Polycyclic Aromatic Hydrocarbons in Water by GC/MS – PBM

Parameter Polycyclic Aromatic Hydrocarbons (PAH) in water

Analytical Method Dichloromethane Liquid-Liquid Extraction, GC/MS

Introduction This method is applicable to the quantitative determination of polycyclic aromatic hydrocarbons in water.

Method Summary This method involves a liquid-liquid extraction using dichloromethane (DCM) followed by gas chromatography mass spectrometry (GC/MS) instrumental analysis.

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

MDL(s) and EMS Analyte Codes

Analyte	Approx. MDL (ug/L)	CAS #	EMS Analyte Code
Acenaphthene	0.01-0.05	83-32-9	PA01
Acenaphthylene	0.01-0.05	208-96-8	PA02
Acridine	0.01-0.05	260-94-6	PA18
Anthracene	0.01-0.05	120-12-7	PA03
Benz(a)anthracene	0.01-0.05	56-55-3	PA04
Benzo(a)pyrene	0.01-0.05	50-32-8	PA05
Benzo(b+j)fluoranthene	0.01-0.05	205-99-2 & 205-82-3	PA39
Benzo(g,h,i)perylene	0.01-0.05	191-24-2	PA07
Benzo(k)fluoranthene	0.01-0.05	207-08-9	PA08
Chloronaphthalene, 2-	0.01-0.05	91-58-7	n/a
Chrysene	0.01-0.05	218-01-9	PA09
Dibenz(a,h)anthracene	0.01-0.05	53-70-3	PA10
Dibenzothiophene	0.01-0.05	132-65-0	PA49
Dimethylbenz(a)anthracene, 7,12-	0.02-0.10	57-97-6	PA23
Fluoranthene	0.01-0.05	206-44-0	PA11
Fluorene	0.01-0.05	86-73-7	PA12
Indeno(1,2,3-cd)pyrene	0.01-0.05	193-39-5	PA13
Methylcholanthrene, 3-	0.02-0.10	56-49-5	PA24
Methylnaphthalene, 1-	0.01-0.05	90-12-0	PA29
Methylnaphthalene, 2-	0.01-0.05	91-57-6	PA28
Naphthalene	0.01-0.05	91-20-3	PA14
Phenanthrene	0.01-0.05	85-01-08	PA15
Pyrene	0.01-0.05	120-00-0	PA16
Quinoline	0.01-0.05	91-21-5	PA19
Methylated Naphthalene	0.10-0.50	n/a	n/a

Other PAH, NPAH, or heterocyclic analytes may also be analyzed by this method, subject to validation and achievement of DQOs.

EMS Method Code(s)

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

Matrix

fresh water, seawater, wastewater

Interferences and Precautions

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

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 the same mass/charge (m/z) ratio as target compounds are potential sources of interference. Alkylated PAHs commonly cause interferences on unsubstituted low molecular weight PAHs.

d) Quinoline and acridine are nitrogen containing PAH and are subject to protonation and subsequent reduced extraction efficiency. Samples must be neutral or basic (pH 6 to 10) to ensure adequate extraction efficiency. Further, these compounds show low recovery if silica gel cleanup is employed.

Sample Handling and Preservation

Container: Amber glass, with Teflon lined lid.

Preservation: Preservation with acid is preferred (e.g. use 1g solid NaHSO4, 1 mL 1:1 HCl, or 1 mL 1:1 H2SO4 per 250 mL).

Stability

Holding Time: Extract samples within 14 days after sample collection if preserved, or within 7 days if unpreserved. Extracts may be held up to 40 days prior to instrumental analysis.

Storage: Store samples and extracts at ≤6ºC (freezing of water samples is acceptable but not recommended due to risk of container breakage). Store extracts at ≤6ºC away from direct sunlight. Allow extracts to warm to room temperature prior to sub-sampling for analysis.

Procedure

Reagents:

a) Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), and Iso-octane or Toluene.
b) Silica gel, activated (optional – refer to US EPA Method 3630C for guidance)
c) Sodium sulfate, anhydrous, reagent grade.
d) Potassium Hydroxide, reagent grade or equivalent

Extraction:

a) Measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials, surface film, or non-aqueous phase layer (NAPL). If solids content is too great for extraction in this manner, then the solids should be extracted separately from the water phase and the extracts combined. Ensure sample pH is between 6 to 10. If necessary, adjust pH using saturated KOH solution or phosphoric acid.

b) Spike the sample with a minimum of three deuterated PAH surrogates, including naphthalene-d8. Include at least one deuterated nitrogen containing PAH surrogate (e.g. acridine-d9, quinoline-d7) unless acridine and quinoline isotopes are used as isotope dilution standards. Refer to the Quality Control section.

c) Add between 25 and 100 mL of DCM to the sample bottle and rinse contents into the separatory funnel. Shake vigorously for one minute with frequent venting. Allow layers to separate and drain the DCM (bottom layer) through sodium sulfate into a glass collection flask.

d) Repeat step c) twice more.

e) Concentrate the combined extracts to a known final volume using an appropriate

concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator) ensuring that method performance requirements are met. It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Silica Gel Clean-Up (Optional):

Silica gel cleanup may be employed to reduce instrumental interferences by removing non-polar and/or polar materials from the extract that may co-elute with analytes or deteriorate instrument condition. Silica gel clean-up is generally not necessary for water samples. Standard silica gel clean-up techniques are not suitable for nitrogen containing PAHs, e.g. quinoline or acridine.

a) In-situ or column silica gel clean-up using silica gel may be employed following the guidelines described in the following reference:

   - USEPA Method 3630C, "Silica Gel Cleanup", Revision 3, December 1996

b) Concentrate the cleaned-up extract to a known final volume using an appropriate concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kudurna Danish, or equivalent) ensuring that method performance requirements are met (separate method validation of test procedure with silica gel clean-up is required where used). It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Instrumental Analysis:

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

- USEPA Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", Revision 5, July 2014 (or as updated from time to time).

GC/MS must be used. Selective ion monitoring (SIM) mode is commonly employed to achieve lower detection limits. Refer to USEPA Method 8270D for guidelines on establishing quantitation and confirmation ions for PAH compounds.

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

The use of internal standards is required. Internal standards can vastly improve method precision. Deuterium labeled PAHs are recommended (e.g. anthracene-d10, benzo(a)pyrene-d12, etc.) and should be selected to encompass the mass range of the test analytes. Internal standards must not introduce significant interferences on test analytes or surrogates.

Isotope dilution techniques may be utilized to improve method performance.

Analysis and Calculation of Methylated Naphthalene

For purposes of the BC approved marine water quality guidelines, methylated naphthalene refers to the aggregate summed concentration of all mono, di, tri, and tetramethyl naphthalenes.

For GCMS data acquisition and calculations, use quantitation and qualifier ions as indicated in the table below.

Isomer Type	Quantitation Ion (m/z)	Qualifier Ion (m/z)	Calibration Reference
1-Methylnaphthalene	142	141	1-Methylnaphthalene
2-Methylnaphthalene	142	141	2-Methylnaphthalene
Dimethylnaphthalenes	156	141	128 ion RF for Naphthalene
Trimethylnaphthalenes	170	155	128 ion RF for Naphthalene
Tetramethylnaphthalenes	184	169	128 ion RF for Naphthalene

Performance Requirements

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

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

For Initial Validations, averages of at least 8 spikes or certified reference materials (CRMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Average accuracy must be between 80-120% for heavy molecular weight PAH compounds (MW>175), between 70-120 % for light molecular weight PAH compounds (MW<175) and nitrogen containing PAHs (e.g. quinoline and acridine), and between 60-120% for 3-methylcholanthrene, 7,12-dimethylbenz(a)anthracene, and for any other PAH, NPAH, or heterocyclic analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

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

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50 – 140%
Field Duplicates	Recommended One per batch (max 20 samples) (requires 2nd sample bottle)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	Recommended One per batch (max 20 samples) (requires 2nd sample bottle)	50 – 140%
Surrogate Compounds	All samples	50 – 140% Not applicable where valid surrogate recoveries cannot be obtained due to interferences.
Calibration Verification Standard (CVS)	1 per initial calibration	80-120% recovery
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run.	80-120% recovery for mid-level standards.

Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50-200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards (IDS)	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. No corrective actions are required for field duplicate DQO exceedances.		

Lab Duplicates: Lab Duplicates are not possible for this method, because whole sample analysis is required. Field Duplicates may be conducted using multiple sample containers.

Field Duplicates: Recommended. Replicate all components of the test from start to finish. Field Duplicate precision represents the combined variability of sampling and analysis processes.

Matrix Spike: Recommended. Requires second sample container due to whole sample analysis requirement. Matrix effects can also be evaluated in all samples using PAH surrogate results. Matrix Spikes are only necessary to evaluate parameter-specific matrix issues.

Surrogate Compounds: Required**.** At minimum, three surrogate compounds are required for each sample and quality control sample. Surrogates must include naphthalene-d8. A nitrogen-heterocyclic surrogate (e.g., acridine-d9, quinoline-d7) is required unless acridine and quinoline isotopes are used as isotope dilution standards. Surrogates should be selected to encompass the mass range of the test analytes.

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

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least every twelve hours). A control standard may serve the same purpose.

Isotope Dilution Standards (IDS): Optional. Required only if necessary to meet LCS DQOs and Accuracy Performance Requirements.

Prescribed Elements

The following components of this method are mandatory:

a) Analysis must be by GC/MS. At least one qualifier ion per analyte must be monitored (two recommended where possible).
b) Initial calibrations must include at least four points.
c) Internal standards must be used, except under extenuating circumstances (e.g. where interferences are evident on internal standard peaks).
d) The entire contents of the sample container must be analyzed, including any accompanying suspended or settled material and any surface film that may exist (with the exception that up to 20% of total sample volume may be removed from the sub-surface after inversion and mixing, if required to create room for extraction using alternate in-bottle extraction methods). Should this not be possible, the client must be contacted for direction and any method deviations must be qualified on the final report.
e) All Performance Requirements and Quality Control requirements must be met.
f) If acridine or quinoline is to be reported, a nitrogen-heterocyclic (e.g. acridine-d9 or quinoline-d7) must be used as surrogate or as isotope dilution standard, and sample pH must be between 6 to 10 prior to extraction. Alternative ranges for acceptable pH may be established through validation studies. Acceptable recovery of the nitrogen-heterocyclic surrogate or ID standard in a sample may be used as validation that sample pH was appropriate.
g) Methylated naphthalene calculation protocols are prescribed, but the listed qualifier ions are recommended.

Apart from these limitations, and provided performance requirements are met, laboratories

may introduce modifications to this method in order to improve quality or efficiency.

References

1. USEPA Method 8270D, “Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)”, Revision 5, July 2014.
2. USEPA Method 3510C, “Separatory Funnel Liquid-Liquid Extraction”, Revision 3, December 1996.
3. USEPA Method 3630C, “Silica Gel Cleanup”, Revision 3, December 1996.
4. British Columbia Ministry of Water, Land and Air Protection, “Polycyclic Aromatic Hydrocarbons (PAHs) in Water by GC/MS/SIM”, November 2002 *(Previous version of this method prior to conversion to PBM format).*
5. US EPA Statement of Work for Determination of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Environmental Samples Related to BP Oil Spill, 2010 (reference for calculation protocol for methylated naphthalenes).

Revision History

July 10, 2017	Additional analytes added to support 2017 CSR updates. PAHs without CSR water standards were removed. Preservation guidance updated for consistency with current MOE preservative and hold time requirements. Definition and calculation protocols added for Methylated Naphthalene (for marine water quality guideline). DQOs for optional Matrix Spikes added. QC DQOs were revised to align with CCME methods guidance. Wider method validation DQOs added for challenging analytes and non-listed PAHs and heterocyclics. Required minimum number of surrogates reduced from four to three. Requirement for use of internal standards was added for consistency with soils method. Cancelled requirement for an NPAH surrogate if isotope dilution is used for both acridine and quinoline. Format updated to 2017 version.
March 31, 2005	2002 version was replaced and converted to PBM format.