

Polycyclic Aromatic Hydrocarbons in Soil by GC/MS – PBM

Parameter	Polycyclic Aromatic Hydrocarbons (PAH) in soil
Analytical Method	Dichloromethane / Acetone Soxhlet extraction (PBM), GC/MS
Introduction	This method is applicable to the quantitative determination of polycyclic aromatic hydrocarbons in solids.
Method Summary	<p>This method involves a Soxhlet extraction of a chemically dried soil using 1:1 DCM/Acetone followed by gas chromatography mass spectrometry (GC/MS) instrumental analysis.</p> <p>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.</p>

MDL(s) and EMS Analyte Codes*	Analyte	Approx. MDL (ug/g)	CAS #	EMS Analyte Code
	Acenaphthene	0.01-0.05	83-32-9	PA01
	Acenaphthylene	0.01-0.05	208-96-8	PA02
	Anthracene	0.01-0.05	120-12-7	PA03
	Benz(a)anthracene	0.01-0.05	56-55-3	PA04
	Benzo(a)pyrene	0.01-0.05	50-32-8	PA05
	Benzo(b+j)fluoranthenes	0.01-0.05	205-99-2 & 205-82-3	PA39
	Benzo(g,h,i)perylene	0.01-0.05	191-24-2	PA07
	Benzo(k)fluoranthene	0.01-0.05	207-08-9	PA08
	Chloronaphthalene, 2-	0.01-0.05	91-58-7	n/a
	Chrysene	0.01-0.05	218-01-9	PA09
	Dibenz(a,h)anthracene	0.01-0.05	53-70-3	PA10
	Dibenzothiophene	0.01-0.05	132-65-0	PA49
	Dibenzo(a,e)pyrene	0.01-0.05	191-65-4	PAD1
	Dimethylbenz(a)anthracene, 7,12-	0.02-0.10	57-97-6	PA23
	Fluoranthene	0.01-0.05	206-44-0	PA11
	Fluorene	0.01-0.05	86-73-7	PA12
	Indeno(1,2,3-cd)pyrene	0.01-0.05	193-39-5	PA13
	Methylcholanthrene, 3-	0.02-0.10	56-49-5	PA24
	Methylnaphthalene, 1-	0.01-0.05	90-12-0	PA29
	Methylnaphthalene, 2-	0.01-0.05	91-57-6	PA28
	Naphthalene	0.01-0.05	91-20-3	PA14
	Phenanthrene	0.01-0.05	85-01-08	PA15
	Pyrene	0.01-0.05	120-00-0	PA16
	Quinoline	0.01-0.05	91-21-5	PA19

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

EMS Method Code(s)*	Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.
Matrix	Soil, Sediment, Sludge
Interferences and Precautions	<p>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.</p> <p>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.</p>

- 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.

Sample Handling and Preservation

Container: Glass, with Teflon or foil lined lid. Wide-mouth sample jars recommended.

Preservation: None.

Stability

Holding Time: Extract samples within 14 days after sample collection. Extracts may be held up to 40 days before instrumental analysis.

Storage: Store samples and extracts at $\leq 6^{\circ}\text{C}$ (freezing of soil samples is acceptable but not recommended due to risk of container breakage). Store extracts at $\leq 6^{\circ}\text{C}$ away from direct light. 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), Acetone, and Iso-Octane or Toluene.
- b) Silica gel, activated (optional – refer to US EPA Method 3630C for guidance).
- c) Sodium sulfate, anhydrous, reagent grade.

Extraction:

- a) Accurately weigh a representative 10 – 20 gram sub-sample of wet soil into a beaker.
- b) Spike the sample with a minimum of 3 deuterated PAH surrogates. Refer to Quality Control section for requirements.
- c) Add 5 – 10 grams of granular anhydrous sodium sulfate, and mix in thoroughly with sample. Add more sodium sulfate if sample has a high moisture content. Let the sample stand for ~20 minutes while moisture adsorbs to the sodium sulfate. Mix well until the sample appears dry and free flowing.
- d) Add an appropriate amount of 1:1 DCM/Acetone to the Soxhlet apparatus.
- e) Turn on Soxhlet heaters, and allow samples to extract for at least 16 hours, ensuring that 4 to 6 cycles per hour are achieved.
- f) Cool and disassemble Soxhlet apparatus. Add about 1-2mL of a low volatility keeper solvent such as toluene or iso-octane to sample extracts prior to solvent reduction steps to prevent loss of volatile PAH components during evaporative concentration.
- g) Concentrate extracts to a known final volume using an appropriate concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator).

Silica Gel Clean Up (Optional):

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

- a) In-situ or column silica gel cleanup using silica gel may be employed using the following reference as guidance:
 - USEPA Method 3630C, "Silica Gel Cleanup", Revision 3, December 1996
- b) Concentrate the cleaned-up extract to a known, accurate final volume using an appropriate concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish, or equivalent), ensuring that method performance requirements are met (separate method validation of test procedure with silica gel clean-up is required where used). It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of more volatile PAH components.

Instrumental Analysis:

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

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

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

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

The use of internal standards is required. Internal standards can vastly improve method precision. Deuterium labeled PAHs are recommended (e.g. anthracene-d10, benzo(a)pyrene-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.

Performance Requirements

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

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

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

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

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

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

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

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50 – 140%
Lab Duplicates (DUP)	One per batch (max 20 samples)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material	One per batch (max 20 samples)	50 - 140%

Surrogate Compounds	All samples	50 - 140% Not applicable where valid surrogate recoveries cannot be obtained due to interferences.
Calibration Verification Standard (CVS) – 2 nd source	One per batch (max 20 samples)	80-120% recovery
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run, and at the end of each run.	80-120% recovery for mid-level standards.
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50-200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards (IDS)	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%.

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to RM DQOs if targets are < 10x MDL (derive lab-specific DQOs in this case) or to MS results where sample background exceeds spike amount.

Surrogate Compounds: Required. At minimum, three surrogate compounds are required for each sample and quality control sample. Surrogates must include naphthalene-d8. If nitrogen compounds are routinely reported, a deuterated nitrogen PAH must also be included (e.g., acridine-d9, quinoline-d7). Surrogates should be selected to encompass the mass range of the test analytes.

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

Prescribed Elements

The following components of this method are mandatory:

- Analysis must be by GC/MS. At least one qualifier ion per analyte must be monitored (two recommended where possible).
- Initial calibrations must include at least four points.
- Internal standards must be used, except under extenuating circumstances (e.g. where interferences are evident on internal standard peaks).
- All Performance Requirements and Quality Control requirements must be met.
- At least three surrogates must be used, which must include d8-naphthalene. If acridine or quinoline is reported, a deuterated nitrogen-containing PAH surrogate must be used (e.g. acridine-d9 or quinoline-d7).
- The specified equivalence procedure must be followed for non-Soxhlet extraction procedures.

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

Equivalence Procedure for Alternate Extraction Techniques

If alternative extraction techniques are employed, equivalence to the Soxhlet extraction procedure must be demonstrated by the extraction and analysis of two PAH Reference Materials (RMs) by the reference technique and by the lab's alternative technique. Equivalence is defined as where the grand average of the recoveries of all normally reported PAH analytes lies within 85-115% of the Soxhlet method, for each RM (i.e. determine the average recovery of each individual PAH analyte, and calculate a single grand average of all of these results to represent the overall method recovery for each RM), and where no single PAH analyte has a recovery outside of 50-150% of the Soxhlet

method.

The following RMs may be suitable for this purpose, while available:

1. National Resource Council of Canada CRMs:
 - HS3B, HS4B, HS5 (availability may be limited)
2. Resource Technology Corporation CRMs:
 - CRM104, CRM140, CRM141, CRM170, CRM171, CRM172, CNS391
3. National Institute of Standards and Technology SRMs:
 - SRM 1941B
4. In-House produced RMs:
 - Must be sufficiently homogeneous (e.g. pulverized to < 100 um)
 - Must be natural materials (i.e. unspiked soils or sediments)

Prior to extraction by either method, each reference material must be wetted with water to a 25% moisture content (e.g. 7.5 g RM + 2.5 mL water). Extractions must be conducted at least in triplicate by each method. Equivalence is determined versus the results obtained using the reference method, not against the certified values of the RM.

Successful results for the equivalence procedure must be demonstrated prior to the use of any alternative method, and must be maintained on file indefinitely in case of audit by BC MOE or clients.

Each reference material assessment must include at least 80% of the laboratory's routinely reported PAH analytes (parameters where the results from both methods are below 5 times the laboratory's reported detection limit may be excluded).

Calculation of Grand Averages:

- a) For the first RM, determine the average measured concentration of each individual PAH analyte by the alternative method and by the Soxhlet reference method (using averages of triplicates or more).
- b) Use the results from above to calculate the average recovery of each individual PAH analyte for the alternative method versus the Soxhlet method.
- c) Calculate the grand average of the recoveries for all analytes in the RM. For each RM, this result must be between 85-115%.
- d) Repeat this assessment for the second RM.

The equivalence test described above need not be repeated for new substances added to the CSR as of 2017 if successful equivalence test data is available for previously listed substances.

References

1. USEPA SW846 Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", Revision 5, July 2014.
2. USEPA SW846 Method 3540C "Soxhlet Extraction", Revision 3, December 1996.
3. USEPA SW846 Method 3630C, "Silica Gel Cleanup", Revision 3, December 1996.

Revision History

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| July 10, 2017 | Additional analytes added to support 2017 CSR updates. Matrix Spikes (or RM) added to QC requirements, and QC DQOs were revised to align with CCME methods guidance. Method validation DQOs were adjusted to support additional more challenging analytes and non-listed PAHs and heterocyclics. Required minimum number of surrogates reduced from four to three. Allowance for isotope dilution formally added. Format updated to 2017 version. |
| June 26, 2009 | 2002 version was replaced and converted to PBM format. |
| Nov 2002 | Method adopted from Manual supplement #1. EMS Codes assigned. |