.

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 potential error may exceed 1-2%.

Calculations

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 calibration standard. $VH_{S(oX-10)}$ is quantitated against the 1,2,4-trimethylbenzene calibration standard.

If any VH-range Surrogate Compounds are added to samples, the contribution to VH of those Surrogates must be subtracted from calculated VH results. Because Surrogate Compounds frequently experience FID interference, it is most practical to subtract the actual spiked concentrations of Surrogate Compounds from calculated VH concentrations. No Surrogate Compounds within the VH-range should be added such that their concentration exceeds the Reporting Detection Limit for VH_{S6-10}.

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) - Actual Surrogate Conc* (µg/g)

* Only Surrogates (if any) that elute within the VH_{S6-10} range are subtracted.

$VH_{S(6-oX)}$ (µg/g) = $(A_{(6-oX)} \times TEV \times Dil) / (CF_{m-Xylene} \times DryWt)$

$VH_{S(oX-10)}$ (µg/g) = $(A_{(oX-10)} \times TEV \times Dil) / (CF_{1,2,4-Trimethylbenzene} \times DryWt)$

where:

$A_{(6-oX)}$	=	Total area between nC6 and ortho-xylene for the sample chromatogram.
$A_{(oX-10)}$	=	Total area between ortho-xylene and nC10 for the sample chromatogram.
$CF_{m-Xylene}$	=	Calibration Factor for meta-xylene standard (mL/µg)
$CF_{1,2,4-Trimethylbenzene}$	=	Calibration Factor for 1,2,4-trimethylbenzene standard (mL/µg)
TEV	=	Total Extract Volume, ***including sample moisture*** (mL). e.g.: For a 10.0 g sample of 20.0% moisture extracted with 20.0 mL Methanol, TEV = 22.0 mL*.
Dil	=	Dilution factor of sample extract (unitless)
DryWt	=	Dry weight of sample extracted (g)

* Calculate TEV using the approximation: [(water volume) + (methanol volume) = (total extract volume)]

When reporting to BCMELP, report VH_{S6-10} results for solids samples in units of µg/g (ppm).

Diluting High Level Sample Extracts

Where sample results exceed the linear working range of the GC/FID system, they must be diluted and re-analyzed at a more appropriate extract concentration. Note that over-dilution of extracts can introduce significant error to VH results. Diluted extracts should be prepared such that their VH_{S6-10} areas fall within the linear working range of the GC/FID system, as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section.

Where sample extracts are diluted prior to analysis, or where less than one-half the normal amount of sample is extracted, Reporting Detection Limits must be increased accordingly.

Method Validation

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) and the Method Performance Check Spike (see the Method Performance Check Spike section).

Calculation of Actual VH_S Concentrations of a Petroleum 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 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:

a) determination of GC/FID linear range for VH_{S6-10} (i.e. calibration range),
b) determination of VH_{S6-10} Instrument Detection Limits (IDLs),
c) preparation of DL Check Standards and Method Spike Solutions,
d) 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 petroleum product solution:

a) Prepare the petroleum product 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 *$[Gasoline_{grav}]$.*

b) Perform replicate analyses of the petroleum product solution prepared in (a) using the instrumental conditions specified within this method. A minimum of 7 replicates is recommended. Do not dilute the solution prior to analysis. Determine the average measured concentration of VH_{S6-10} using the calculations specified in the Calculations section. In the example below, the measured VH_{S6-10} concentration is denoted as *$[VH_{S6-10,measured}]$*, where the square brackets denote concentration. Percent Relative Standard Deviations (%RSDs) of these values may also be determined, and may be useful to set statistical warning and control limits for some applications.

c) Calculate the percentage that the VH_{S6-10} range represents of the total petroleum product concentration. Example (for a given source of gasoline):

$$\%VH_{S6-10} \text{ in gasoline} = 100\% \times [VH_{S6-10,measured}] \ / \ [Gasoline_{grav}]$$

where:

[ ]	=	symbol for concentration
$[VH_{S6-10}$, measured]	=	measured $[VH_{S6-10}]$ of a solution of gasoline in methanol.
$[Gasoline_{grav}]$	=	actual [Gasoline] in wt of gasoline / volume methanol for the same solution.
Units	=	same for both concentrations (e.g. µg/mL).

Note: The percentage of VH_{S6-10} in gasoline is considerably less than 100% (typically about 50%) because not all components of gasoline fall within the nC6 - nC10 boiling point range.

d) To calculate the *Actual VH_{S6-10} Concentrations* of other concentrations of the same product, use the VH_{S6-10} percentage relative to the total petroleum product concentration as follows (the gasoline example is continued):

Actual VH_{S6-10} conc. in Gasoline = (%VH_{S6-10} in Gasoline) / 100% x *[$Gasoline_{grav}$]*

where:

[$Gasoline_{grav}$] = the conc. of Gasoline (in wt. Gasoline / volume methanol) of any solution.

Establishing 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 50,000 µg/mL 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. 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. These are referred to below as *Calculated VH_{S6-10} Results*.

Follow the procedure in the Calculation of Actual VH_S Concentration of a Petroleum Reference Solution section to calculate the *Actual VH_{S6-10} Concentrations* for all of the above solutions.

Make a plot of *Calculated VH_{S6-10} Results* (y-axis) versus *Actual VH_{S6-10} Concentrations* (x-axis), and determine the linear working range of VH_{S6-10}.

Instrument accuracy for VH_{S6-10} is measured as *Calculated VH_{S6-10} Results* / *Actual VH_{S6-10} Concentrations.* As VH_{S6-10} concentration approaches the Instrument Detection Limit (IDL), instrument accuracy decreases because the less abundant components of the petroleum hydrocarbon blend (e.g. gasoline) cease to be detected. For the purposes of this method, the Instrument Detection Limit for the VH_{S6-10} parameter is defined as the lowest VH_{S6-10} concentration at which instrument accuracy consistently falls within the range of 70-130%. However, a gasoline chromatogram at the IDL must still resemble chromatograms of higher concentrations. At the IDL, any chromatographic peak that normally comprises more than 5% of total VH_{S6-10} area must still be visible as a distinct peak; this requirement takes precedence over the 70-130% accuracy requirement.

The IDL is expressed in units of *Actual VH_{S6-10} Concentration*.

Establishing Method Detection Limits
Determine the Method Detection Limits (MDLs) at the 95% confidence level for VH_{S6-10}, using the procedure outlined in the British Columbia Environmental Laboratory Manual (5). This method requires the use of the procedure described below, which is one of several generic approaches described in the BC Environmental Laboratory Manual.

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 sediment/soil matrix (of 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 (see the Gasoline Method Spike Solution section).

Calculate the Method Detection Limit (MDL) at the 95% confidence level for VH_{S6-10} using the calculations described in the BC Environmental Laboratory Manual (5).

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 VH_S Concentration of a Petroleum Reference Solution section. If this condition is not met, repeat the MDL determination at a higher spike level.

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. Reporting Detection Limits for VH_{S6-10} must be greater than or equal to the Method Detection Limits (at the 95% confidence level) that were experimentally determined in-house using the procedure described in the Establishing Method Detection Limits section.

Ensure that calculated Method Detection Limits and Reporting Detection Limits are below any regulatory criteria values or regulatory standards specified by BCMELP or other applicable regulatory body. For BC requirements, refer to BCMELP method “Calculation of Volatile Petroleum Hydrocarbons in Solids or Water” (July, 99).

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:

a) Gasoline product concentration units must be converted to (and from) VH_{S6-10} concentration units.
b) 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:

a) 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 nC6 - nC10 boiling point range.

b) 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 x (Reporting DL for VH_{S6-10}) / (%VH_{S6-10} in Gasoline) x 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)
Units for Total Extract Volume	=	mL

For 20% moisture, 10 wet gram sample weights, and 20 mL Methanol volumes:

Average Dry Sample Weight = 8.0 grams
Average Total Extract Volume = 22.0 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.

c) 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) x (%VH_{S6-10} in gasoline)

Accuracy and Precision

For a limited period of time, individual laboratories may assess their accuracy and/or precision for this method by analyzing replicates of the 1998 BCMELP Hydrocarbon Round Robin samples, and comparing results against single laboratory and interlaboratory consensus values. This is not a formal requirement for the validation of this method, but is strongly recommended.

Alternatively, multiple method spikes of an appropriate petroleum product (unweathered gasoline is recommended) may be used to assess the method, although less information can be derived about accuracy without interlaboratory consensus data. "Accuracy" data gathered from method spikes is limited to a measure of percent recovery (i.e. a measure of extraction losses). Better measures of overall method bias and accuracy are obtained from analysis of BCMELP Interlaboratory Study samples, and from Method Performance Check Spikes.

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.

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 using the same Reference Samples. 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 the GC Analysis Procedure section.

Please note: For the Round Robin data, results are presented for two methods: Direct Injection (DI) and Purge and Trap (P&T). Only the Direct Injection results directly measure the performance of this method. Purge and Trap is an alternative procedure, which may only be used if equivalence to Direct Injection is demonstrated. The Purge and Trap results are included here for comparison only.

Instrument Performance Check Data

Multiple laboratory (Round Robin) data and single laboratory data for Instrument Performance Checks are presented in Table I-15. Direct Injection data was analyzed as described in the Instrument Performance Check section. **Purge and Trap Round Robin results are presented for comparison purposes only.**

Method Performance Check Spike Data

Multiple laboratory (Round Robin) data and single laboratory data for Method Performance Check Spikes are presented in Table I-16. Direct Injection data was analyzed as described in the Method Performance Check Spike section. **Purge and Trap Round Robin results are presented for comparison purposes only.**

Table I-15: VH_S Instrument Performance Check Data

	1998 BCMELP Round Robin Results Direct Injection			Purge & Trap			Single Lab Results Direct Injection		
Relative Response	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Hexane (nC6)[3]	4	0.78	9.0%	2	1.10	28.1%	9	0.81	0.7%
Benzene[1]	5	1.00	4.9%	2	1.14	11.1%	9	1.01	0.5%
Toluene[1]	5	0.99	3.5%	2	1.07	6.5%	9	1.00	0.2%
Octane (nC8) [1]	5	0.91	2.7%	2	0.97	11.2%	9	0.91	0.4%
Ethylbenzene[1]	5	0.99	3.1%	2	1.02	2.4%	9	0.99	0.0%
m,p-Xylene[1]	5	1.00	n/a	2	1.00	n/a	9	1.00	n/a
o-Xylene[2]	5	1.07	2.6%	2	1.12	5.5%	9	1.02	0.2%
1,2,4-Trimethylbenzene[4]	5	1.00	n/a	2	1.00	n/a	9	1.00	n/a
Decane (nC10)[2]	5	0.89	4.3%	2	0.78	10.0%	9	0.96	0.3%

3 Relative response calculated against m,p-Xylene.
4 Relative response calculated against 1,2,4-Trimethybenzene.

Table I-16: VH_S Method Performance Check Spike Data									
	1998 BCMELP Round Robin Results Direct Injection			Purge & Trap			Single Lab Results Direct Injection		
Spike Recovery (%)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Hexane (nC6)	4	102%	4.7%	2	97.3%	8.6%	8	88.0%	10.4%
Benzene	5	104%	4.1%	2	104%	5.3%	8	101%	7.0%
Toluene	5	105%	5.9%	2	102%	0.1%	8	100%	5.8%
Octane (nC8)	5	103%	4.8%	2	103%	3.1%	8	97.5%	8.1%
Ethylbenzene	5	106%	3.9%	2	100%	3.5%	8	100%	5.3%
m,p-Xylene	5	106%	4.0%	2	103%	0.2%	8	100%	5.4%
o-Xylene	5	106%	4.2%	2	102%	0.9%	8	101%	5.9%
1,2,4-Trimethylbenzene	5	109%	3.5%	2	105%	3.6%	8	103%	6.7%
Decane (nC10)	5	105%	4.9%	2	110%	4.8%	8	98.3%	7.2%

Method Detection Limited Data

The Method Detection Limit data reported in Table I-17 was obtained from the 1998 Single Laboratory Validation Study, and was generated as described in the Establishing Method Detection Limits section. The VH_S *target* was determined by direct analysis of the spike solution. Please note that the data presented demonstrates an achievable MDL; each laboratory must determine the MDL that applies to their individual circumstances.

Table I-17: VH_S Method Detection Limits (Single Laboratory Data)														
Units = mg/kg	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**Mean**	**Std. Dev.**	**Target**	**Mean Recovery**	**MDL**
VH_{S6-10}	37.7	31.3	31.3	31.1	28.6	30.6	32.6	31.1	30.7	**31.7**	**2.5**	**30.0**	**106 %**	**9.3**

VH_S Gasoline Method Spike Data

Multiple laboratory (Round Robin) data and single laboratory data for Gasoline Method Spikes are presented in Tables I-18 to I-20. Three different concentrations of gasoline spikes were performed, at 250 mg/kg, 1,250 mg/kg, and 7,180 mg/kg of gasoline in clean sand. Direct Injection data was analyzed as described in the Gasoline Method Spike section. For all samples, 10 grams of a clean sand matrix was wetted with 2 mL of reagent water prior to the addition of a gasoline spike solution. MAH and calculated VPH_S results are also presented for the same samples. **Purge and Trap Round Robin results are presented for comparison purposes only.**

Table I-18: VH_S Gasoline Method Spike Data (250 mg/kg gasoline)

	1998 BCMELP Round Robin Results Direct Injection			Purge & Trap			Single Lab Results Direct Injection		
VH Results (mg/kg)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**%RSD**	**(n)**	**Mean**	**%RSD**
$VH_{S6\text{-}oXylene}$	5	95.7	22.6%	2	147	44.2%	8	111	5.5%
$VH_{SoXylene\text{-}10}$	5	15.5	15.3%	2	15.3	17.9%	8	18.6	8.4%
$VH_{S6\text{-}10}$	5	111	21.5%	2	163	38.3%	8	129	5.6%
VPHs	4	87.3	26.0%	2	138	37.4%	8	93.3	7.6%
	Combined Data						**Direct Injection**		
MAH Results (mg/kg)	**(n)**		**Mean**		**% RSD**		**(n)**	**Mean**	**%RSD**
Benzene	7		2.2		25.9%		8	2.6	3.2%
Toluene	7		11.2		31.5%		8	15.8	3.1%
Ethylbenzene	7		2.7		26.8%		8	3.4	2.1%
m,p-Xylene	7		8.9		26.4%		8	10.3	3.1%
o-Xylene	6		3.3		24.1%		8	4.0	2.7%
Styrene	9		<		n/a		8	<0.01	n/a

Table I-19: VH_S Gasoline Method Spike Data (1,250 mg/kg gasoline)

	1998 BCMELP Round Robin Results Direct Injection			Purge & Trap			Single Lab Results Direct Injection		
VH Results (mg/kg)	**(n)**	**Mean**	**%RSD**	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**%RSD**
$VH_{S6\text{-}oXylene}$	5	449	10.5%	2	710	53.6%	6	554	4.5%
$VH_{SoXylene\text{-}10}$	5	88.9	7.1%	2	87.3	25.4%	6	100	4.6%
$VH_{S6\text{-}10}$	5	538	9.1%	2	797	50.4%	6	654	4.2%
VPHs	4	422	16.5%	2	699	51.7%	6	468	5.6%
	Combined Data						**Direct Injection**		
MAH Results (mg/kg)	**(n)**		**Mean**		**% RSD**		**(n)**	**Mean**	**% RSD**
Benzene	7		8.9		35.5%		6	12.6	1.6%
Toluene	7		46.3		24.7%		6	81.0	1.3%
Ethylbenzene	7		11.5		32.1%		6	17.9	2.0%
m,p-Xylene	7		37.3		25.6%		6	53.4	2.2%
o-Xylene	6		13.9		29.3%		6	20.9	1.4%
Styrene	8		<		n/a		6	<0.05	n/a

Table I-20: VH_S Gasoline Method Spike Data (7,180 mg/kg gasoline)

	Single Lab Results Direct Injection		
VH Results (mg/kg)	**(n)**	**Mean**	**%RSD**
$VH_{S6\text{-}oXylene}$	8	3101	0.7%
$VH_{SoXylene\text{-}10}$	8	517	2.1%
$VH_{S6\text{-}10}$	8	3618	0.7%
VPHs	8	2493	1.4%
MAH Results (mg/kg)	**(n)**	**Mean**	**% RSD**
Benzene	8	81.0	1.2%
Toluene	8	494	1.5%
Ethylbenzene	8	106	2.3%
m,p-Xylene	8	319	2.2%
o-Xylene	8	125	2.6%
Styrene	8	<0.25	n/a

Use of Alternative Methods

This method contains several 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 $VH_{S6\text{-}10}$ 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 BCMELP:

a) 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.

b) "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.

c) Maximum holding time prior to extraction is 7 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

d) Pre-extraction "drying" of samples using anhydrous salts like sodium sulphate or magnesium sulphate is prohibited due to losses of volatile organics that would result.

e) Methanol extraction is required (except for samples that form 2 liquid phases with methanol, where acetone must be used – see the Sample Preparation section).

f) Wherever possible, the same sediment extract must be used for the analysis of both VH_{S6-10} and targeted MAH compounds (i.e. BTEX), so that sub-sampling variability does not affect the calculated VPH result. Although situations may arise where this is not possible, it must be the normal procedure.

g) The ratio of methanol : wet weight of solids being extracted must always be at least 2:1.

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

i) The water content in sample extracts (due to sample moisture) must never exceed 25%.

j) Gas Chromatography with Flame Ionization Detection is required for VH_{S6-10}.

k) GC column must be a capillary column.

l) GC column stationary phase must be 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent).

m) Meta-xylene (or meta and para xylenes) and 1,2,4-trimethylbenzene must be used as the calibration standards for $VH_{S6-10.}$

n) 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.

o) If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control Standard section).

p) Calibration stability must be monitored as described in section the Ongoing Verification of Calibration (Verification Standards) section.

q) 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 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 BCMELP. This information must be available in the event of audit by BCMELP.

Pay particular attention to the results of Instrument Performance Checks (the Instrument Performance Check section) and Method Performance Check Spikes (the Method Performance Check Spike section), since both of these checks 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:

a) Apparatus
b) Reagents and Standards
c) Gas Chromatograph Conditions

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

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:

a) Sample Preparation Procedure (see appropriate section)

An equivalence test for Sample Preparation (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.

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 BCMELP 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:

a) ***At least five unspiked field samples.*** Each sample must contain $VH_{S6\text{-}10}$ at ≥ 3 times the laboratory's routinely reported detection limit (≥ 5 times DL 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 peat samples
   - one or more soil or sediment samples
   - one or more samples with >40% moisture

b) ***At least one set of gasoline spikes into clean matrix samples or field samples.*** Each spiked sample set must be analyzed in triplicate (at minimum) by both the reference method and the modified method. Spike concentrations must correspond to at least five times the laboratory's routinely reported detection limit.

Note: While available, 1998 BCMELP Round Robin Study sample spike solutions (or samples evaluated under future Round Robin Studies) may be analyzed to satisfy this component of the equivalency test.

For both (a) and (b) 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:

a) 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:

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

or,

b) 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].

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 [h].

If 1998 BCMELP Round Robin spike samples are used for (b) above, then the results for the modified method may be compared against the Single Laboratory Results (the Method Performance Data section) or against in-house results generated by the reference method. Note that comparison against the Round Robin Results in the Method Performance Data section is not sufficient to demonstrate method equivalence, due to the small sample population of that study (n=5). Sample results from future Round Robin studies may be used for equivalency comparisons where the study population is six or greater [h].

Test for Precision of Modified Methods

Modified methods must demonstrate a reasonable level of precision on homogeneous samples (e.g. Method Spikes or Reference Materials). Analyze a minimum of 8 replicates of at least one Gasoline Method Spike or Reference Material that contains $VH_{S6\text{-}10}$ at $\geq$ 3 times the laboratory's routine Reporting Detection Limit ($\geq$ 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 [h].

For $VH_{S6\text{-}10}$, the modified method must demonstrate a precision of $\leq$ 20% relative standard deviation.

References

a) Laboratory and Systems Management, Environmental Protection Department, Ministry of Environment, Lands and Parks, Province of British Columbia, 1996, British Columbia Field Sampling Manual, Parts A & D.

b) J.W. Eichelberger et al., Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1992, Method 524.2 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography / Mass Spectrometry, Revision 4.0.

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

d) 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.

f) 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, section 3 (Protocol for Setting Method Detection Limits).

g) Massachusetts Department of Environmental Protection, January 1998, Method for the Determination of Volatile Petroleum Hydrocarbons (VPH).

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 British Columbia Ministry of the Environment, Lands and Parks.

Acknowledgments

Mark Hugdahl and Scott Hannam of ASL Analytical Service Laboratories developed and wrote this method. ASL Analytical Service Laboratories analyzed and compiled the Single Laboratory Data.

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Revision History

March 1997:	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Solids.
1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
July 1999:	Finalization of present method based on results of a vetting round robin.

December 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.

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 (7). The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

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

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

$$V_A = s_A^2 / n_A \qquad V_B = s_B^2 / n_B$$

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.

Calculation of Volatile Petroleum Hydrocarbons in Solids or Water (VPH)

Parameters

Volatile Petroleum Hydrocarbons in water
Volatile Petroleum Hydrocarbons in solids

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
VPH_W	**VPH- F099**
VPH_S	**VPH- F100**

Analytical Methods

Refer to the following VPH precursor methods:

Volatile Hydrocarbons in Water by GC-FID

Monocyclic Aromatic Hydrocarbons (BTEX) in Water by Purge and Trap GC/MS or GC/PID (Non-PBM section of manual)

Monocyclic Aromatic Hydrocarbons (BTEX) in Water by Dynamic Headspace and GC/PID/FID (Non-PBM section of manual)

Volatile Hydrocarbons in Solids by GC-FID

Monocyclic Aromatic Hydrocarbons (BTEX) in Solids by Purge and Trap GC/MS (Non-PBM section of manual)

Monocyclic Aromatic Hydrocarbons (BTEX) in Solids by Dynamic Headspace and GC/PID/FID (Non-PBM section of manual)

Units

water = mg/L
solids = µg/g

Introduction

Volatile Petroleum Hydrocarbons are calculated using the results from selected methods as listed above. The calculation procedure for VPH requires that both Volatile Hydrocarbons (VH) and Monocyclic Aromatic Hydrocarbons (MAHs, including BTEX and styrene) be analyzed using methodologies which have been approved by the Director.

Selected MAHs are subtracted from VH results to produce VPH values. These MAHs are excluded from VPH because they are regulated directly under the British Columbia (BC) Contaminated Site Regulations (CSR). MAHs excluded from VPH for waters are listed in Schedule 6 of the CSR. MAHs excluded from VPH for soils are listed in Schedules 4 and 5 of the CSR. The Procedure section lists the MAHs to be excluded from both waters and soils.

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

Wherever possible, laboratories must use the same sample extract (for sediments) or the same sample aliquot (for waters) to determine both VH and BTEX. This minimizes the potential error in the final VPH result that could otherwise occur due to normal analytical variability.

Procedure

Subtract the total applicable MAHs from the VH_{6-10} result:

$VPH = VH_{6-10} - \Sigma$ MAHs from CSR schedule(s) within VH_{6-10} range

To calculate VPH_W, subtract the individual results for benzene, toluene, ethylbenzene, ortho-xylene, meta-xylene, and para-xylene from the VH_{W6-10} concentration obtained by the approved VH GC/FID method.

To calculate VPH_S, subtract the individual results for benzene, toluene, ethylbenzene, ortho-xylene, styrene, meta-xylene, and para-xylene from the VH_{S6-10} result obtained by the approved VH GC/FID method.

It is strongly recommended that all MAH results be analyzed 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, e.g.:

a) field testing (see below).
b) analysis of samples where no interferences are apparent (i.e. all target analyte peaks are baseline-resolved, Gaussian in shape, and elute within expected retention time windows).
c) analysis of commercial/industrial samples where interferences do not prevent an evaluation of whether or not regulatory standards are exceeded.

Regardless of the GC detector used, wherever suspected interferences prevent the positive identification and/or accurate quantitation of MAH compounds, results must be reported as "<DL", with detection limits elevated to reflect the maximum amount of each compound that may be present (Note: If a non-GC/MS detector is used and the reported detection limit exceeds a regulatory standard value, then re-analysis by GC/MS is required).

Treat any MAH results reported as less than detection limit as Zero (no subtraction).

Report results to BCMELP in units of µg/g dry weight for solids, and in units of µg/L for waters.

Maximum Reporting Detection Limits

This section lists the Maximum Permitted Reporting Detection limits for VPH in soil and water. Higher detection limits may be reported to BCMELP by laboratories or permittees under special circumstances, but acceptance of these results is at the discretion of the Director.

Analyte	Maximum Reporting DL
VPH_S	100 µg/g (dry weight)
VPH_W	100 µg/L

Normal Reporting Detection Limits for VPH must not be less than the Reporting Detection Limit for VH_{6-10}. Validation procedures for VH detection limits are described in the appropriate VH method.

Revision History	March 1997:	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Water.
	1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
	July 1999:	Finalization of present method based on results of a vetting round robin.
	December 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.

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

Parameters

Extractable Petroleum Hydrocarbons$_{(nC10-nC19)}$ in water
Extractable Petroleum Hydrocarbons$_{(nC19-nC32)}$ in water

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
EPH_{W10-19}	**LEPH F065**
EPH_{W19-32}	**HEPH F065**

(Note that the above EMS codes are for precursor and results are not corrected for PAHs.)

Analytical Method

DCM liquid-liquid extraction - Gas Chromatography with Flame Ionization Detection (GC/FID).

Introduction

This method measures the collective concentration of Extractable Petroleum Hydrocarbons (EPH) in water (EPH_W). Extractable Petroleum Hydrocarbons (EPH) are divided into two boiling point ranges, each quantitated against eicosane (nC20). EPH_{W10-19} measures hydrocarbons that elute between n-decane and n-nonadecane, roughly equivalent to a boiling point range of 174°C to 330°C. EPH_{W19-32} measures hydrocarbons that elute between n-nonadecane and n-dotriacontane, roughly equivalent to a boiling point range of 330°C to 467°C.

The two Extractable Petroleum Hydrocarbons (EPH) parameters are the 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 British Columbia Ministry of Environment, Land and Parks (BCMELP) method “Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids and Waters”.

The Extractable Petroleum Hydrocarbons (EPH) method is normally used in conjunction with the BCMELP Volatile Hydrocarbons (VH) method. Together, these methods can generate quantitative values for the concentration of most petroleum products. Note that the correlation of these results with the actual concentration of petroleum product in a sample (i.e. accuracy) may be less than would be achieved for single compound analyses.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC6 through nC10 (e.g. VH captures the majority of most unweathered gasolines, mineral spirits, and paint thinners). Petroleum products that are predominantly captured with the EPH parameters are those whose primary components are within the boiling point range of nC10 through nC32 (e.g. EPH captures the majority of most diesel fuels, lubricating oils, greases, hydraulic oils, waxes). Many petroleum products contain components within both the VH and EPH parameter ranges (e.g. kerosenes, jet fuel, and weathered gasolines). Petroleum products that contain a substantial proportion of hydrocarbons with boiling points greater than nC32 will not be accurately quantitated by either of the VH or EPH methods.

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 EPH results among laboratories. British Columbia Ministry of the 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.

Every laboratory that uses this method, or a modified version of this method, to report EPH, LEPH, or HEPH data to BCMELP must perform an in-house validation of the method as described in the Method Validation section.

This method is not intended to quantitate individual target compounds (i.e. PAHs).

Units

mg/L

Method Summary

Water samples are extracted with dichloromethane (DCM) in a separatory funnel. Extracts are dried, concentrated, and analyzed by capillary column gas chromatography with flame ionization detection.

Matrix

Fresh Water
Waste Water
Marine Water

Interferences and Precautions

Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. **All of solvents, reagents and hardware 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. If further information concerning the chemical composition of sample components is required, a silica gel procedure can be used to fractionate EPH into aliphatic and aromatic components. This procedure can remove some naturally occurring organic components like humic acids. Refer to BCMELP Method “Aliphatic/Aromatic Fractionation of Extractable Petroleum Hydrocarbons in Solids and Waters” (Pending).

This method requires the analysis of the total contents of each sample container, including any hydrocarbons which may be present as solids (or adsorbed to solids) within the sample container, and including any hydrocarbons which may be adsorbed to the surface of the sample container. 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 Reporting Detection Limits is suspected.

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

Collect samples in 500 mL amber glass bottles with Teflon-lined lids. No chemical preservation is required. Store samples at (4 ± 2)°C.

Maximum holding time prior to extraction is 7 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

Because this method analyzes the total contents of each sample container, two 500 mL samples should be taken for each sample location. This allows the laboratory to analyze Field Replicates [a] or Field Splits [a] as desired, and/or to re-analyze any sample if confirmation is required.

Where possible, groundwater samples should contain no visible solids. Sampling staff are referred to the British Columbia Field Sampling Manual [b] to minimize suspended solids in collected water samples.

Apparatus

Glassware and Support Equipment
1 L Separatory funnels
500 mL or 1 L Graduated cylinder
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

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_{W10-19} and EPH_{W19-32}. FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

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

Chromatographic Column
The reference column for this method is a 30 meter, 0.32 mm internal diameter capillary column with a 0.25 um coating of 100% dimethyl siloxane

(e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified.

Reagents and Standards

Reagents

Acetone (2-propanone)
Dichloromethane (DCM)
Sodium sulphate, Anhydrous
Iso-octane (2,2,4-trimethyl-pentane)
Organic free reagent water

Calibration Standard Stock Solution

Prepare a Calibration Standard Stock Solution in DCM containing 1,000 µg/mL of each of decane (nC10), dodecane (nC12), hexadecane (nC16), nonadecane (nC19), eicosane (nC20), dotriacontane (nC32), naphthalene, phenanthrene, and pyrene. This mixture may be purchased commercially or prepared from neat standards. Ensure all components are fully dissolved before use. Warm the solution and/or place in an ultrasonic bath if necessary to re-dissolve any precipitated components. Store refrigerated at $(4 \pm 4)^{\circ}C$.

Calibration Standard

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

Control Standard Stock Solution

Prepare a Control Standard Stock Solution containing 5,000 µg/mL of eicosane (nC20) in iso-octane. This solution may also contain other target analytes, and may be purchased commercially or prepared from neat compounds**. It must be prepared from a different source than the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions). Store refrigerated at (4 ± 4)°C.**

Control Standard

Prepare a 250 µg/mL Control Standard by diluting the 5,000 µg/mL Control Standard Stock Solution in iso-octane.

Diesel / Motor Oil Stock Solution

Prepare a 100,000 µg/mL stock solution of 1:1 diesel (fuel #2) : motor oil (non-synthetic 10W30) by combining 50,000 µg/mL of each product in iso-octane. Prepare the solution by weight (e.g. weigh 0.250g diesel plus 0.250g motor oil into a 5.00 mL volumetric flask). Any unweathered, fresh source of these products is acceptable. Store refrigerated at $(4 \pm 4)^{\circ}C$.

Note: The 100,000 µg/mL concentration above can be referred to as the "product concentration" of the solution, where the product is in this case a diesel/motor oil mixture. It is important to note that the product concentration of the solution is not equivalent to its total EPH_W concentration (i.e. EPH_{W10-19} + EPH_{W19-32}).

Detection Limit Check Standard

Dilute the 100,000 µg/mL Diesel / Motor Oil Stock Solution to prepare a Detection Limit (DL) Check Standard in iso-octane. Prepare the standard at a concentration that is approximately equal to the extract concentrations that correspond to the Reporting Detection Limits for each of EPH_{W10-19} and EPH_{W19-32}. This standard is required for Initial Calibration QC (see the Detection Limit section). Store refrigerated at $(4 \pm 4)^{\circ}C$.

Refer to the Detemination of DL Check Standard Concentration and EPH Targets section under Method Validation for the procedure to determine an appropriate concentration for this solution.

Diesel / Motor Oil Method Spike Solution
If Diesel/Motor Oil Method Spikes will be analyzed (see the Diesel/Motor Oil Method Spike section), prepare a Diesel/Motor Oil Method Spike Solution at a suitable concentration by diluting the Diesel/Motor Oil Stock Solution into iso-octane. Concentrations ranging from 1,000 - 20,000 µg/mL of diesel/motor oil may be appropriate, depending on the desired Method Spike concentrations. Store refrigerated at (4 ± 4)°C.

Quality Control (QC)

Table I-7 summarizes all the required and recommended calibration and QC components of this method. Each of these components is described in detail in this section.

Table I-7: Summary of EPH_W QC and Calibration Requirements and Recommendations

QC Component	Minimum Frequency	Minimum Acceptance Criterion
Instrument Performance QC		
Instrument Performance Check	**Every 12 hours, and at end of analysis batch if >6 hrs from previous check.**	**Relative response ratios must be 0.7-1.3 for all components**
Calibration QC and Verification		
Instrument blank	**1/analysis batch**	None
Control Standard	**1/analysis batch**	**Within 15% of expected concentration**
Detection Limit Check Standard	**1/analysis batch**	**50 – 150% of EPH targets**
Ongoing Verification of Calibration	**Every 12 hours, and at end of analysis batch if >6 hrs from previous check.**	**Within 25% of previous std & Within 35% of initial calibration, (in continuing calibration mode).**
Method QC		
Method Blank	**1/preparation batch**	**< reported detection limit**
Method Performance Check Spike	**1/preparation batch**	***Average* recoveries must be: 65-120% for nC10, nC12, naphthalene, 80-120% for all other components.**
Diesel / Motor Oil Method Spike	Not required	None
Laboratory and Field Sample Replicates	Not required	None
Surrogate Compounds	Not required	None

General QC Requirements

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

Samples are prepared in a set that is referred to as a preparation batch, and are analyzed by GC in a set that is referred to as an analysis batch.

If any of the specified acceptance criteria for Instrument Performance QC, Initial Calibration QC, or Method 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_{W10-19} and EPH_{W19-32} 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.

Instrument Performance QC

Instrument Performance Check

REQUIRED – Perform this check whenever a Calibration Standard or Verification Standard is analyzed. See the Ongoing Verification of Calibration section for required frequency.

The 50 µg/mL Calibration Standard is used for initial calibration (Initial Calibration section) and for ongoing verification of calibration (see Ongoing Verification of Calibration section). In addition, it is used for the Instrument Performance Check to do the following:

a) Measure and control relative response ratios of specified EPH components,
b) Determine retention time windows for EPH integration ranges,
c) Confirm resolution of decane (nC10) from the solvent peak.

One essential purpose of the Instrument Performance Check is to ensure that the GC/FID response factors of EPH components throughout its boiling point range are roughly equal. If excessive relative bias exists among EPH 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 eicosane (nC20). For all compounds within the mixture, these ratios should normally fall between 0.80 and 1.20. Acceptance criteria for relative response ratios are 0.7 – 1.3 for all components of the Instrument Performance Check. **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 analysis batch of no more than 100 samples. Inject an iso-octane solvent blank to the GC system to establish the chromatographic baseline. All GC parameters must be identical to those of samples run in the same analysis batch.

Control Standard

REQUIRED - minimum 1 per analysis batch of no more than 100 samples.

Analyze a Control Standard (see the Control Standard section) containing eicosane (nC20), 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, and to verify calibration linearity if single-point calibration is used. Where possible, the Control Standard should be traceable to national chemical metrology standards.

If single-point calibration is used, the concentration of the Control Standard must differ from the concentration of the Calibration Standard by at least a factor of five.

Note: At concentrations above ~ 50-100 µg/mL, chromatographic peak shapes may be distorted due to column phase overload, but FID responses are not normally affected.

If the calculated concentration of eicosane in the Control Standard 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 analysis batch of no more than 100 samples. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low level solution of diesel / motor oil.

Analyze a Detection Limit Check Standard that contains both EPH_{W10-19} and EPH_{W19-32} at concentrations that are approximately equivalent to the EPH_{W10-19} and EPH_{W19-32} Reporting Detection Limits for the method (see the Detection Limit Check Standard section).

The procedure for determining the target concentrations for this standard is described under Method Validation in the Determination of DL Check Standard Concentration and EPH Target section. **Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the EPH_{W10-19} and EPH_{W19-32} targets (calculated as described in** the Determination of DL Check Standard Concentration and EPH Targets section). **Data reports must be qualified if this acceptance criterion is not met for the analysis batch in which the samples were run.**

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 50 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).

Method Performance Check Spike
REQUIRED - minimum 1 per preparation batch of no more than 50 samples. Prepare a Method Performance Check Spike by fortifying reagent water with the Calibration Standard Stock Solution, at a concentration of 0.10 µg/mL of each component.

Spike 50 uL of the 1,000 µg/mL Calibration Standard Stock Solution into approximately 1 mL of acetone, and quantitatively transfer the acetone solution to 500 mL of reagent water. Extract and analyze as described in the Sample Preparation Procedure and GC Analysis Procedure sections.

Calculate the spike recovery of each component of the mixture by quantitation against the appropriate component of the Calibration Standard (i.e. calculate naphthalene against naphthalene). **Spike recoveries must normally be between 65% and 120% for decane, dodecane, and naphthalene, and between 80% and 120% for all other components of the Method Performance Check Spike. Where recoveries fall significantly outside this range with unknown cause, or with known cause that may impact samples, then samples from the same preparation batch must be repeated, or their data reports must be qualified.**

Diesel/Motor Oil Method Spike
OPTIONAL. Prepare a Diesel / Motor Oil Method Spike by fortifying reagent water with a known amount of diesel / motor oil in acetone. Spikes may be prepared at any reasonable concentration, depending on the objective.

Dispense an accurate volume of the Diesel / Motor Oil Method Spike Solution (see the Diesel/Motor Oil Method Spike Solution section) into approximately 1 mL of acetone, and quantitatively transfer the acetone solution to a reagent water sample. Extract and analyze as described in the Sample Extraction Procedure and GC Analysis Procedure sections.

Determine the targets for EPH_{W10-19} and EPH_{W19-32} by directly analyzing several replicates of the Diesel/Motor Oil Method Spike Solution diluted to a concentration that equals the amount of diesel/motor oil spiked (in µg) divided by the final extract volume for the spike.

A Diesel/Motor Oil Method Spike prepared in this way provides information about method precision and about method bias (accuracy), where bias is in this case a measure of extraction efficiency and losses associated with the extraction process. Acceptance criteria are at the discretion of the laboratory.

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 are normally Field Sample Replicates [a] or Field Sample Splits [a], since the entire contents of each sample must be analyzed along with the solvent rinsings from the sample bottle. 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*

OPTIONAL. The use of one or more Surrogate Compounds for EPH is at the discretion of the laboratory. Surrogates that elute outside the EPH retention time ranges are recommended so that they do not need to be subtracted from integrated EPH peak areas. Surrogate Compounds listed in other published hydrocarbon methods include ortho-terphenyl, chloro-octadecane and 5-alpha androstane.

Note that sample interferences will often preclude the accurate measurement of any surrogate by FID. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

*Surrogate Compounds have chemical characteristics similar to those of analytes, but provide analytical response that is distinct from analytes. They are added to samples prior to sample preparation. Surrogate percent recovery measurements are used as Method QC to estimate sample preparation losses and matrix effects. They are only useful when not subject to measurement interferences.

Sample Preparation Procedure

Sample Extraction Procedure

Laboratories are required to analyze the total contents of all water samples submitted for analysis by this method. If visible solids are present in a sample, the laboratory must do one of the following:

a) Physically separate the solids from the water, extract both portions separately, and combine the two extracts prior to GC analysis. Or,
b) Thoroughly mix the solids with the aqueous sample phase, and extract the entire sample in the separatory funnel. This option is only applicable where emulsions do not prevent an efficient extraction of the sample.

Prepare section. Use 500 mL of reagent water for the Method Blank, Method Performance Check Spike, and Diesel/Motor Oil Method Spike samples.

Accurately measure the entire contents of the 500 mL glass sample bottle into a separatory funnel.

Rinse the sample bottle with 50 mL of DCM, and add the rinsings to the separatory funnel.

Extract the sample by shaking for two minutes; vent the separatory funnel frequently to release pressure. Allow the phases to separate. Transfer the extract through anhydrous sodium sulphate and into a Kuderna-Danish collection flask (or round bottom flask).

Repeat the extraction two more times, each time using 50 mL of DCM, and combine the extracts in the Kuderna-Danish collection flask (or round bottom 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 1.00 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 or larger final extract volumes may be appropriate for higher level samples.

Extracts for this method must never be reduced to volumes below 0.5 mL, or severe losses of volatile EPH 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.

Transfer a portion of the extract to a GC autosampler vial and analyze by GC/FID. Store remaining extract at (4 ±4)°C for at least 40 days in case re-analysis is required.

Aliphatic/Aromatic Fractionation Procedure
If fractionation of Extractable Petroleum Hydrocarbons (or of LEPH or HEPH) into aliphatic and aromatic components is required, follow the procedure outlined in BCMELP Method "Aliphatic / Aromatic Fractionation of Extractable Petroleum Hydrocarbons in Solids and Waters" (Pending).

GC Analysis Procedure

Gas Chromatograph Conditions

GC Column:	DB-1, 30m, 0.32 mm id, 0.25um 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)
	3.4 mL/minute @ 320°C (63 cm/sec linear velocity)
Constant flow:	not recommended
Injector temp:	280°C
Injection solvent:	iso-octane
Injection volume:	2 uL
Injection mode:	splitless
GC liner type:	4 mm id splitless liner with silanized glass wool
Initial inlet purge:	OFF
Inlet purge on time:	1.0 minutes
FID temperature:	320°C
Oven program:	Initial Temp 65°C (hold 2.0 minutes)
	15°C /min to 320°C (hold 10 minutes)
FID gas flows:	as recommended by manufacturer

Initial Calibration
Analyze a 50 µg/mL Calibration Standard at the beginning of each new analytical batch (see the Calibration Standard Stock Solution section).

Calibration is by single or multi-point external standard technique, using eisocane (nC20).

A continuing calibration is recommended (i.e. reslope the calibration with each Verification Standard). Changes in response between standards must be monitored and controlled (see the Ongoing Verification of Calibration section).

Linear calibration must be used for this method. Either single or multi-point calibrations are acceptable, due to the linear response of GC/FID systems. If single-point calibration is used, linearity must be verified using a Control

Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control 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, ensuring that all specified acceptance criteria are met.

For each analysis batch, verify that the initial calibration is adequate by performing all tests specified in the Initial Calibration QC, ensuring that all specified acceptance criteria are met.

Calculate the Calibration Factor (CF) for eicosane in the Calibration Standard using the equation below. The Calibration Factor is based on the concentration of analyte in the solution that is injected onto the GC:

$$CF_{nC20} \text{ in mL/µg} = \frac{\text{Area of nC20 peak}}{\text{nC20 concentration (µg/mL in iso-octane)}}$$

Ongoing Verification of Calibration (Verification Standards)
After initial calibration, the Calibration Factor (CF_{nC20}) must be verified, at minimum, after every 12 hours of continuous operation. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

Use a Calibration Standard as a Verification Standard (see the Calibration Standard section).

Under a continuing calibration mode, if the Calibration Factor changes by more than 25% from the previous standard, or by more than 35% from the initial calibration standard, then corrective action must be taken, and samples analyzed after the last acceptable standard must be re-run.

Alternatively, an initial calibration may be used for as long as the Calibration Factor remains within 15% of its initial value. If this criterion is exceeded, the calibration may be updated using the Verification Standard Calibration Factor, but only if the continuing calibration acceptance criteria specified above are satisfied.

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 EPH_{W10-19} and EPH_{W19-32}
The Extractable Petroleum Hydrocarbons parameters are defined to include all GC/FID peaks eluting between decane (nC10) and dotriacontance (nC32). EPH_W is evaluated as two separate analytes: EPH_{W10-19} includes those hydrocarbons that elute between decane nonadecane, EPH_{W19-32} includes those hydrocarbons that elute between nonadecane and dotriacontane. Each EPH_W parameter is reported and considered independently (i.e. they are not normally summed).

Determine the total integrated peak area of each EPH_W range, where:

a) The EPH_{W10-19} range begins at the apex of the nC10 peak and ends at the apex of the nC19 peak.

b) The EPH_{W19-32} range begins at the apex of the nC19 peak and ends at the apex of the nC32 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch, and should be established using marker compound concentrations that do not overload the liquid phase of the GC column.

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 EPH areas must be visually verified, and must be manually corrected where potential error may exceed 1-2%.

Calculations

EPH_{W10-19} and EPH_{W19-32} concentrations are calculated by comparing total areas for each range to the response of the eicosane (nC20) calibration standard.

If any EPH-range Surrogate Compounds are added to samples, the contribution to EPH of those Surrogates must be subtracted from calculated EPH results. Because Surrogate Compounds frequently experience FID interference, it is most practical to subtract the actual spiked concentrations of Surrogate Compounds from calculated EPH concentrations. No Surrogate Compounds within the EPH-range should be added such that their concentration exceeds the Reporting Detection Limit for either of EPH_{W10-19} or EPH_{W19-32}.

Use the following equations to calculate EPH_{W10-19} and EPH_{W19-32}:

EPH_{W10-19} (µg/mL) = A_{10-19} x FV x Dil / (CF_{nC20} x Vol) – Actual Surrogate Conc* (µg/mL)

EPH_{W19-32} (µg/mL) = A_{19-32} x FV x Dil / (CF_{nC20} x Vol) – Actual Surrogate Conc* (µg/mL)

* Only Surrogates (if any) that elute within a given range are subtracted from that range.

where:

$A_{(10-19)}$ = Total area between nC10 and nC19 for the sample chromatogram.
$A_{(19-32)}$ = Total area between nC19 and nC32 for the sample chromatogram.
CF_{nC20} = Calibration Factor for nC20 standard (mL/µg)
FV = Final volume of sample extract (mL)
Dil = Dilution factor of sample extract (unitless)
Vol = Volume of sample extracted (mL)

When reporting to BCMELP, report EPH_{W10-19} and EPH_{W19-32} results for water samples in units of µg/L (ppb). Multiply µg/mL (ppm) results (as calculated above) by 1,000 to convert results to units of µg/L.

Diluting High Level Sample Extracts

Where sample results exceed the linear working range of the GC/FID system, they must be diluted and re-analyzed at a more appropriate extract concentration. Note that over-dilution of extracts can introduce significant error to EPH results. Diluted extracts should be prepared such

that their EPH_{W10-19} and EPH_{W19-32} areas fall within the linear working range of the GC/FID system, as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section.

Where sample extracts are diluted prior to analysis, or where less than one-half the normal amount of sample is extracted, Reporting Detection Limits must be increased accordingly.

Method Validation

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate EPH_W 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) and the Method Performance Check Spike (see the Method Performance Check Spike section).

Calculation of Actual EPH_W Concentrations of a Petroleum Reference Solution
This procedure describes how to calculate the *Actual EPH_W Concentrations* for solutions of petroleum products where only the total weight/volume concentration of the petroleum product is explicitly known. *Actual EPH_W concentrations* of a petroleum product can only be measured experimentally, whereas the 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 EPH_W Concentrations are required within this method for the following purposes:

a) determination of GC/FID linear range for EPH_{W10-19} and EPH_{W19-32} (i.e. calibration range),
b) determination of EPH_W Instrument Detection Limits (IDLs),
c) preparation of DL Check Standards and Method Spike Solutions,
d) calculation of EPH_W targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual EPH_W Concentration* of a petroleum product solution:

a) Prepare the petroleum product solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for EPH_{W10-19} and EPH_{W19-32} (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 *$[Diesel_{grav}]$.*

b) Perform replicate analyses of the petroleum product solution prepared in (1.) using the instrumental conditions specified within this method. A minimum of 7 replicates is recommended. Do not dilute the solution prior to analysis. Determine the average measured concentrations of EPH_{W10-19} and EPH_{W19-32} using the calculations specified in Calculations section (use a value of 1 for Final Volume, Dilution, and Sample Volume). In the example below, the measured EPH_{W10-19}

concentration is denoted as *[$EPH_{W10\text{-}19,measured}$]*, where the square brackets denote concentration. Percent Relative Standard Deviations (%RSDs) of these values may also be determined, and may be useful to set statistical warning and control limits for some applications.

c) Calculate the percentage that each EPH range represents of the total petroleum product concentration. Example (for $EPH_{W10\text{-}19}$ in a given source of diesel):

$$\%EPH_{W10\text{-}19} \text{ in diesel} = 100\% \times [EPH_{W10\text{-}19,measured}] \ / \ [Diesel_{grav}]$$

where:

[ ]	= symbol for concentration
[$EPH_{W10\text{-}19}$, measured]	= measured [$EPH_{W10\text{-}19}$] of a solution of diesel in iso-octane
$Diesel_{grav}$]	= actual [Diesel] in weight of diesel / volume iso-octane for the same solution.
Units	= same for both concentrations (e.g. µg/mL).

Note: The sum of the percentages of the $EPH_{W10\text{-}19}$ and $EPH_{W19\text{-}32}$ compositions in diesel and/or motor oil are normally less than 100% (typically 80-90%) because not all components of diesel fall within the nC10 to nC32 boiling point range.

d) To calculate the *Actual EPH_W Concentrations* of other concentrations of the same product, use the EPH_W percentages relative to the total petroleum product concentration as follows (the $EPH_{W10\text{-}19}$ in diesel example is continued):

$$Actual\ EPH_{W10\text{-}19}\ Conc.\ in\ Diesel. = (\%EPH_{W10\text{-}19} \text{ in Diesel}) / 100\% \times [Diesel_{grav}]$$

where:

[$Diesel_{grav}$] = the conc. of diesel (in weight diesel / volume iso-octane) of any solution.

Establishing Instrument Calibration Working Range and Estimated IDLs
Establish the linear working range of the GC/FID system for $EPH_{W10\text{-}19}$ and $EPH_{W19\text{-}32}$ using a series of dilutions of the 100,000 µg/mL 1:1 Diesel:Motor Oil Stock Solution prepared in iso-octane. Analyze diesel/motor oil 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 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 the 1:1 diesel:motor oil mixture. Calculate $EPH_{W10\text{-}19}$ and $EPH_{W19\text{-}32}$ results for each solution using the procedure described in Calculations section. These are referred to below as *Calculated EPH_W Results*.

Follow the procedure in the Calculation of Actual EPH_W Concentrations of a Petroleum Reference Solution section to calculate the *Actual $EPH_{W10\text{-}19}$* and *$EPH_{W19\text{-}32}$ Concentrations* for all of the above solutions.

Make a plot of *Calculated $EPH_{W10\text{-}19}$ Results* (y-axis) versus *Actual $EPH_{W10\text{-}19}$ Concentrations* (x-axis), and determine the linear working range of $EP_{10\text{-}19}$.

Make a plot of *Calculated EPH_{W19-32} Results* (y-axis) versus *Actual EPH_{W19-32} Concentrations* (x-axis), and determine the linear working range of EPH_{W19-32}.

Instrument accuracy for EPH parameters is measured as *Calculated EPH_W Results* / *Actual EPH_W Concentrations.* As EPH concentration approaches the Instrument Detection Limit (IDL), instrument accuracy decreases because the less abundant components of the petroleum hydrocarbon blend cease to be detected. For the purposes of this method, the Instrument Detection Limit for each EPH parameter is defined as the lowest EPH concentration at which instrument accuracy consistently falls within the range of 70-130%. However, a diesel/motor oil chromatogram at the IDL must still resemble chroma-tograms of higher concentrations. At the IDL, any chromatographic peak that normally comprises more than 5% of total EPH_{W10-19} or EPH_{W19-32} area must still be visible as a distinct peak; this requirement takes precedence over the 70-130% accuracy requirement.

The IDL is expressed in units of *Actual EPH_{W10-19} or EPH_{W19-32} Concentration*.

Establishing Method Detection Limits

Determine the Method Detection Limits (MDLs) at the 95% confidence level for both EPH_{W10-19} and EPH_{W19-32}, using the procedure outlined in Section A of this manual. This method requires the use of the procedure described below, which is one of several generic approaches described in Section A of this manual.

Consider the normal final volume of extracts produced by this method, and select a concentration for method spikes of diesel/motor oil into water that should result in extracts with concentrations of between one and three times the estimated IDLs for EPH_{W10-19} and EPH_{W19-32} (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 Diesel/Motor Oil Method Spike Solution to prepare these method spikes (see the Diesel/Motor Oil Method Spike Solution section).

Calculate the Method Detection Limit (MDL) at the 95% confidence level for both EPH_{W10-19} and EPH_{W19-32} using the calculations described in Section A of this manual.

Average recoveries of the MDL Method Spikes for EPH_{W10-19} and EPH_{W19-32} must be between 60-140%, where recovery is defined as calculated EPH result / spiked (actual) EPH concentration. If this condition is not met, repeat the MDL determination at a higher spike level.

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. It is a requirement of this method that Reporting Detection Limits for EPH_{W10-19} and EPH_{W19-32} are greater than or equal to the Method Detection Limits (at the 95% confidence level) that were experimentally determined in-house using the procedure described in the Establishing Method Detection Limits section.

Ensure that calculated Method Detection Limits and Reporting Detection Limits are below any regulatory criteria values or regulatory standards

specified by BCMELP or other applicable regulatory body. For BC requirements, refer to BCMELP method "Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids or Water".

Determination of DL Check Standard Concentration and EPH Targets
Use the procedure that follows to select a suitable concentration of 1:1 diesel:motor oil in iso-octane for the DL Check Standard. This procedure involves two separate conversions of units:

a) Diesel/motor oil product concentration units must be converted to (and from) EPH concentration units.

b) Sample concentration units (e.g. µg/mL of water) must be converted to sample extract concentration units (e.g. µg/mL of iso-octane).

Results from the Calculation of Actual EPH_W Concentrations of a Petroleum Reference Solution and Establishing Instrument Calibration Working Range and Estimated IDLs sections may initially be used for step 1, but this determination should be repeated if the source of the diesel/motor oil changes:

a) Calculate the percentages of the total 1:1 diesel:motor oil concentration that each of EPH_{W10-19} and EPH_{W19-32} represent, using the procedure described in the Calculation of Actual VH_S Concentration of a Petroleum Reference Solution section. Typically, EPH_{W10-19} and EPH_{W19-32} each represent about 35-45% of the total diesel/motor oil concentration. The sum of the 2 percentages is normally less than 100% because not all components of diesel and motor oil fall within the nC10 - nC32 boiling point range.

b) Determine the concentrations of diesel/motor oil in iso-octane that correspond to each of the EPH_{W10-19} and EPH_{W19-32} Reporting Detection Limits. Use the calculated percentages from (a) to calculate this diesel/motor oil concentration. The normal sample volume extracted, and the normal extract final volume are required to convert method units to the *equivalent* solution concentration units:

[Diesel/Motor Oil] equiv. to EPH_{W10-19} DL =

100 x [(Reporting DL for EPH_{S10-19}) / (%EPH_{10-19} in Diesel/Motor Oil)] x (Sample Volume / Extract Volume)

[Diesel/Motor Oil] equiv. to EPH_{W19-32} DL =

100 x [(Reporting DL for EPH_{W19-32}) / (%EPH_{19-32} in Diesel/Motor Oil)] x (Sample Volume / Extract Volume)

where:

Units for [Diesel/Motor Oil] = ppm (µg/mL of iso-octane)
Units for Reporting DL for EPH = ppm (e.g. µg/mL of water
Sample Volume and Extract Volume must be in same units (i.e. mL).

Select a concentration for the Detection Limit Check Standard that is approximately equal to both of the concentrations determined above. Then, a single DL Check Standard can be used to simultaneously verify that the Reporting Detection Limits for both EPH_{W10-19} and EPH_{W19-32} remain valid.

c) Calculate the targets for EPH_{W10-19} and EPH_{W19-32} in the Detection Limit Check Standard by multiplying the concentrations selected in (a) by the EPH_W percentages from (b).

Target for EPH_{W10-19}= (DL Std. Diesel:Motor Oil conc.) x (%EPH_{W10-19} in Diesel/Motor Oil)

Target for EPH_{W19-32} = (DL Std. Diesel:Motor Oil conc.) x(%EPH_{W19-32} in Diesel/Motor Oil)

Accuracy and Precision

For a limited period of time, individual laboratories may assess their accuracy and/or precision for this method by analyzing replicates of the 1998 BCMELP Hydrocarbon Round Robin samples, and comparing results against single laboratory and interlaboratory consensus values. This is not a formal requirement for the validation of this method, but is strongly recommended.

Alternatively, multiple method spikes of an appropriate petroleum product (a 1:1 blend of unweathered diesel/motor oil is recommended) may be used to assess the method, although less information can be derived about accuracy without interlaboratory consensus data. "Accuracy" data gathered from method spikes is limited to a measure of percent recovery (i.e. a measure of extraction losses). Better measures of overall method bias and accuracy are obtained from analysis of BCMELP Interlaboratory Study samples, and from Method Performance Check Spikes.

Determine Method Spike targets using *Actual EPH_W Concentrations* of the spike solution by following the procedure outlined in the Calculation of Actual EPH_W Concentrations of a Petroleum Reference Solution section.

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 the GC Analysis section, except for minor differences in the GC oven temperature program.

EPH_W Instrument Performance Check Data

Multiple laboratory (Round Robin) data and single laboratory data for Instrument Performance Checks are presented in Table I-8. These samples were analyzed as described in the Instrument Performance Check section.

Table I-8: EPHw Instrument Performance Check Data

	Round Robin Results			Single Lab Results		
Relative Response	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Decane (nC10)	6	0.99	8.3%	8	0.99	0.8%
Naphthalene	6	1.03	7.0%	8	1.02	1.0%
Dodecane (nC12)	4	0.97	2.8%	8	1.01	1.6%
Hexadecane (nC16)	7	0.99	2.8%	8	0.99	0.8%
Phenanthrene	7	1.04	5.7%	8	1.00	1.3%
Nonadecane (nC19)	7	1.00	0.8%	8	0.99	0.7%
Eicosane (nC20)	7	1.00	n/a	8	1.00	n/a
Pyrene	7	1.08	1.5%	8	1.01	3.6%
Benzo(a)pyrene	6	0.82	19.6%	-	-	-
Triacontane (nC30)	6	0.92	15.5%	8	0.98	5.6%
Dotriacontane (nC32)	7	0.87	16.0%	8	0.92	8.4%

EPH_W Method Performance Check Spike Data

Multiple laboratory (Round Robin) data and single laboratory data for Method Performance Check Spikes are presented in Table I-9. These samples were analyzed as described in the Method Performance Check Spike section.

Table I-9: EPHw Method Performance Check Data

	Round Robin Results			Single Lab Results		
Spike Recovery (%)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Decane (nC10)	6	54.9%	18.6%	8	85.6%	4.5%
Naphthalene	6	82.7%	31.3%	8	101%	5.2%
Dodecane (nC12)	4	69.3%	15.3%	8	99.0%	5.0%
Hexadecane (nC16)	7	92.1%	18.1%	8	105%	5.5%
Phenanthrene	7	93.1%	17.1%	8	105%	6.1%
Nonadecane (nC19)	7	94.7%	17.9%	8	105%	5.6%
Eicosane (nC20)	7	95.4%	17.0%	8	105%	5.6%
Pyrene	7	93.9%	15.0%	8	106%	7.1%
Benzo(a)pyrene	6	99.9%	19.9%	8	111%	6.0%
Triacontane (nC30)	6	94.8%	19.3%	8	110%	6.1%
Dotriacontane (nC32)	7	97.8%	20.4%	8	102%	5.5%

Method Detection Limited Data

The Method Detection Limit data reported in Table I-10 was obtained from the 1998 Single Laboratory Validation Study, and was generated as described in the Establishing Method Detection Limits section. The EPH_W *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-10: EPH_W Method Detection Limits (Single Laboratory Data)

Units = µg/L	#1	#2	#3	#4	#5	#6	#7	#8	Mean	Std. Dev.	Target	Mean Recovery	MDL
EPH_{W10-19}	146	151	129	159	130	159	156	175	**151**	**15.5**	**235**	**64 %**	**59**
EPH_{W19-32}	302	343	284	329	268	340	308	326	**313**	**26.9**	**294**	**106 %**	**102**

EPH_W Diesel / Motor Oil Method Spike Data

Multiple laboratory (Round Robin) data and single laboratory data for Diesel Method Spikes are presented in Tables I-10 and I-11. Two different concentrations of diesel/motor oil spikes were performed, at 5,000 µg/L and 25,000 µg/L in reagent water. These samples were analyzed as described in the Diesel/Motor Oil Method Spike section, except using Diesel instead of a Diesel/Motor Oil mixture. PAH and calculated $LEPH_W$ and $HEPH_W$ results also presented for the same samples.

Table I-11: EPHw Low Level Method Spike Data

	Round Robin Results			Single Lab Results		
EPH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
EPH_{W10-19}	7	3147	29.5%	8	3384	8.4%
EPH_{W19-32}	7	579	16.9%	8	565	8.3%
LEPHw	7	3143	29.5%	8	3380	8.4%
HEPHw	7	579	16.9%	8	565	8.3%
PAH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Naphthalene	8	1.72	40.7%	8	0.91	13.1%
Acenaphthene	5	0.49	67.1%	8	<0.5	n/a
Fluorene	8	0.78	53.8%	8	0.71	3.8%
Phenanthrene	8	1.30	45.0%	8	1.52	3.0%
Anthracene	6	<	n/a	8	0.21	7.2%
Acridine	5	<	n/a	8	<0.1	n/a
Fluoranthene	6	<	n/a	8	<0.05	n/a
Pyrene	6	0.20	62.8%	8	0.16	6.8%
Benz(a)anthracene	6	<	n/a	8	<0.05	n/a
Benzo(a)pyrene	7	<	n/a	8	<0.05	n/a

Table I-12: EPHw High Level Method Spike Data

	Round Robin Results			Single Lab Results		
EPH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
EPH_{W10-19}	7	16325	18.4%	8	17428	4.7%
EPH_{W19-32}	7	2978	17.2%	8	3341	4.8%
LEPHw	7	16304	18.4%	8	17407	4.7%
HEPHw	7	2978	17.2%	8	3340	4.8%
PAH Results (µg/L)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Naphthalene	8	9.56	38.4%	8	8.12	19.9%
Acenaphthene	6	2.62	59.1%	8	<3	n/a
Fluorene	8	3.73	47.4%	8	3.99	1.2%
Phenanthrene	8	6.36	43.4%	8	7.74	1.8%
Anthracene	4	<	n/a	8	0.98	3.4%
Acridine	6	<	n/a	8	<0.5	n/a
Fluoranthene	7	<	n/a	8	<0.2	n/a
Pyrene	6	0.85	54.8%	8	0.76	2.3%
Benz(a)anthracene	7	<	n/a	8	<0.05	n/a
Benzo(a)pyrene	7	<	n/a	8	<0.05	n/a

Use of Alternative Methods

This method contains several prescribed and required elements that may not be modified. These requirements are necessary due to the nature of method-defined 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_W 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 BCMELP:

a) 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.

b) "REQUIRED" QC elements from the Quality Control (QC) section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.

c) Maximum holding time prior to extraction is 7 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

d) Unless data is qualified, samples must be analyzed as "totals". See the Sample Extraction Procedure section for available options for the handling of samples that contain visible solids.

e) Sample bottles must be solvent rinsed during the extraction process.

f) Liquid-liquid solvent extraction is required.

g) Solid Phase Extraction (SPE) and Solid Phase Micro Extraction (SPME) are expressly prohibited for this method due to potential relative biases.

h) Use of a low volatility "keeper" solvent is required during solvent removal steps (an aliphatic keeper solvent like iso-octane is required for samples where aliphatic/aromatic fractionation is to be done).

i) Gas Chromatography with Flame Ionization Detection is required for measurement of EPH_W.

j) GC column must be a capillary column.

k) GC column stationary phase must be 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent).

l) 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.

m) nC20 (at a minimum concentration of 50 µg/mL) must be used as the calibration standard for both EPH_W ranges (see the Calibration Standard Stock Solution section).

n) If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control Standard section).

o) Calibration stability must be monitored as described in the Ongoing Verification of Calibration (Verification Standards) section.

p) EPH_W method detection limits and reporting limits must be based on a diesel/motor oil blend (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 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 BCMELP. This information must be available in the event of audit by BCMELP.

Pay particular attention to the results of Instrument Performance Checks (see Instrument Performance Check section) and Method Performance Check Spikes (see the Method Performance Check Spike section), since both of these checks 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:

a) Apparatus
b) Reagents and Standards
c) Gas Chromatograph Conditions

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

Modifications Where Equivalence Testing is Required:
Except where expressly disallowed in the Prescribed Element 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 Preparation Procedure (See appropriate section)
An equivalence test for Sample Preparation (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.

Note: 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 diesel or diesel/motor oil spikes into clean matrix samples or field samples. At least three concentrations of diesel or diesel/motor oil spikes must be investigated. At minimum, Method Spike Samples must be analyzed with targets for both EPH_{W10-19} and EPH_{W19-32} lying within the following ranges:

a) 1-5x Reported Detection Limit
b) 50-250x Reported Detection Limit

Note: For 1:1 diesel/motor oil spikes, targets for EPH_{W10-19} and EPH_{W19-32} are of similar magnitude. For diesel spikes, the EPH_{W10-19} target is typically about 5-6 times higher than the EPH_{W19-32} target. Therefore, with diesel spikes, up to four different spike concentrations may be necessary to cover the two ranges above for both EPH_{W10-19} and EPH_{W19-32}.

Each spiked sample set must be analyzed in triplicate (at minimum) by both the reference method and the modified method.

While available, 1998 BCMELP Round Robin Study sample spike solutions may be analyzed to satisfy a portion of this component of the equivalency test. Results for the modified method may then be compared against the Single Laboratory Results (in the Method Performance Data section), against the Round Robin Results (in the Use of Alternative Methods 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 [h].

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:

a) 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:

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

or,

b) 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].

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 [h].

Test for Precision of Modified Methods

Modified methods must demonstrate a reasonable level of precision on homogeneous samples (e.g. Method Spikes). Analyze a minimum of 8 replicates of at least one Diesel or Diesel/Motor Oil Method Spike that contains both EPH_{W10-19} and EPH_{W19-32} at ≥ 3 times the laboratory's routine Reporting 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 [h].

For both EPH_{W10-19} and EPH_{W19-32}, the modified method must demonstrate a precision of $\leq$ 20% relative standard deviation.

References

a) 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.

b) 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 E.

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

d) 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, section 3 (Protocol for Setting Method Detection Limits).

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

f) British Columbia Ministry of Environment, Lands and Parks, February 1996, Extractable Petroleum Hydrocarbons in Water by GC/FID.

g) British Columbia Ministry of Environment, Lands and Parks, June 1993, Hydrocarbons, Total Extractable (Dichloromethane) in Water by Gas Chromatograph (GC).

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 British Columbia Ministry of the Environment, Lands and Parks.

Acknowledgments

Mark Hugdahl and Scott Hannam of ASL Analytical Service Laboratories developed and wrote this method. ASL Analytical Service Laboratories analyzed and compiled the Single Laboratory Data.

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BCMELP 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.

Revision History	March 1997:	Initial publication of Version 1.0 for EPH Water.
	1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
	July 1999:	Finalization of present method based on results of a vetting round robin.
	December 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.

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 (7). The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

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

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

$$V_A = s_A^2 / n_A \qquad V_B = s_B^2 / n_B$$

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.

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

Parameters

Extractable Petroleum Hydrocarbons$_{(nC10\text{-}nC19)}$ in solids
Extractable Petroleum Hydrocarbon$_{s(nC19\text{-}nC32)}$ in solids

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
$EPH_{S10\text{-}19}$	**LEPH F086**
$EPH_{S19\text{-}32}$	**HEPH F086**

(Note that the above EMS codes are for results not corrected for PAHs.)

Analytical Method

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

Introduction

This method measures the collective concentration of Extractable Petroleum Hydrocarbons in solids (EPH_S). Extractable Petroleum Hydrocarbons (EPH) are divided into two boiling point ranges, each quantitated against eicosane (nC20). $EPH_{S10\text{-}19}$ measures hydrocarbons that elute between n-decane and n-nonadecane, roughly equivalent to a boiling point range of 174°C to 330° C. $EPH_{S19\text{-}32}$ measures hydrocarbons that elute between n-nonadecane and n-dotriacontane, roughly equivalent to a boiling point range of 330°C to 467° C.

The two Extractable Petroleum Hydrocarbons (EPH) parameters are the 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 British Columbia Ministry of Environment, Land and Parks (BCMELP) method “Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids and Waters”.

The Extractable Petroleum Hydrocarbons (EPH) method is normally used in conjunction with the BCMELP Volatile Hydrocarbons (VH) method. Together, these methods can generate quantitative values for the concentration of most petroleum products. Note that the correlation of these results with the actual concentration of petroleum product in a sample (i.e. accuracy) may be less than would be achieved for single compound analyses.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC6 through nC10 (e.g. VH captures the majority of most unweathered gasolines, mineral spirits, and paint thinners). Petroleum products that are predominantly captured with the EPH parameters are those whose primary components are within the boiling point range of nC10 through nC32 (e.g. EPH captures the majority of most diesel fuels, lubricating oils, greases, hydraulic oils, waxes). Many petroleum products contain components within both the VH and EPH parameter ranges, (e.g. kerosenes, jet fuel, and weathered gasolines). Petroleum products that contain a substantial proportion of hydrocarbons with boiling points greater than nC32 will not be accurately quantitated by either of the VH or EPH methods.

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 EPH results among laboratories. British Columbia Ministry of the 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.

Every laboratory that uses this method, or a modified version of this method, to report EPH, LEPH, or HEPH data to BCMELP must perform an in-house validation of the method as described in the Method Validation section.

This method is not intended to quantitate individual target compounds (i.e. PAHs).

Units

µg/g

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.

Matrix

Soil
Sediment
Marine Sediment

Interferences and Precautions

Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. **All solvents, reagents and hardware 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. If further information concerning the chemical composition of sample components is required, a silica gel procedure can be used to fractionate EPH into aliphatic and aromatic components. This procedure can remove some naturally occurring organic components like humic acids. Refer to BCMELP Method “Aliphatic / Aromatic Fractionation of Extractable Petroleum Hydrocarbons in Solids and Waters” (Pending).

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 Reporting Detection Limits is suspected.

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

Collect samples in glass wide-mouth jars with Teflon-lined lids. No chemical preservation is recommended. Store samples away from direct sunlight at (4 $\pm$ 2)°C.

Maximum holding time prior to extraction is 14 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

Sampling staff are referred to the British Columbia Field Sampling Manual [2] for additional sample collection guidelines.

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 uL splitless or on-column injections is strongly recommended.

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

Reagents and Standards

Reagents
Hexane
Acetone (2-propanone)
Iso-octane (2,2,4-trimethyl-pentane)
Reagent water (organic free)

Diatomaceous earth drying reagent (e.g. Hydromatrix)
Sodium sulphate, Anhydrous
Sodium chloride
Clean soil/sediment matrix (e.g. Ocean Construction Sakrete "Play 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.

Calibration Standard Stock Solution
Prepare a Calibration Standard Stock Solution in DCM containing 1,000 µg/mL of each of decane (nC10), dodecane (nC12), hexadecane (nC16), nonadecane (nC19), eicosane (nC20), dotriacontane (nC32), naphthalene, phenanthrene, and pyrene. This mixture may be purchased commercially or prepared from neat standards. Ensure all components are fully dissolved before use. Warm the solution and/or place in an ultrasonic bath if necessary to re-dissolve any precipitated components. Store refrigerated at $(4 \pm 4)°C$.

Calibration Standard: Prepare a 50 µg/mL Calibration Standard in iso-octane by diluting the 1,000 µg/mL stock standard. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at $(4 \pm 4)°C$.

Control Standard Stock Solution
Prepare a Control Standard Stock Solution containing 5,000 µg/mL of eicosane (nC20) in iso-octane. This solution may also contain other target analytes, and may be purchased commercially or prepared from neat compounds. **It must be prepared from a different source than the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions). Store refrigerated at $(4 \pm 4)°C$.**

Control Standard: Prepare a 250 µg//mL Control Standard by diluting the 5,000 µg//mL Control Standard Stock Solution in iso-octane.

Diesel / Motor Oil Stock Solution
Prepare a 100,000 µg/mL stock solution of 1:1 diesel (fuel #2) : motor oil (non-synthetic 10W30) by combining 50,000 µg/mL of each product in iso-octane. Prepare the solution by weight (e.g. weigh 0.250g diesel plus 0.250g motor oil into a 5.00 mL volumetric flask). Any unweathered, fresh source of these products is acceptable. Store refrigerated at $(4 \pm 4)°C$.

Note: The 100,000 µg/mL concentration above can be referred to as the "product concentration" of the solution, where the product is in this case a diesel/motor oil mixture. It is important to note that the product concentration of the solution is not equivalent to its total EPH_S concentration (i.e. EPH_{S10-19} + EPH_{S19-32}).

Detection Limit Check Standard: Dilute the 100,000 µg/mL Diesel / Motor Oil Stock Solution to prepare a Detection Limit (DL) Check Standard in iso-octane. Prepare the standard at a concentration that is approximately equal to the extract concentrations that correspond to the Reporting Detection Limits for each of EPH_{S10-19} and EPH_{S19-32}. This standard is required for Initial Calibration QC (see Detection Limit Check section). Store refrigerated at $(4 \pm 4)°C$.

Refer to Determination of DL Check Standard Concentration and EPH Targets section for the procedure to determine an appropriate concentration for this solution.

Diesel / Motor Oil Method Spike Solution: If Diesel/Motor Oil Method Spikes will be analyzed (see Diesel/Motor Oil Method Spike section) prepare a Diesel/Motor Oil Method Spike Solution at a suitable concentration by diluting the Diesel/Motor Oil Stock Solution into iso-octane. Concentrations ranging from approximately 1,000 - 20,000 µg/mL of diesel/motor oil may be appropriate, depending on the desired Method Spike concentrations. Store refrigerated at (4 ±4)°C.

Quality Control (QC)

Table I-1 summarizes all the required and recommended calibration and QC components of this method. Each of these components is described in detail in this section.

Table I-1: Summary of EPH_S QC and Calibration Requirements and Recommendations

QC Component	Minimum Frequency	Minimum Acceptance Criterion
Instrument Performance QC		
Instrument Performance Check	**Every 12 hours, and at end of analysis batch if >6 hrs from previous check.**	**Relative response ratios must be 0.7-1.3 for all components**
Calibration QC and Verification		
Instrument blank	**1/analysis batch**	None
Control Standard	**1/analysis batch**	Within 15% of expected concentration
Detection Limit Check Standard	**1/analysis batch**	50 – 150% of EPH targets
Ongoing Verification of Calibration	**Every 12 hours, and at end of analysis batch if >6 hrs from previous check.**	**Within 25% of previous std & Within 35% of initial calibration, (in continuing calibration mode).**
Method QC		
Method Blank	**1/preparation batch**	**< reported detection limit**
Method Performance Check Spike	**1/preparation batch**	***Average* recoveries must be: 65-120% for nC10, nC12, naphthalene, 80-120% for all other components.**
Diesel / Motor Oil Method Spike	**Not required**	None
Laboratory and Field Sample Replicates	**Not required**	None
Surrogate Compounds	**Not required**	None
Reference Material	**1/preparation batch**	At discretion of laboratory

General QC Requirements

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

Samples are prepared in a set that is referred to as a preparation batch, and are analyzed by GC in a set that is referred to as an analysis batch.

If any of the specified acceptance criteria for Instrument Performance QC, Initial Calibration QC, or Method 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_{S10-19} and EPH_{S19-32} 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.

Instrument Performance QC

Instrument Performance Check
REQUIRED – Perform this check whenever a Calibration Standard or Verification Standard is analyzed. See Ongoing Verification of Calibration section for required frequency.

The 50 µg/mL Calibration Standard is used for initial calibration (see Initial Calibration section) and for ongoing verification of calibration (see Ongoing Verification of Calibration section). In addition, it is used for the Instrument Performance Check to do the following:

a) Measure and control relative response ratios of specified EPH components,
b) Determine retention time windows for EPH integration ranges,
c) Confirm resolution of decane (nC10) from the solvent peak.

One essential purpose of the Instrument Performance Check is to ensure that the GC/FID response factors of EPH components throughout its boiling point range are roughly equal. If excessive relative bias exists among EPH 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 eicosane (nC20). For all compounds within the mixture, these ratios should normally fall between 0.80 and 1.20. Acceptance criteria for relative response ratios are 0.7 – 1.3 for all components of the Instrument Performance Check. **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 analysis batch of no more than 100 samples. Inject an iso-octane solvent blank to the GC system to establish the chromatographic baseline. All GC parameters must be identical to those of samples run in the same analysis batch.

Control Standard
REQUIRED - minimum 1 per analysis batch of no more than 100 samples. Analyze a Control Standard (see Control Standard section) containing eicosane (nC20), 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, and to verify calibration

linearity if single-point calibration is used. Where possible, the Control Standard should be traceable to national chemical metrology standards.

If single-point calibration is used, the concentration of the Control Standard must differ from the concentration of the Calibration Standard by at least a factor of five.

Note: At concentrations above ~ 50-100 µg/mL, chromatographic peak shapes may be distorted due to column phase overload, but FID responses are not normally affected.

If the calculated concentration of eicosane in the Control Standard 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 analysis batch of no more than 100 samples. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low level solution of diesel / motor oil.

Analyze a Detection Limit Check Standard that contains both EPH_{S10-19} and EPH_{S19-32} at concentrations that are approximately equivalent to the EPH_{S10-19} and EPH_{S19-32} Reporting Detection Limits for the method (see Detection Limit Check Standard section).

The procedure for determining the target concentrations for this standard is described under Method Validation in Determination of DL Check Standard Concentration and EPH Targets section. **Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the EPH_{S10-19} and EPH_{S19-32} targets (calculated as described in the Determination of DL Check Standard Concentration and EPH Targets section). Data reports must be qualified if this acceptance criterion is not met for the analysis batch in which the samples were run.**

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 50 samples. Prepare a Method Blank using a clean soil/sediment matrix. 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).

Method Performance Check Spike
REQUIRED - minimum 1 per preparation batch of no more than 50 samples. Prepare a Method Performance Check Spike by fortifying a clean soil/sediment matrix (containing 20% moisture) with the Calibration Standard Stock Solution, at a concentration of 25 µg/g of each component.

Spike 250 uL of the 1,000 µg/mL Calibration Standard Stock Solution into approximately 1 mL of iso-octane, and quantitatively transfer the iso-octane solution to 10 grams of clean soil/sediment matrix and 2.0 mL of reagent water. Dry the spiked sample with diatomaceous earth (unless associated samples are not to be dried). Once drying is complete, transfer the sample immediately to a Soxhlet apparatus and wet the sample with extraction solvent. Extract and analyze as described in Sample Preparation Procedure and GC Analysis Procedure sections.

Note: Dispensing the spike solution in a 1mL volume of iso-octane helps to prevent losses of volatile EPH components (iso-octane simulates the presence of organic matter, which is otherwise not present in a clean sand matrix). It is strongly recommended that the drying process be completed as quickly as possible, using the procedure described above.

Calculate the spike recovery of each component of the mixture by quantitation against the appropriate component of the Calibration Standard (i.e. calculate naphthalene against naphthalene). **Spike recoveries must normally be between 65% and 120% for decane, dodecane, and naphthalene, and between 80% and 120% for all other components of the Method Performance Check Spike. Where recoveries fall significantly outside this range with unknown cause, or with known cause that may impact samples, then samples from the same preparation batch must be repeated, or their data reports must be qualified.**

Diesel/Motor Oil Method Spike
OPTIONAL. Prepare a Diesel/Motor Oil Method Spike by fortifying a clean sediment/soil matrix (containing approximately 20% water) with an accurate volume of the Diesel/Motor Oil Method Spike Solution (see Diesel/Motor Oil Method Spike Solution section). Extract and analyze as described in Sample Preparation Procedure and GC Analysis Procedure sections. Spikes may be prepared at any reasonable concentration, depending on the objective.

Determine the targets for EPH_{S10-19} and EPH_{S19-32} by directly analyzing several replicates of the Diesel/Motor Oil Method Spike Solution diluted to a concentration that equals the amount of diesel/motor oil spiked (in µg) divided by the final extract volume for the spike.

A Diesel/Motor Oil Method Spike prepared in this way provides information about method precision and about method bias (accuracy), where bias is in this case a measure of losses associated with the extraction process. Acceptance criteria are at the discretion of the laboratory.

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 [3], 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*
OPTIONAL. The use of one or more Surrogate Compounds for EPH is at the discretion of the laboratory. Surrogates that elute outside the EPH retention time ranges are recommended so that they do not need to be subtracted from integrated EPH peak areas. Surrogate Compounds listed in other published hydrocarbon methods include ortho-terphenyl, chloro-octadecane and 5-alpha androstane.

Note that sample interferences will often preclude the accurate measurement of any surrogate by FID. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

*Surrogate Compounds have chemical characteristics similar to those of analytes, but provide analytical response that is distinct from analytes. They are added to samples prior to sample preparation. Surrogate percent recovery measurements are used as Method QC to estimate sample preparation losses and matrix effects. They are only useful when not subject to measurement interferences.

Reference Materials

REQUIRED - minimum 1 per preparation batch of no more than 50 samples. Acceptance criteria are at the discretion of the laboratory. 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.

RTC CRM 355-100 (TPH in Soil). A diesel-contaminated terrestrial soil, produced specifically for this method by Resource Technology Corporation of Laramie, Wyoming.

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

Sample Preparation Procedure

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

It is strongly recommended that samples be sub-sampled, weighed, dried, and transferred to Soxhlet thimbles (with solvent) in very small batches (ideally this is performed one sample at a time). The longer a sample is exposed to air, the more volatile components are lost. This is especially true after the drying step has been initiated. Sediment samples must not be permitted to warm to room temperature during the sub-sampling process. 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).

Using a top-loading balance, 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 and add a few mL of hexane:acetone to the thimble to prevent loss of volatiles. Do not dry samples with anhydrous salts like sodium sulphate or magnesium sulphate.

Note: Drying with anhydrous salts is a chemical process that takes minutes or even hours to complete. Drying with diatomaceous earth is a rapid physical process. Longer drying times translate to more loss of volatiles. Drying with anhydrous salts can cause total loss of nC10 - nC12 components, with significant losses occurring up to nC16.

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, Method Performance Check Spike, 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 sulphate 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 (not normally required for typical BCMELP applications).

Extracts for this method must never be reduced to volumes below 0.5 mL, or severe losses of volatile EPH components may result.

Transfer a portion of the extract to a GC autosampler vial and analyze by GC/FID. Store remaining extract at $(4 \pm 4)^{\circ}C$ for at least 40 days in case re-analysis is required.

Aliphatic/Aromatic Fractionation Procedure
If fractionation of Extractable Petroleum Hydrocarbons (or of LEPH or HEPH) into aliphatic and aromatic components is required, follow the procedure outlined in BCMELP Method "Aliphatic / Aromatic Fractionation of Extractable Petroleum Hydrocarbons in Solids and Waters" (Pending).

GC Analysis Procedure

Gas Chromatograph Conditions:

GC Column:	DB-1, 30m, 0.32 mm id, 0.25um 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)
	3.4 mL/minute @ 320°C (63 cm/sec linear velocity)
Constant flow:	not recommended
Injector temp:	280°C
Injection solvent:	iso-octane
Injection volume:	2 uL
Injection mode:	splitless
GC liner type:	4 mm id splitless liner with silanized glass wool
Initial inlet purge:	OFF
Inlet purge on time:	1.0 minutes
FID temperature:	320°C
Oven program:	Initial Temp 65°C (hold 2.0 minutes)
	15°C /min to 320°C (hold 10 minutes)
FID gas flows:	as recommended by manufacturer

Initial Calibration
Analyze a 50 µg/mL Calibration Standard at the beginning of each new analytical batch (see the Calibration Standard section).

Calibration is by single or multi-point external standard technique, using eisocane (nC20).

A continuing calibration is recommended (i.e. reslope the calibration with each Verification Standard). Changes in response between standards must be monitored and controlled (see the Ongoing Verification of Calibration section).

Linear calibration must be used for this method. Either single or multi-point calibrations are acceptable, due to the linear response of GC/FID systems. If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control 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, ensuring that all specified acceptance criteria are met. For each analysis batch, verify that the initial calibration is adequate by performing all tests specified in the Initial Calibration QC section ensuring that all specified acceptance criteria are met.

Calculate the Calibration Factor (CF) for eicosane in the Calibration Standard using the equation below. The Calibration Factor is based on the concentration of analyte in the solution that is injected onto the GC:

$$CF_{nC20} \text{ in mL/µg} = \frac{\text{Area of nC20 peak}}{}$$

nC20 concentration (µg/mL in iso-octane)

Ongoing Verification of Calibration (Verification Standards)
After initial calibration, the Calibration Factor (CF_{nC20}) must be verified, at minimum, after every 12 hours of continuous operation. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

Use a Calibration Standard as a Verification Standard (see the Calibration Standard section).

Under a continuing calibration mode, if the Calibration Factor changes by more than 25% from the previous standard, or by more than 35% from the initial calibration standard, then corrective action must be taken, and samples analyzed after the last acceptable standard must be re-run.

Alternatively, an initial calibration may be used for as long as the Calibration Factor remains within 15% of its initial value. If this criterion is exceeded, the calibration may be updated using the Verification Standard Calibration Factor, but only if the continuing calibration acceptance criteria specified above are satisfied.

See the Instrument Performance QC section for requirements that must be satisfied with each Calibration Standard and Verification Standard.

Integration of Total Areas for EPH_{S10-19} and EPH_{S19-32}
The Extractable Petroleum Hydrocarbons parameters are defined to include all GC/FID peaks eluting between decane (nC10) and dotriacontance (nC32). EPH_S is evaluated as two separate analytes: EPH_{S10-19} includes those hydrocarbons that elute between decane nonadecane, EPH_{S19-32} includes those hydrocarbons that elute between nonadecane and dotriacontane. Each EPH_S parameter is reported and considered independently (i.e. they are not normally summed).

Determine the total integrated peak area of each EPH_S range, where:

a) The EPH_{S10-19} range begins at the apex of the nC10 peak and ends at the apex of the nC19 peak.
b) The EPH_{S19-32} range begins at the apex of the nC19 peak and ends at the apex of the nC32 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch, and should be established using marker compound concentrations that do not overload the liquid phase of the GC column.

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 EPH areas must be visually verified, and must be manually corrected where potential error may exceed 1-2%.

Calculations

EPH_{S10-19} and EPH_{S19-32} concentrations are calculated by comparing total areas for each range to the response of the eicosane (nC20) calibration standard.

If any EPH-range Surrogate Compounds are added to samples, the contribution to EPH of those Surrogates must be subtracted from calculated EPH results. Because Surrogate Compounds frequently experience FID interference, it is most practical to subtract the actual spiked concentrations of Surrogate Compounds from calculated EPH concentrations. No Surrogate Compounds within the EPH-range should be added such that their concentration exceeds the Reporting Detection Limit for either of EPH_{S10-19} or EPH_{S19-32}.

Use the following equations to calculate EPH_{S10-19} and EPH_{S19-32}:

EPH_{S10-19} (µg/g) = A_{10-19} x FV x Dil / (CF_{nC20} x DryWt) – Actual Surrogate Conc* (µg/g)

EPH_{S19-32} (µg/g) = A_{19-32} x FV x Dil / (CF_{nC20} x DryWt) – Actual Surrogate Conc* (µg/g)

* Only Surrogates (if any) that elute within a given range are subtracted from that range.

where:

$A_{(10-19)}$ = Total area between nC10 and nC19 for the sample chromatogram.
$A_{(19-32)}$ = Total area between nC19 and nC32 for the sample chromatogram.
CF_{nC20} = Calibration Factor for nC20 standard (mL/µg)
FV = Final volume of sample extract (mL)
Dil = Dilution factor of sample extract (unitless)
DryWt = Dry weight of sample extracted (g)

When reporting to BCMELP, report EPH_{S10-19} and EPH_{S19-32} results for solids samples in units of µg/g.

Diluting High Level Sample Extracts
Where sample results exceed the linear working range of the GC/FID system, they must be diluted and re-analyzed at a more appropriate extract concentration. Note that over-dilution of extracts can introduce significant error to EPH results. Diluted extracts should be prepared such that their EPH_{S10-19} and EPH_{S19-32} areas fall within the linear working range of the GC/FID system, as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section.

Where sample extracts are diluted prior to analysis, or where less than one-half the normal amount of sample is extracted, Reporting Detection Limits must be increased accordingly.

Method Validation

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 method meets the relative response equivalency requirements of the method by performing the EPH_S Instrument Performance Check (see Quality Control section) and the EPH_S Method Performance Check Spike (see Quality Control section).

Calculation of Actual EPH_S Concentrations of a Petroleum Reference Solution

This procedure describes how to calculate the *Actual EPH_S Concentrations* for solutions of petroleum products where only the total weight/volume concentration of the petroleum product is explicitly known. *Actual EPH_S concentrations* of a petroleum product can only be measured experimentally, whereas the concentration of the petroleum product is simply determined by dividing the weight of product by the volume of solvent in which it is prepared.

Actual EPH_S Concentrations are required within this method for the following purposes:

a) determination of GC/FID linear range for EPH_{S10-19} and EPH_{S19-32} (i.e. calibration range),
b) determination of EPH_S Instrument Detection Limits (IDLs),
c) preparation of EPH_S DL Check Standards and Method Spike Solutions,
d) calculation of targets for EPH_S DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual EPH_S Concentration* of a petroleum product solution:

a) Prepare the petroleum product solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for EPH_{S10-19} and EPH_{S19-32} (see 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 *$[Diesel_{grav}]$.*

b) Perform replicate analyses of the petroleum product solution prepared in (a) using the instrumental conditions specified within this method. A minimum of 7 replicates is recommended. Do not dilute the solution prior to analysis. Determine the average measured concentrations of EPH_{S10-19} and EPH_{S19-32} using the calculations specified in the Calculation section (use a value of 1 for Final Volume, Dilution, and Sample Volume). In the example below, the measured EPH_{S10-19} concentration is denoted as *$[EPH_{S10-19,measured}]$*, where the square brackets denote concentration. Percent Relative Standard Deviations (%RSDs) of these values may also be determined, and may be useful to set statistical warning and control limits for some applications.

c) Calculate the percentage that each EPH range represents of the total petroleum product concentration. Example (for EPH_{S10-19} in a given source of diesel):

$$\%EPH_{S10-19} \text{ in diesel} = 100\% \times ([EPH_{S10-19,measured}] / [Diesel_{grav}]$$

where:

[ ]	=	symbol for concentration
EPH_{S10-19}, measured]	=	measured [EPH_{S10-19}] of a solution of diesel in iso-octane
[$Diesel_{grav}$]	=	actual [Diesel] in weight of diesel / volume iso-octane for the same solution.
Units	=	same for both concentrations (e.g. µg/mL).

Note: The sum of the percentages of the EPH_{S10-19} and EPH_{S19-32} compositions in diesel and/or motor oil are normally less than 100% (typically 80-90%) because not all components of diesel fall within the nC10 to nC32 boiling point range.

d) To calculate the *Actual EPH_S Concentrations* of other concentrations of the same product, use the EPH_S percentages relative to the total petroleum product concentration as follows (the EPH_{S10-19} in diesel example is continued):

Actual EPH_{S10-19} Conc. in Diesel (%EPH_{S10-19} in Diesel) / 100% x *[$Diesel_{grav}$]*

where:

[$Diesel_{grav}$] = the conc. of diesel (in weight diesel / volume iso-octane) of any solution.

Establishing Instrument Calibration Working Range and Estimated IDLs
Establish the linear working range of the GC/FID system for EPH_{10-19} and EPH_{19-32} using a series of dilutions of the 100,000 µg/mL 1:1 Diesel:Motor Oil Stock Solution prepared in iso-octane. Analyze diesel/motor oil 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 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 the 1:1 Diesel: Motor Oil mixture. Calculate EPH_{S10-19} and EPH_{S19-32} results for each solution using the procedure described in Calculation section. These are referred to below as *Calculated EPH_S Results*.

Follow the procedure in the Method Validation section to calculate the *Actual EPH_{S10-19}* and *EPH_{S19-32} Concentrations* for all of the above solutions.

Make a plot of *Calculated EPH_{S10-19} Results* (y-axis) versus *Actual EPH_{S10-19} Concentrations* (x-axis), and determine the linear working range of EPH_{S10-19}.

Make a plot of *Calculated EPH_{S19-32} Results* (y-axis) versus *Actual EPH_{S19-32} Concentrations* (x-axis), and determine the linear working range of EPH_{S19-32}.

Instrument accuracy for EPH parameters is measured as *Calculated EPH_S Results* / *Actual EPH_S Concentrations.* As EPH concentration approaches the Instrument Detection Limit (IDL), instrument accuracy decreases because the less abundant components of the petroleum hydrocarbon blend cease to be detected. For the purposes of this method, the Instrument Detection Limit for each EPH parameter is defined as the lowest EPH concentration at which instrument accuracy consistently falls within the range of 70-130%. However, a diesel/motor oil chromatogram at the IDL must still resemble chromatograms of higher concentrations. At the IDL, any chromatographic peak that normally comprises more than 5% of total EPH_{S10-19} or EPH_{S19-32} area must still be visible as a distinct peak; this requirement takes precedence over the 70-130% accuracy requirement.

The IDL is expressed in units of *Actual EPH_{S10-19} or EPH_{S19-32} Concentration*.

Establishing Method Detection Limits
Determine the Method Detection Limits (MDLs) at the 95% confidence level for both EPH_{S10-19} and EPH_{S19-32}, using the procedure outlined in Section A of this manual. This method requires the use of the procedure described below, which is one of several generic approaches described in Section A.

Consider the normal final volume of extracts produced by this method, and select a concentration for method spikes of diesel/motor oil into a clean sediment/soil matrix (of 20% moisture) that should result in extracts with concentrations of between one and three times the estimated IDLs for EPH_{S10-19} and EPH_{S19-32} (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 Diesel/Motor Oil Method Spike Solution to prepare these method spikes (see the Diesel/Motor Oil Method Spike Solution section).

Calculate the Method Detection Limit (MDL) at the 95% confidence level for both EPH_{S10-19} and EPH_{S19-32} using the calculations described in Section A of this manual.

Average recoveries of the MDL Method Spikes for EPH_{S10-19} and EPH_{S19-32} must be between 60-140%, where recovery is defined as calculated EPH_S result / spiked (actual) EPH_S concentration. If this condition is not met, repeat the MDL determination at a higher spike level.

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. It is a requirement of this method that Reporting Detection Limits for EPH_{S10-19} and EPH_{S19-32} are greater than or equal to the Method Detection Limits (at the 95% confidence level) that were experimentally determined in-house using the procedure described in the Establishing Method Detection Limits section.

Ensure that calculated Method Detection Limits and Reporting Detection Limits are below any regulatory criteria values or regulatory standards specified by BCMELP or other applicable regulatory body. For BC requirements, refer to BCMELP method “Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids or Water”.

Determination of DL Check Standard Concentration and EPH Targets
Use the procedure that follows to select a suitable concentration of 1:1 Diesel:Motor Oil Stock Solution for the DL Check Standard. This procedure involves two separate conversions of units:

a) Diesel/motor oil product concentration units must be converted to (and from) EPH concentration units.
b) Sample concentration units (e.g. µg/g of solids) must be converted to sample extract concentration units (e.g. µg/mL of iso-octane).

Results from sections Calculations of Actual EPHs Concentrations of a Petroleum Reference Solution and Establishing Instrument Calibration Working Range and Estimated IDLs may initially be used for step (a), but this
determination should be repeated if the source of the diesel/motor oil changes:

a) Calculate the percentages of the total 1:1 diesel:motor oil concentration that each of EPH_{10-19} and EPH_{19-32} represent, using the procedure described in the Calculation of Actual EPHs Concentrations of a Petroleum Reference Solution section. Typically, EPH_{10-19} and EPH_{19-32} each represent about 35-45% of the total diesel/motor oil concentration. The sum of the 2 percentages is normally less than 100% because not all components of diesel and motor oil fall within the nC10 - nC32 boiling point range.

b) Determine the concentrations of diesel/motor oil that correspond to each of the EPH_{10-19} and EPH_{19-32} Reporting Detection Limits. Use the calculated percentages from (a) to calculate this diesel/motor oil concentration. The normal sample volume extracted, and the normal extract final volume are required to convert method units to the *equivalent* solution concentration units:

[Diesel/Motor Oil] equiv. to EPH_{S10-19} DL =

100 x [(Reporting DL for EPH_{S10-19}) / (%EPH_{10-19} in Diesel/Motor Oil)] x (Sample Weight / Extract Volume)

[Diesel/Motor Oil] equiv. to EPH_{S19-32} DL =

100 x [(Reporting DL for EPH_{S19-32}) / (%EPH_{19-32} in Diesel/Motor Oil)] x (Sample Weight / Extract Volume)

where:

Units for [Diesel/Motor Oil]	=	ppm (µg/mL of iso-octane)
Units for Reporting DL for EPH	=	ppm (e.g. µg/g dry weight of sample)
Units for Sample Weight	=	grams (dry weight)
Units for Extract Volume	=	mL

Select a concentration for the Diesel/Motor Oil DL Check Standard that is approximately equal to both of the concentrations determined above. Then, a single DL Check Standard can be used to simultaneously verify that the Reporting Detection Limits for both EPH_{S10-19} and EPH_{S19-32} remain valid.

c) Calculate the targets for EPH_{S10-19} and EPH_{S19-32} in the EPH_S Detection Limit Check Standard by multiplying the concentrations selected in (b) by the EPH_S percentages from (a).

Target for EPH_{S10-19} = (DL Std. Diesel:Motor Oil conc.) x (%EPH_{S10-19} in Diesel/Motor Oil)

Target for EPH_{S19-32} = (DL Std. Diesel:Motor Oil conc.) x (%EPH_{S19-32} in Diesel/Motor Oil)

Accuracy and Precision

Individual laboratories may assess their accuracy and/or precision for this method by analyzing replicates of the 1998 BCMELP Hydrocarbon Round Robin samples, and comparing results against single laboratory and interlaboratory consensus values (these samples are commercially available Reference Materials - see Reference Materials section). This is not a formal requirement for the validation of this method if used without significant modification, but is strongly recommended.

Alternatively, multiple method spikes of an appropriate petroleum product (a 1:1 blend of unweathered diesel/motor oil is recommended) may be used to assess method accuracy and precision, although less information can be

derived about accuracy without interlaboratory consensus data. “Accuracy” data gathered from method spikes is limited to a measure of recovery (i.e. a measure of extraction losses). Better measures of overall method bias and accuracy are obtained from analysis of BCMELP Interlaboratory Study samples, and from Method Performance Check Spikes.

For Method Spikes, determine targets using *Actual EPH_S Concentrations* of the spike solution by following the procedure outlined in Calculation of Actual EPHs Concentrations of a Petroleum Reference Solution section.

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-2. These samples were analyzed as described in the Instrument Performance Check section.

Table I-2: EPHs Instrument Performance Check Data

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

EPH_S Method Performance Check Spike Data: Multiple laboratory (Round Robin) data and single laboratory data for EPH_S Method Performance Check Spikes are presented in Table I-3. These samples were analyzed as described in the Method Performance Check Spike section.

Table I-3: EPHs Method Performance Check Spike Data						
	Round Robin Results			Single Lab Results		
Spike Recovery (%)	**(n)**	**Mean**	**% RSD**	**(n)**	**Mean**	**% RSD**
Decane (nC10)	4	41.6%	89.0%	8	89.1%	4.6%
Naphthalene	4	43.6%	52.2%	8	92.0%	3.5%
Dodecane (nC12)	3	40.9%	60.7%	8	92.0%	3.6%
Hexadecane (nC16)	6	80.9%	15.2%	8	95.4%	2.8%
Phenanthrene	6	75.1%	25.8%	8	94.9%	3.5%
Nonadecane (nC19)	6	83.6%	20.1%	8	96.5%	1.7%
Eicosane (nC20)	6	83.4%	23.7%	8	97.0%	1.5%
Pyrene	6	68.2%	41.8%	8	96.3%	1.7%
Benzo(a)pyrene	3	68.2%	45.0%	8	73.6%	6.5%
Triacontane (nC30)	3	88.0%	8.4%	8	97.0%	1.7%
Dotriacontane (nC32)	5	94.7%	17.9%	8	96.6%	1.7%

Method Detection Limit Data: The EPH_S Method Detection Limit data reported in Table I-4 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-4: EPH_S Method Detection Limits (Single Laboratory Data)													
units = mg/kg	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**Mean**	**Std. Dev.**	**Target**	**Mean Recovery**	**MDL**
EPH_{S10-19}	52.0	51.2	45.7	42.6	42.1	51.4	51.8	37.3	**46.8**	**5.7**	**44.6**	**105%**	**21**
EPH_{S19-32}	56.1	52.9	54.2	51.3	55.4	55.9	58.4	51.7	**54.5**	**2.4**	**51.7**	**105%**	**9.1**

EPH_S Reference Material Data

Multiple laboratory (Round Robin) data and single laboratory data for EPH_S Reference Materials are presented in Tables I-5 and I-6. 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-5: EPHs Reference Material - RTC CRM 355-100

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

Table I-6: 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 several prescribed and required elements that may not be modified. These requirements are necessary due to the nature of method-defined 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_S 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.

Prescribed Elements

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

a) 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.

b) "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.

c) Maximum holding time prior to extraction is 14 days after sampling. Maximum holding time for refrigerated extracts is 40 days. Where holding times are exceeded, data must be qualified.

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

e) All samples with > 40% moisture content must be dried with diatomaceous earth before extraction (as described in the Sample Extraction Procedure section). Drying with diatomaceous earth is recommended for all samples.

f) Anhydrous salts may not be used to dry sediment samples prior to extraction.

g) 1:1 hexane:acetone solvent is required as the extraction solvent.

h) 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).

i) Use of a low volatility "keeper" solvent is required during solvent removal steps (an aliphatic keeper solvent like iso-octane is required for samples where aliphatic/aromatic fractionation is to be done).

j) Gas Chromatography with Flame Ionization Detection is required for measurement of EPH_S.

k) GC column must be a capillary column.

l) GC column stationary phase must be 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent).

m) 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.

n) nC20 (at a minimum concentration of 50 µg/mL) must be used as the calibration standard for both EPH_S ranges (see the Calibration Standard Stock Solution section).

o) If single-point calibration is used, linearity must be verified using a Control Standard with a concentration that differs from the Calibration Standard concentration by at least a factor of five (see the Control Standard section).

p) Calibration stability must be monitored as described in the Ongoing Verification of Calibration section.

q) EPH_S method detection limits and reporting limits must be based on a diesel/motor oil blend (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 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 BCMELP. This information must be available in the event of audit by BCMELP.

Pay particular attention to the results of Instrument Performance Checks and Method Performance Check Spikes (see appropriate sections), since both of these checks 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 Use of Alternative Methods section or elsewhere, changes to the following components of this method are permitted if all specified quality control requirements of the method are achieved:

a) Apparatus
b) Reagents and Standards
c) Gas Chromatograph Conditions

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

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.

Note: 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 BCMELP 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:

a) ***At least five unspiked field samples.*** 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 peat samples
- one or more soil or sediment samples
- one or more samples with >40% moisture

b) ***At least two soil / sediment Reference Materials.*** While available, the two RMs analyzed within the 1998 BCMELP Hydrocarbon Round Robin must be used to satisfy this requirement:
- Resource Technology Corporation RTC 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 the RTC 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 [4].

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, one of the following must be satisfied:

i) 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:

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

or,

ii) 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 [4].

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 [4].

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 Reporting 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 [4].

For both EPH_{S10-19} and $EPH_{S19-32,}$ the modified method must demonstrate a precision of ≤ 20% relative standard deviation.

References

a) Laboratory and Systems Management, Environmental Protection Department, Ministry of Environment, Lands and Parks, Province of British Columbia, 1996, British Columbia Field Sampling Manual, Parts A & D.
b) Canadian Standards Association, January 1995, Requirements for the Competence of Environmental Laboratories, CAN/CSA-Z753.
c) Massachusetts Department of Environmental Protection, January 1998, Method for the Determination of Extractable Petroleum Hydrocarbons (EPH).
d) 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 British Columbia Ministry of the Environment, Lands and Parks.

Acknowledgments

Mark Hugdahl and Scott Hannam of ASL Analytical Service Laboratories developed and wrote this method. ASL Analytical Service Laboratories analyzed and compiled the Single Laboratory Data.

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)" [3].

BCMELP 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.

Revision History	March 1997:	Initial publication of Version 1.0 for EPH in Soil
	1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
	July 1999:	Finalization of present method based on results of a vetting round robin.
	December 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.

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 (7). The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

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

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

$$V_A = s_A^2 / n_A \qquad V_B = s_B^2 / n_B$$

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.

Silica Gel Fractionation of Extractable Petroleum Hydrocarbons

Parameters and Analyte Symbols

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

Analytical Method

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

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 $EPH_{10\text{-}19}$ and $EPH_{19\text{-}32}$ 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 the 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
Waste Water
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 x 10 mm i.d. glass chromatography columns with 250mL reservoir
Teflon stop-cocks for above
Kuderna-Danish Concentrator system (or rotary evaporator)
250 mL Kuderna-Danish (KD) flasks (or round bottom flasks)
Nitrogen blowdown system
Micro-syringes
Oven (Capable of 130^{o}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^{o}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 ug/mL of each of decane (nC10), dodecane (nC12), hexadecane (nC16), nonadecane (nC19), eicosane (nC20), dotriacontane (nC32), naphthalene, phenanthrene, and pyrene. This mixture may be purchased commercially or prepared from neat standards. Ensure all components are fully dissolved before use. Warm the solution and/or place in an ultrasonic bath if necessary to re-dissolve any precipitated components. Store refrigerated at (4 $\pm$ 4)^{o}C.

EPH Fractionation Performance Check Solution

Prepare a 50 ug/mL EPH Performance Check Solution in iso-octane by diluting the 1,000 ug/mL Calibration Standard Stock Solution. Warm the solution and mix well before use to ensure complete dissolution of all components. Store refrigerated at (4 $\pm$ 4)°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 (3). Required and recommended QC elements are described within this section.

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

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

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

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

Weigh (7.0 $\pm$ 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 $\pm$ 1) mL of hexane or pentane to column, open the stopcock and begin collecting the aliphatic fraction (F1). Turn off the stopcock when the solvent reaches the top of the packing. [Note: If 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 $\pm$ 2) mL of 50:50 DCM:Hexane or 50:50 DCM:Pentane to the column, open the stopcock and collect the aromatic fraction (F2). Collect this fraction until the column is completely drained.

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

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

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

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

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 nC16 through nC32, including phenanthrene and pyrene, and between 70% and 115% for nC10, nC12, and naphthalene.

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

b) Method Detection Limits

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

Table 1: EPH MDL's to be applied to Aliphatic/Aromatic EPH parameters

Fractionated EPH parameter:	Code	Use MDL for
Aliphatic-EPH_{10-19} in water	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 $\geq$ 3 times the laboratory's routinely reported detection limits ($\geq$ 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 $\geq$ 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:

$$\mathbf{RPD = |(X_1 - X_2) / mean_{(X1, X2)}| * 100\%}$$

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 (7). This test is summarized in Appendix I.

If results for one or more samples do not meet one of the above criteria, additional replicates of the same samples may be analyzed, with the tests applied to the larger populations. If necessary, either the Dixon or Grubbs outlier tests may be used to discard outlier datapoints (7).

Test for Precision of Modified Methods

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

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

Where necessary, outlier data points may be discarded if they satisfy either the Dixon or Grubbs outlier tests (7).

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

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 & 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)" (4).

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.

Calculation of Light and Heavy Extractable Petroleum Hydrocarbons in Solids or Water (LEPH & HEPH)

Parameters

Light Extractable Petroleum Hydrocarbons in water
Heavy Extractable Petroleum Hydrocarbons in water

Light Extractable Petroleum Hydrocarbons in solids
Heavy Extractable Petroleum Hydrocarbons in solids

Analyte Symbols and EMS Codes

Analyte Symbol	EMS Code
$LEPH_W$	**LEPH F064**
$HEPH_W$	**HEPH F064**
$LEPH_S$	**LEPH F085**
$HEPH_S$	**HEPH F085**

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

Analytical Methods

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

water = mg/L
solid = µg/g

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 Hydrocarbons (EH) and Polycyclic Aromatic Hydrocarbons (PAHs) be analyzed using methodologies which have been approved by theDirector.

Selected PAHs are subtracted from EH 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 Site Regulations (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 should be subtracted from LEPH, and which should be subtracted from HEPH, for both waters and soils.

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

Procedure

Subtract the total applicable PAHs from the appropriate EH 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 $LEPH_W$, subtract the individual results for acenaphthene, acridine, anthracene, fluorene, naphthalene, and phenanthrene from the EPH_{W10-19} concentration obtained by the approved EPH GC/FID method.

To calculate $LEPH_S$, subtract the individual results for naphthalene and phenanthrene from the EPH_{S10-19} concentration obtained by the approved EPH GC/FID method.

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

To calculate $HEPH_S$, subtract the individual results for benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, and pyrene from the EH_{S19-32} 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 to BCMELP in units of µg/g dry weight for solids, and in units of µg/L for waters.

Maximum Reporting Detection Limits

This section lists the Maximum Permitted Reporting Detection limits for LEPH and HEPH in soil and water. Higher detection limits may be reported to BCMELP by laboratories or permittees under special circumstances, but acceptance of these results is at the discretion of the Director.

Analyte Symbol	Maximum Reporting DL
$LEPH_S$	500 µg/g (dry weight)
$LEPH_W$	250 µg/L
$HEPH_S$	500 µg/g (dry weight)
$HEPH_W$	250 µg/L

Normal Reporting Detection Limits for LEPH and HEPH must not be less than the Reporting Detection Limits for EPH_{10-19} and EPH_{19-32}. Validation procedures for EPH detection limits are described in the appropriate EPH method.

Revision History

March 1997:	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Solids and similarly for water.
1998 - 1999:	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
July 1999:	Finalization of present method based on results of a vetting round robin.
December 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'. Former methods superseded.

Oil and Grease in Water - Combined Hexane Extraction

Parameter

Oil and grease.

Analytical Method

Combined hexane extraction, gravimetric.

EMS Code

0003 X372

Introduction

Oil and Grease is any material recovered as a substance soluble in hexane. 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. Unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oils 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

Particulates are separated from the sample by filtration and then extracted with hexane using a Soxhlet extractor. The liquid phase is then extracted with hexane and this extract is subsequently combined with the Soxhlet extract. The hexane is evaporated from the combined extract and the residue is weighed. Note: The definition of oil and grease is based on the procedure used. Thus, the source of the oil and/or grease, the solvent used and the presence of extractable non-oily matter will influence the results obtained.

MDL

1 mg/L

Matrix

Fresh water
Wastewater
Marine water

Liquid - liquid extraction is sufficient for most samples with TSS < 500 mg/L. If TSS >500 mg/L, then use the combined Soxhlet and liquid-liquid extraction method.

Interferences and Precautions

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 from co-extractives which are not oil and grease. A low bias results from the poor extraction efficiency of hexane.

Sample Handling and Preservation

Bottle - 1 L glass, preferably wide mouth.
Preservation - conc. HCl, 3 mL/L to pH <2 (to inhibit bacterial growth).
Collect a representative sample in a wide mouthed glass bottle that has been rinsed with the solvent. Do not rinse the bottle with sample. Collect a separate sample for an oil and grease determination and do not subdivide in the laboratory.

Stability

Holding time - analyze within 14 days of collection.
Storage - store at 4°C until analyzed

Procedure

Apparatus

a) Extraction apparatus; Soxhlet extractor (containing a 33 x 94 mm extraction thimble) fitted with an Allihn condenser and a 250 mL flat bottom flask.
b) Distillation apparatus; condenser and connector (fitted with the 250 mL flat bottom flask).
c) Hot plate.
d) Filtration apparatus; two litre vacuum flask fitted with a 12 cm Buchner funnel (containing two 11 cm cheesecloth discs overlaid with 11 cm Whatman No. 42 filter paper).
e) Drying oven.
f) Desiccator provided with desiccant.
g) Analytical balance, sensitive to 0.1 mg.

Reagents

a) n-Hexane; highest purity pesticide grade.
b) Diatomaceous earth filter aid suspension: add 10 g filter aid to one litre deionized water.
c) Compressed air, dry.

Procedure

Note: 1) Samples are collected in hexane-rinsed one litre glass bottles.
2) The extraction flasks (flat bottom 250 mL) used in the procedure are dried to constant weight at 105°C, cooled in a desiccator and weighed.

a) Prepare a filter consisting of two cheesecloth discs overlaid with filter paper. Place the assembled filter in the Buchner funnel and wet the filter with distilled water. Under vacuum, apply 100 mL filter aid suspension to the prepared filter - the filter must be completely covered with the filter aid. Wash the filter with three successive portions of 100 mL distilled water. Dry the filter under vacuum.
b) Determine the volume of sample to be analyzed by visual comparison with a pre-graduated one litre glass bottle.
c) Filter the sample under vacuum and continue until no more water is removed from the filter.
d) Extract filtrate using Oil and Grease in Water - Direct Extraction procedure.
e) Remove the filter from the funnel with a pair of forceps and carefully place in an extraction thimble.
f) Wipe all areas of both the funnel and collection bottle, exposed to the sample, with strips of cheesecloth soaked in hexane. Add the cheesecloth to the extraction thimble.
g) Dry the extraction thimble in an oven at 105°C and then place the thimble in the Soxhlet extractor.
h) Add 125 mL hexane to the extraction flask and connect to the Soxhlet extractor.
i) Extract for 2-4 hr. Ensure that at least 25 cycles of hexane have passed through the extractor.
j) Combine hexane from direct extraction with hexane from Soxhlet extraction.
k) Distill off the hexane until 3-5 mL remains.
l) Pass dry filtered air into the flask until no hexane remains.
m) Heat the extraction flask in an oven at 105°C until dry; desiccate and weigh.

Note: Repeat the foregoing procedure with a distilled water blank. Determine any increase in weight of the pre-weighed flask and use this value as a blank correction.

Calculation

$$\text{Oil and Grease, mg/L} = \frac{1000\,[\,(W1 - W2) - C\,]}{\text{mL sample}}$$

where:

W1 = wt of flask + residue (mg)

W2 = wt of flask (mg)

C = wt contribution from blank (mg)

Precision

MOE Synthetic samples	Standard Deviation
(spike at 7.8 mg/L)	0.36 mg/L
(spike at 27.56 mg/L)	1.93 mg/L

Accuracy

None listed.

Quality Control

Blanks: 1 blank per batch or 1 in 14.
All balances should be calibrated with Class "A" weights.

References

a) "Standard Methods For the Examination of Water and Wastewater", 13th Edition, American Public Health Association, New York, 1971.
b) "ASTM Standards, Part 23", American Society for Testing and Materials, Philadelphia, 1971.

Revision History

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

Oil and Grease in Water - Direct Hexane Extraction

Parameter

Oil and grease

Analytical Method

Hexane extraction, gravimetric.

EMS Code

0003 X055

Introduction

Oil and Grease is any material recovered as a substance soluble in hexane. 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. Unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oils 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. If the sample has high suspended solids, the combined extraction procedure should be used.

Summary

The sample is placed in a separatory funnel and extracted with hexane into a tared flask. The hexane is evaporated from the extract and the residue is dried at 105°C, cooled and weighed.

MDL

1 mg/L

Matrix

Fresh water
Wastewater
Marine water

Liquid-liquid extraction is sufficient for most samples with TSS < 500 mg/L. If TSS >500 mg/L, then use the combined Soxhlet and liquid-liquid extraction method.

Interferences and Precautions

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 from co-extractives which are not oil and grease. A low bias results from the poor extraction efficiency of hexane.

Sample Handling and Preservation

Bottle - 1 L glass, preferably wide mouth
Preservation - 3 mL/L of conc. HCl to pH<2 (to inhibit bacterial growth)

Collect a representative sample in a wide mouthed glass bottle that has been pre-rinsed with solvent. Do not rinse the bottle with sample. Collect a separate sample for an oil and grease determination and do not subdivide in the laboratory.

Stability

Holding time - extract within 30 days of collection.
Storage - store at 4°C until analyzed

Procedure

Apparatus

a) Separatory funnels; 2 litre.
b) Filtration apparatus; 52 mm glass filtering funnels (containing folded Whatman No. 40 filter paper).
c) Distillation apparatus; condenser and connector fitted with a 250 mL flat bottom flask.
d) Hot plate.
e) Drying oven.
f) Desiccator provided with desiccant.
g) Analytical balance, sensitive to 0.1 mg.

Reagents

a) Hexane; highest purity pesticide grade.
b) Sodium sulfate; anhydrous (granular).
c) Methanol.
d) Aerosol OT.
e) Compressed air; dry.

Procedure

Note: The extract collection flasks in the procedure are dried to constant weight at 105°, cooled in a desiccator and weighed.

a) Determine the volume of the sample to be analyzed by visual comparison with a pre-graduated one litre glass bottle.
b) Add the sample to a 2 litre separatory funnel.
c) Wash the oil and grease bottle with 25 mL hexane and add to the separatory funnel.
d) Shake the separatory funnel for 2 min. and allow to settle.
e) If the phases separate, continue with the procedure. If not, add 2 drops of Aerosol OT; mix and allow to settle. If the emulsion disperses, continue with the procedure. If it persists, add 5 mL methanol; mix and allow to settle.
f) Run off the bottom (aqueous) layer into the original oil and grease sample bottle.
g) Run the solvent layer through a prepared filter (folded filter paper containing 25-30 g anhydrous sodium sulfate) into a 125 mL Erlenmeyer flask. Rinse the filter with 10 mL hexane.
h) Starting with the aqueous layer in the oil and grease bottle repeat steps b - g twice more.
i) Rinse the separatory funnel with 15 mL hexane and filter into the Erlenmeyer flask through the prepared filter. Rinse the filter with 10 mL hexane.
j) Transfer the hexane extract from the Erlenmeyer flask to a pre-weighed 250 mL flat bottom flask. Use two 10 mL portions of hexane to rinse the Erlenmeyer flask.
k) Distill the hexane off until only 3-5 mL remains.
l) Pass dry filtered air into the flask until no hexane remains. Heat the flask in an oven at 105°C until dry; desiccate and weigh.

Note: Repeat the procedure with a distilled water blank. Determine any increase in weight of the pre-weighed flask and use this value as a blank correction.

Calculation

$$\text{Oil and Grease, mg/L} = \frac{1000\,[\,(W1 - W2) - C\,]}{\text{mL sample}}$$

where:
W1 = wt of flask + residue (mg)
W2 = wt of flask (mg)
C = wt contribution from blank (mg)

Precision

MOE Synthetic samples

(spiked at 8.11 mg/L)	SD = 0.82 mg/L
(spiked at 35.6 mg/L)	SD = 1.56 mg/L

BCR Synthetic samples

(spiked at 16.7 mg/L)	SD = 0.54 mg/L
(spiked at 4.36 mg/L)	SD = 0.40 mg/L

Accuracy

None listed.

Quality Control

1 blank per batch or 1 in 14
All balances should be calibrated with Class "A" weights.

References

a) Standard Methods For the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York, 1971.
b) ASTM Standards, Part 23, American Society for Testing and Materials, Philadelphia, 1971.

Revision History

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

Oil and Grease (Mineral) in Water by Direct Extraction: Roller Method

Parameter	Oil and Grease (Mineral)
Analytical Method	Direct Extraction (Roller Mixing)
EMS Code	
Introduction	Oil and Grease is any material recovered as a substance soluble in hexane. It may include material other than animals 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. Unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oils 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	The sample is placed in a 4 L bottle and extracted with hexane by rolling overnight. The hexane is evaporated from the separated extract and the residue is weighed. It is to be noted that the definition of oil and grease is based on the procedure used. Thus, the source of oil and/or grease, the solvent used and the presence of extractable nonoily matter will influence the result obtained.
MDL	1 mg/L
Matrix	Fresh Water Wastewater
Interferences and Precautions	An oil which volatilizes at 70°C will be lost.
Sample Handling and Preservation	Unfiltered: Field 2 mL/L 50% v/v sulphuric acid Unfiltered: Lab 2 mL/L 50% v/v sulphuric acid Collect a representative sample in a wide mouthed glass bottle that has been rinsed with the solvent. Do not rinse the bottle with sample. Collect a separate sample for an oil and grease determination and do not subdivide in the laboratory.
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) 4 L bottles
b) Sodium Sulfate; anhydrous (granular).
c) Hot plate.
d) Drying oven.
e) Desiccator provided with desiccant.
f) Analytical balance, sensitive to 0.1 mg.
g) Wheaton Modular Cell Production Roller Apparatus Model III.
h) Either a 2 L separatory funnel or a custom cap for 4 L bottle with a spigot for draining liquid.
i) 250 mL flat bottom flasks.

Reagents

a) Hexane; highest purity pesticide grade.
b) Filtration apparatus; 52 mm glass filtering funnels (containing folded Whatman No. 40 filter paper).
c) Silica gel; column chromatography grade, 70 - 230 mesh, activated by heating in muffle furnace at 550°C for 2 - 2.5 hours. Store in sealed bottle.
d) Nitrogen; dry.

Procedure

Note: a) The flat bottom 250 mL flasks used in the procedure are dried to constant weight at 70°C; desiccated and weighed.

a) Add the sample to a 4 L cylinder bottle.

b) Thoroughly rinse the oil and grease bottle with 4 x 25 mL hexane and add to the 4 L bottle.
c) Mix the bottle overnight (minimum of 16 h) on a roller mixer, then allow to settle.
d) Transfer to 2 L separatory funnel or bottle with stop cock attached. Run off the bottom aqueous layer into the oil and grease bottle. Measure the volume of the original sample.
e) Prepare filter to contain a bottom layer of 10 - 20 g of activated silica, then a top layer of 10 - 15 g of anhydrous sodium sulfate. Run the solvent layer through this filter and rinse with 10 mL hexane.
f) Evaporate solvent at low heat on a hot plate (35% of maximum setting) in a fume hood until only 3 - 5 mL of hexane remains.
g) Pass dry nitrogen into the flask until no hexane remains.
h) Heat the flask in a drying oven at 70°C for 30 minutes; desiccate overnight or to constant weight, and weigh.

Calculation

$$\text{Oil and Grease, mg/L} = \frac{1000\,[W1 - W2]}{\text{mL sample}} \times 1000$$

where: W1 = wt of flask + residue, in g.
W2 = wt of flask, in g.

Precision

Commercial reference samples at concentrations from 13 to 374 mg/L Oil and Grease gave coefficients of variation of 9%.

Accuracy

Commercial reference samples at concentrations from 13 to 374 mg/L Oil and Grease gave average recovery of 103% compared to consensus values supplied.

Quality Control

a) Repeat the foregoing procedure with deionized water blank. Determine any increase in weight of the pre-weighed flask and report this value as a blank.

b) Run one duplicate per batch. Record duplicate results in a control database with duplicate control chart linked to it.
Note: Because of inhomogenous nature of oil and grease samples, splitting samples for duplicate analysis will not give a good estimate of precision.

c) Run a standard reference material at least every 3 months, and record data in a control chart database with linked control chart.

References

a) American Public Health Association. Standard Methods. Thirteenth Edition. New York (1971).
b) American Society for Testing and Materials. ASTM Standards, Part 23. Philadelphia (1971).

Revision Dates

November 2002. Method adopted from Manual Supplement #1. EMS Code assigned.

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 Na2SO4 + silica gel into a preweighed disposable 25 mm x 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 animals 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 watts and pulsing capability.
b) 125mL honey jars with PTFE lined caps.
c) Disposable glass 25 mm x 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 1/3 of the filter with Na2SO4. Place the funnel into a preweighed (to 0.0001g) 25 mm x 200 mm disposable glass test tube and pour the extract through the filter. Rinse the jar with 2 x 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

$$\textbf{Min. O\&G(in µg/g)} = \frac{1{,}000{,}000 \times (\text{Final Wt,g} - \text{Initial Wt,g})}{(\text{Wt,g of Sample} \times (100 - \%\text{Moisture})/100)}$$

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

a) 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, 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 it's 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 (ug/g)
Oil and Grease	50
Oil and Grease (Mineral)	50

Matrix

Soil (Marine)
Sediment Solids (concrete, wood chips, etc.)

Interferences and Precautions

Naturally occuring 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 degrees celsius.

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

$$\textbf{Min. O\&G(in µg/g)} = \frac{1{,}000{,}000 \times (\text{Final Wt,g} - \text{Initial Wt,g})}{(\text{Wt,g of Sample} \times (100 - \%\text{Moisture})/100)}$$

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.

Volatile Organic Compounds (VOC) in Water by Purge and Trap GC/MS

Parameter Volatile organic compounds (EPA-624)

Analytical Method Purge and trap GC/MS

Introduction This method is applicable to the qualitative and quantitative determination of VOC in water samples.

Method Summary The sample is analyzed by purge and trap gas chromatography /mass spectrometry. The procedure involves purging the volatile compounds from the sample with an inert gas, and trapping them on a solid sorbant. The trap is then heated and the compounds are flushed onto the gas chromatographic column. Analysis is accomplished by separation of the components by gas chromatography and detection/quantitation by mass spectrometry.

MDL and EMS Codes

Compound	µg/L	EMS Code
Benzene	0.5	**B020 X384**
Bromodichloromethane	0.8	**B012 X384**
Bromoform	0.8	**B013 X384**
Bromomethane	2.0	(will be defined on request)
Carbon Tetrachloride	0.8	(will be defined on request)
Chlorobenzene	0.5	**C010 X384**
Chloroethane	2.0	**C003 X384**
2-Chloroethylvinyl Ether	1.0	(will be defined on request)
Chloroform	0.8	**C032 X384**
Chloromethane	2.0	**C070 X384**
Dibromochloromethane	0.8	**C033 X384**
Dichloromethane	4.0	**M041 X384**
1,1-Dichloroethane	0.8	**C021 X384**
1,2-Dichloroethane	0.5	**C022 X384**
1,1-Dichloroethylene	0.5	**C024 X384**
1,2-Dichloroethylene	0.5	**C023 X384**
1,2-Dichloropropane	0.8	**C025 X384**
cis-1,3-Dichloropropene	0.5	**C027 X384**
trans-1,3-Dichloropropene	0.5	**C028 X384**
Ethylbenzene	0.5	**B021 X384**
Styrene	0.5	**S010 X384**
1,1,2,2-Tetrachloroethane	0.8	**C080 X384**
Tetrachloroethene	0.8	**T030 X384**
1,1,1-Trichloroethane	0.6	**T016 X384**
Trichloroethene	0.3	**T029 X384**
Trichlorofluoromethane	0.5	**T070 X384**
Toluene	1.5	**T001 X384**
Vinyl Chloride	2.9	(to be defined on request)

Matrix
Fresh Water
Wastewater
Marine Water
Sludge

Interferences and Precautions

Proper sample containers should be used at all times to reduce loss of components by evaporation. Samples can be contaminated by diffusion of some volatile organic compounds through the septum (particularly fluorocarbons and dichloromethane). Samples should be stored accordingly, so as to reduce the possibility of contamination. 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 if low level samples are analyzed after high level samples. Frequent bakeout of the analytical system and analysis of reagent water should be performed in these circumstances to ensure a contamination-free system.

Sample Handling and Preservation

Container - 40 mL volatile vial with Teflon-lined septum
Preservation - if the sample contains residual chlorine, add sodium thiosulphate to reduce the chlorine and prevent formation of halogenated compounds after sampling (10 mg $Na_2S_2O_3$ per 40 mL sample is sufficient for up to 5 ppm Cl_2).

Preservation - pH <2 with H_2SO_4 or HCl or 0.1% $CuSO_4$.

Do not rinse the vial with sample. Collect the sample with as little aeration as possible, filling the vial to just overflowing. Cap the vial and ensure no bubbles are present. If $Na_2S_2O_3$ has been added, shake vial vigorously for one minute. Samples should be collected in duplicate to allow for a second analysis if dilution is required.

Stability

Holding Time - analyze within 14 days of sampling
Storage - store at 4°C until analyzed

Principle or Procedure

See Method 624, Purgeables, EPA 40 CFR Ch. 1 (7-1-90 Edition).
SW 846 5030/8240 or 8021, EPA 524.

Precision

None listed.

Accuracy

None listed.

Quality Control

Blanks: A transportation blank may be carried along with the samples to check for contamination during handling. One method blank should be included per analytical batch.
Replicates: duplicate vials should be used to confirm positives.
Recovery control: one spike should be included per analytical batch.
If a second analysis is required for dilution purposes, a second sample vial which has not been opened should be used.

References

a) Code of Federal Regulations, Title 40, Chapter 1 (Environmental Protection Agency), Part 136, App. A, Method 624 - Purgeables, July 1, 1990.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

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	(*)

Parameter Group MISA 23	Detection Limits (µg/L) for Standards in Reagent Water	
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.

Polycyclic Aromatic Hydrocarbons (PAHs) In Water by GC/MS/SIM

Parameter Polyclyclic Aromatic Hydrocarbons in water.

Analytical Method Extraction, silica gel, GC/MS/SIM.

EMS Code
Extraction, GC/FID **PAH- X377**
Extraction, HPLC/UV-UVF **PAH- X378**
Extraction, GC/MS **PAH- X379**

Introduction This method is applicable to the quantitative determination of polyclyclic aromatic hydrocarbons in water.

Summary Water samples are liquid liquid extracted with dichloromethane (DCM). The extract is then cleaned up by silica gel column chromatography and analyzed by gas chromatography mass spectroscopy using selected ion monitoring (SIM).

MDL

Polyclyclic Aromatic Hydrocarbons (PAHs)	mg/L
Naphthalene	0.00001
Acenaphthylene	0.00001
Acenaphthene	0.00001
Fluorene	0.00001
Phenanthrene	0.00001
Anthracene	0.00001
Fluoranthene	0.00001
Pyrene	0.00001
Benz(a)anthracene	0.00001
Chrysene	0.00001
Benzo(b+k)fluoranthene	0.00001
Benzo(a)pyrene	0.00001
Indeno(123-cd)pyrene	0.00001
Dibenz(ah)anthracene	0.00001
Benzo(ghi)perylene	0.00001

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 baseline. 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 extent of the matrix interferences will vary from source to source.

c) Components coeluting with and having fragments with m/z same as target compounds are potential sources of interference.

Sample Handling and Preservation

Bottle: 1L amber glass, narrow mouth, heat treated 350°C.
Preservation: unfiltered and unpreserved.

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 and 2000 mL
b) Round bottom flasks, 250 and 500 mL
c) Glass filter funnels
d) Glass columns 1.2 cm x 30 cm with 150 mL reservoir
e) Pipettes, 2 mL
f) Rotary evaporator
g) Graduated cylinders, 1000 mL
h) Graduated centrifuge tubes, 15 mL

Reagents

a) Solvents, distilled in glass or Pesticide grade
   1) Dichloromethane
   2) Isooctane
b) Silica gel, heated at 350°C overnight then deactivated with 5% water (w/w).
c) Sodium sulphate, anhydrous, reagent grade, heat treated at 600°C for 6 hr.

Procedure

a) Measure 800 mL of water into a 1000 mL separatory funnel.
b) Spike the sample with 50 µL of 20 ppm perdeuterated PAH surrogates (naphthalene d8, acenaphthene d10, phenanthrene d10, chrysene d10, and perylene d12).
c) Add 100 mL of dichloromethane and shake vigorously for one minute. Allow layers to separate and drain the DCM, through sodium sulfate supported in a glass funnel by glass wool, into a 500 mL round bottom flask.
d) Re-extract the aqueous layer with 2 x 60 mL DCM. Add the DCM to the round bottom flask.
e) Concentrate the combined extracts to 2 mL using a rotary evaporator. **Note: some of the PAH are very volatile, so bath temperature should be 35°C . Also do NOT let go dry.**
f) Prepare a 10 g silica gel column (30 cm x 1.0 mm, with 150 mL reservoir) topped with 1 cm of sodium sulfate in dichloromethane. Clean by running 50 mL of DCM through the column. Discard DCM.
g) Load sample when the solvent has just reached the top of the sodium sulfate. Elute with 40 mL of DCM and collect.
h) Add 1 mL of isooctane and concentrate the sample to 2 mL using a rotary evaporator.
i) Transfer to a 15 mL graduated centrifuge tube and concentrate under a gentle stream of nitrogen to 1 mL.
j) Spike extract with 50 µL of 20 ppm anthracene d10 and benzo(a)pyrene d12, and transfer to a 2 mL GC autosampler vial for GC-MS analysis.

Instrument Conditions

Instrument	HP 5890 gas chromatograph with HP5970 mass selective detector
Column	DB5, 30 m x 0.25 mm i.d.
Carrier gas	Helium
Head pressure	10 psi
Column flow rate	30 cm/s @ 100°
Scan mode	Selective ion monitoring (SIM)
Scan rate	1 scan/sec (minimum)
Injector temperature	250°C
Injection volume	1 µL
Injection mode	Splitless
Initial temperature	50°C
Initial time	1 min
Temperature program	25°C/min to 100°C, then 8°C/min to 300°C
Final hold	19 min

Selective Ion Masses	Quantitation Ions	Confirmation Ions
Natives		
Naphthalene	128	129, 64
Acenaphthylene	152	153, 76
Acenaphthene	154	152, 150
Fluorene	166	167, 82
Phenanthrene	178	179, 89
Anthracene	178	179, 89
Fluoranthene	202	203, 200
Pyrene	202	203, 200
Benz(a)anthracene	228	299, 226
Chrysene	228	299, 226
Benzo(b+k)fluoranthene	252	250, 126
Benzo(a)pyrene	252	250, 126
Indeno(123-cd)pyrene	276	277, 138
Dibenz(ah)anthracene	278	279, 139
Benzo(ghi)perylene	276	277, 138
Internal Standards		
Anthracene d10	188	
Benzo(a)pyrene d12	264	
Surrogates		
Naphthalene d8	136	
Acenaphthene d10	164	
Phenanthrene d10	188	
Chrysene d12	240	
Perylene d12	264	

GCMS Calibration

a) To each prepared calibration standard mixture, add a known constant amount of the two internal deuterated standards to yield a resulting concentration of 1 µg/mL and dilute to volume. 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-MS system.

b) Analyze constant amount (usually 1 µL) of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each PAH and internal standard, and calculate the relative response factor (RRF) for each PAH using the following equation:

$$RRF = (A_x C_{is}) / (A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the PAH to be measured.

C_x = Concentration of the PAH, (ng/µL)

A_{is} = Area of the characteristic ion for 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 may be prepared.

e) The retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

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 mid-scale calibration standard. This is the same check that is applied during the initial calibration, but one instead of five working standards is evaluated. Analyze the one working standard under the same conditions the initial calibration curve was evaluated. Analyze 1 µL of each of the midscale calibration standard and obtain the RRF. Calculate the percent difference between the current RRF and average RRF using the following equation:

$$\% \text{ Difference} = (RRF_c - RRF_i) / RRF_i \times 100$$

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 fivepoint calibration **MUST** be generated. This criterion **MUST** be met before sample analysis begins.

12 - Hour Calibration Verification

A calibration standard at midlevel concentration containing all PAHs 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-MS 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 fivepoint curve **MUST** be generated.

Calculation

Concentration of $PAH_X = (A_X/A_{IS}) \times (W_{IS}/RRF_X) / Vol$

where:

A_x	=	Area of the characteristic ion for PAH_x, the PAH to be measured
A_{is}	=	Area of the characteristic ion for the internal standard
W_{is}	=	Amount of internal standard added to the final extract
RRF_x	=	Relative response factor of PAH_x from a calibration run
Vol	=	Initial sample volume

Precision

Three blank waters spiked with PAHs at 0.002 mg/L gave the following results:

PAH	RSD
Naphthalene	3.2%
Acenaphthylene	0.0%
Acenaphthene	0.0%
Fluorene	3.0%
Phenanthrene	5.9%
Anthracene	3.0%
Fluoranthene	5.6%
Pyrene	5.4%
Benz(a)anthracene	7.7%
Chrysene	8.6%
Benzo(b+k)fluoranthene	1.4%
Benzo(a)pyrene	2.8%
Indeno(123-cd)pyrene	9.0%
Dibenz(ah)anthracene	4.6%
Benzo(ghi)perylene	4.0%

Accuracy

Three blank waters spiked with PAHs at 0.002 mg/L gave the following results:

PAH	RSD
Naphthalene	86%
Acenaphthylene	96%
Acenaphthene	96%
Fluorene	94%
Phenanthrene	96%
Anthracene	94%
Fluoranthene	100%
Pyrene	104%
Benz(a)anthracene	110%
Chrysene	98%
Benzo(b+k)fluoranthene	103%
Benzo(a)pyrene	102%
Indeno(123-cd)pyrene	94%
Dibenz(ah)anthracene	62%
Benzo(ghi)perylene	70%

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 more frequent. 800 mL of sample is spiked with a known concentration of PAH. The spike level should be at a concentration near, but above, the minimum detection limit. 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 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 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 MDC). Replicate outside the limits are required to be repeated.

Surrogates:
Acceptable surrogate recoveries are 40 - 130%.

References

a) C.V. Breder, AOAC Official Methods of Analysis (1984), p. 408
b) "Handbook of Polycyclic Aromatic Hydrocarbons", Alf Bjorseth, ed., Marcel Dekker, Inc., New York, 1983.

Revision Date: November 2002. Method adopted from Manual Supplement #1. EMS Code assigned.

Polycyclic Aromatic Hydrocarbons (PAHs) In Solids by GC/MS/SIM

Parameter Polyclyclic Aromatic Hydrocarbons in soil, sediments or solids.

Analytical Method -S02 - soxhlet, silica gel, GC/MS/SIM.

EMS Code

Introduction This method is applicable to the quantitative determination of polycyclic aromatic hydrocarbons in soil.

Summary Soil samples are ground with anhydrous sodium sulphate and soxhlet extracted with dichloromethane. The extract is then cleaned up by silica gel column chromatography and analyzed by gas chromatography - mass spectroscopy using selected ion monitoring (SIM).

MDL

Polyclyclic Aromatic Hydrocarbons (PAHs)	µg/g
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.001
Fluoranthene	0.001
Pyrene	0.001
Benz(a)anthracene	0.001
Chrysene	0.001
Benzo(b+k)fluoranthene	0.001
Benzo(a)pyrene	0.001
Indeno(123-cd)pyrene	0.001
Dibenz(ah)anthracene	0.001
Benzo(ghi)perylene	0.001

Matrix Soil Sediment Solids

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 baseline. 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 extent of the matrix interferences will vary from source to source.
c) Components co-eluting with and having fragments with m/z same as target compounds are potential sources of interference.

Sample Handling and Preservation

Bottle: 0.5L wide mouth amber glass, heat treated 350°C.
Preservation: 4°C.

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) Soxhlets, minimum 200 mL bed volume
b) Round bottom flasks, 250 and 500 mL
c) Glass filter funnels
d) Glass columns 1.2 cm x 30 cm with 150 mL reservoirs
e) Pipettes, 2 mL
f) Rotary evaporator
b) Graduated centrifuge tubes, 15 mL

Reagents

a) Solvents, distilled in glass or Pesticide grade
    1) Dichloromethane
    2) Isooctane
b) Silica gel, heated at 350°C overnight then deactivated with 5% water (w/w).
c) Sodium sulphate, anhydrous, reagent grade, heat treated at 600°C for 6 hr.

Procedure

a) Determine the moisture content of the soil by oven drying (105°C) 10 g of wet soil.
b) Accurately weigh 15 - 20 g (wet weight) of soil and place it in a mortar containing 50 g of anhydrous sodium sulphate. Grind the mixture until it flows like dry sand, and transfer to a soxhlet extractor.
c) Spike the sample with 50 µL of 20 ppm perdeuterated PAH surrogates (naphthalene d8, acenaphthene d10, phenanthrene d10, chrysene d10, and perylene d12).
d) Soxhlet extract for a minimum of 16 hours with dichloromethane (DCM).
e) Remove the solvent from the heat and concentrate to 2 mL using a rotary evaporator.
    Note: some of the PAH are very volatile, so bath temperature should not be above 35°C. Also do NOT let go dry.
f) Prepare a 10 g silica gel column (30 cm x 1.0 mm, with 150 mL reservoir) topped with 1 cm of sodium sulfate in dichloromethane (DCM). Clean by running 50 mL of DCM through the column. Discard DCM.
g) Load sample when the solvent has just reached the top of the sodium sulfate. Elute with 40 mL of DCM and collect.
h) Add 1 mL of isooctane to the eluted sample and concentrate the sample to 2 mL using a rotary evaporator.
i) Transfer to a 15 mL graduated centrifuge tube and concentrate under a gentle stream of nitrogen to 1 mL.
j) Spike extract with 50 µL of 20 ppm anthracene d10 and benzo(a)pyrene d12, and transfer to a 2 mL GC autosampler vial for GCMS analysis.

Instrument Conditions:

Instrument	HP 5890 gas chromatograph with HP5970 mass selective detector
Column	**DB5, 30 m x 0.25 mm i.d.**
Carrier gas	Helium
Head pressure	10 psi
Column flow rate	30 cm/s @ 100°C
Scan mode	Selective ion monitoring (SIM)
Scan rate	1 scan/sec (minimum)
Injector temperature	250°C
Injection volume	1 µL
Injection mode	Splitless
Initial temperature	50°C
Initial time	1 min
Temperature program	25°C/min to 100°C, then 8°C/min to 300°C
Final hold	19 min

Selective Ion Masses	**Quantitation Ions**	**Confirmation Ions**
Natives		
Naphthalene	128	129, 64
Acenaphthylene	152	153, 76
Acenaphthene	154	152, 150
Fluorene	166	167, 82
Phenanthrene	178	179, 89
Anthracene	178	179, 89
Fluoranthene	202	203, 200
Pyrene	202	203, 200
Benz(a)anthracene	228	299, 226
Chrysene	228	299, 226
Benzo(b+k)fluoranthene	252	250, 126
Benzo(a)pyrene	252	250, 126
Indeno(123cd)pyrene	276	277, 138
Dibenz(ah)anthracene	278	279, 139
Benzo(ghi)perylene	276	277, 138
Internal Standards		
Anthracene d10	188	
Benzo(a)pyrene d12	264	
Surrogates		
Naphthalene d8	136	
Acenaphthene d10	164	
Phenanthrene d10	188	
Chrysene d12	240	
Perylene d12	264	

GCMS Calibration

a) To each prepared calibration standard mixture add a known constant amount of the two internal deuterated standards to yield a resulting concentration of 1 µg/mL and dilute to volume. 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-MS system.

b) Analyze constant amount (usually 1 µL) of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each PAH and internal standard, and calculate the relative response factor (RRF) for each PAH using the following equation:

$$RRF = (A_x C_{is}) / (A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the PAH to be measured
C_x = Concentration of the PAH, (ng/µL)
A_{is} = Area of the characteristic ion for 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.

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 mid-scale calibration standard. This is the same check that is applied during the initial calibration, but one instead of five working standards is evaluated. Analyze the one working standard under the same conditions the initial calibration curve was evaluated. Analyze 1 µL of each of the midscale calibration standard and obtain the RRF. Calculate the percent difference between the current RRF and average RRF using the following equation:

$$\% \text{ Difference} = (RRF_c - RRF_i) / RRF_i \times 100$$

where:

RRF_i = Average relative response factor from initial calibration using midscale standard

RF_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 fivepoint calibration **MUST** be generated. This criterion **MUST** be met before sample analysis begins.

12 - Hour Calibration Verification

A calibration standard at midlevel concentration containing all PAHs 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-MS 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 fivepoint curve **MUST** be generated.

Calculation

Concentration of $PAH_x = (A_x/A_{is}) \times (W_{is}/RRF_x) / Wt$

where:

A_x	=	Area of the characteristic ion for the PAH to be measured.
A_x	=	Area of the characteristic ion for PAH_x, the PAH to be measured.
A_{is}	=	Area of the characteristic ion for the internal standard
W_{is}	=	Amount of internal standard added to the final extract
RRF_x	=	Relative response factor of PAH_x from a calibration run
Wt	=	Initial sample dry weigh

Precision

Relative standard deviation was 11% at a concentration of 0.01 µg/g.

Accuracy

Recovery was 95% at a concentration of 0.01 µg/g.

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. 800 mL of sample is spiked with a known concentration of PAH. The spike level should be at a concentration near, but above, the minimum detection limit. Calculate the % recovery as follows:

% Recovery = [recovered amount] / [spiked amount] x 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). Replicate outside the limits are required to be repeated.

Surrogates:
Acceptable surrogate recoveries are 40 - 130%.

References

a) "Handbook of Polycyclic Aromatic Hydrocarbons", Alf Bjorseth, ed., Marcel Dekker, Inc., New York, 1983.

Revision Dates: November 2002. Method adopted from Manual supplement #1. EMS Codes 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 x 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 x 0.25 mm i.d., 0.025 µm film thickness, or DB5, 30 m x 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 ofanalysis. 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 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

Apparatus

a) Separatory funnels, 500 mL
b) Flasks, Erlenmeyer, 500 mL
c) Flasks, round bottom 250 mL and 500 mL
d) Glass filter funnels
e) Glass columns 1.4 cm x 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 x 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 x 0.25 mm i.d., 0.025 µm film thickness, or
	DB5, 30 m x 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:

$$RRF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:

A_x = Area of the PCB to be measured.

C_x = Area of the internal standard

A_{is} = Concentration of the PCB, (ng/µL)

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 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 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.

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 X 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.

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

Compound	Type	mg/L
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
Methidathion	OP	0.0002
Methoxychlor	OC	0.0002
Methyl Parathion	OP	0.0002
Metolachlor	H	0.0002
Metobromuron	H	0.0005
Metribuzin	H	0.0001
Mevinphos	OP	0.0005
Mirex	OC	0.0002
Monuron	H	0.0005
Naled	OP	0.0001
Nitrofen	H	0.0001
Nonachlor, trans-	OC	0.0001
Omethoate	OP	0.0003
Oxychlordane	OC	0.0001
Oxyfluorfen	H	0.0001
Parathion	OP	0.0002
Phorate	OP	0.0002
Phosalone	OP	0.0005
Phosmet	OP	0.0003

Compound	Type	mg/L
Phosphamidon	OP	0.0005
Prometryne	H	0.0002
Pronamide	H	0.0001
Propanil	H	0.0002
Propazine	H	0.0002
Ronnel	OP	0.0005
Simazine	H	0.0002
Sulfotep	OP	0.0002
Terbacil	H	0.0005
Terbofos	OP	0.0002
Terbutryn	H	0.0002
Terbutylazine	H	0.0005
Tetrachlorvinphos	OP	0.0002
Tetradifon	OC	0.0001
Triallate	H	0.0001
Trifluralin	H	0.0001
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

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

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 mg/L - 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 and Preservation	Glass (1.0 L). Add 5 mL 8% $CuSO_4$ /L and H_3PO_4 to pH <4. 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.

Revision Date: December 31, 2000

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.

Polychlorinated Dibenzo(p) Dioxins And Dibenzo-Furans In Water And In 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 quantiation 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 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 x 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 x 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 Teflonlined 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 13C12 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 x 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 x 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 13C-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 13C-1,2,3,4-TCDD. Recoveries of the hexa through octa surrogate standards are calculated using the 13C-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 13C-121,2,3,4-TCDD or 13C12-1,2,3,7,8,9-H6CDD;

C_c = concentration of the native standard (pg/mL);

C_{sc} = concentration of the appropriate surrogate standard (pg/mL);

C_{rc} = concentration of 13C12-1,2,3,4-TCDD or 13C12-1,2,3,7,8,9-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 fivepoint 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 13C-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 13C-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 X (pg);
A_k	=	quantification ion (single or both ions) peak area for the "k"th homologous isomer of analyte X (n = 1 for isomer-specific analysis);
V	=	Initial weight or volume of sample (g or L)
Q_{ss}	=	amount of surrogate standard X added to the sample (pg);
A_{ss}	=	quantification ion (single or both ions) peak area for surrogate standard X 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/ul)**
13C-2,3,7,8-TCDD	100
13C-1,2,3,7,8-PeCDD	100
13C-1,2,3,6,7,8-HxCDD	100
13C-1,2,3,4,6,7,8-HpCDD	100
13C-OCDD	200
13C-2,3,7,8-TCDF	100
13C-1,2,3,7,8-PeCDF	100
13C-1,2,3,6,7,8-HxCDF	100
13C-1,2,3,4,6,7,8-HpCDF	100

Internal Standards:	
13C-1,2,3,4-TCDD	100
13C-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	13C-TCDF
	317.9389	M + 2	13C-TCDF
	319.8965	M	TCDD
	321.8936	M + 2	TCDD
	327.8850	M	37Cl-TCDD
	331.9368	M	13C-TCDD
	333.9339	M + 2	13C-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	13C-PeCDF
	353.8970	M + 4	13C-PeCDF
	355.8546	M + 2	PeCDD
	357.8516	M + 4	PeCDD
	367.8949	M + 2	13C-PeCDD
	369.8919	M + 4	13C-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	13C-HxCDF
	385.8610	M + 2	13C-HxCDF
	389.8157	M + 2	HxCDD
	391.8127	M + 4	HxCDD
	401.8559	M + 2	13C-HxCDD
	403.8529	M + 4	13C-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	13C-HpCDF
	419.8220	M + 2	13C-HpCDF
	423.7766	M + 2	HpCDD
	425.7737	M + 4	HpCDD
	435.8169	M + 2	13C-HpCDD
	437.8140	M + 4	13C-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	13C-OCDD
	471.7750	M + 4	13C-OCDD
	513.6775	M + 4	DCDPE
	454.9728	LOCKMASS	PFK

H	=	1.007825
C	=	12.000000
13C	=	13.003355
F	=	18.9964
O	=	15.994915
35Cl	=	34.968853
37Cl	=	36.965903

Note: Lock masses may change with different types of PFK

TABLE 3

THEORETICAL ION ABUNDANCE RATIOS AND THEIR 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 13C-HxCDF only**
7	M / M + 2	0.44	0.37	0.51	**use for 13C-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

	CS1 - Low	CS2 - Low	CS3 - Low CS1 - High	CS4 - Low CS2 - High	CS5- Low CS3 - High	Initial Calibration	Continuing Calibration
Unlabeled Analytes:	**pg/ul**	**pg/ul**	**pg/ul**	**pg/ul**	**pg/ul**	**% RSD**	**% 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:							
13C-2,3,7,8-TCDD	100	100	100	100	100	25	25
13C-1,2,3,7,8-PeCDD	100	100	100	100	100	25	25
13C-1,2,3,6,7,8-HxCDD	100	100	100	100	100	25	25
13C-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	30	30
13C-OCDD	100	100	100	100	100	30	30
13C-2,3,7,8-TCDF	100	100	100	100	100	30	30
13C-1,2,3,7,8-PeCDF	100	100	100	100	100	30	30
13C-1,2,3,6,7,8-HxCDF	100	100	100	100	100	30	30
13C-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	30	30
Internal Standards:							
13C-1,2,3,4-TCDD	100	100	100	100	100		
13C-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 (8). The case where the standard deviations of the two populations differ is summarized below. An alternative test, for where the standard deviations of the two populations do not significantly differ, is summarized in the reference text and may also be used.

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

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

$$V_A = s_A^2 / n_A \qquad V_B = s_B^2 / n_B$$

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.