Chlorinated and Non-Chlorinated Phenols in Soils - PBM

Parameter

Chlorinated Phenols, Non-Chlorinated Phenols, Nitrophenols in Soils

Analytical Method

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

Introduction

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

Method Summary

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

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

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

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/g)	EMS Analyte Code
Non-Chlorinated Phenols			
2,4-Dimethylphenol	105-67-9		D048
2,6-Dimethylphenol	576-26-1		n/a
3,4-Dimethylphenol	95-65-8		n/a
Hydroquinone (Catechol)	123-31-9		n/a
2-Methylphenol (ortho-Cresol)	95-48-7		PH33
3-Methylphenol (meta-Cresol)	108-39-4		PH37
4-Methylphenol (para-Cresol)	106-44-5		PH37
Phenol	108-95-2		0119
Nitrophenols			
2,4-Dinitrophenol	51-28-5		D049
2-Methyl-4,6-Dinitrophenol	534-52-1		D047
2-Nitrophenol	88-75-5		N030
4-Nitrophenol	100-02-7		N031
Chlorinated Phenols			
2-Chlorophenol	95-57-8		C035
3-Chlorophenol	108-43-0		C054
4-Chlorophenol	106-48-9		C055
2,3-Dichlorophenol	576-24-9		D073
2,4-Dichlorophenol	120-83-2		D050
2,5-Dichlorophenol	583-78-8		D075
2,6-Dichlorophenol	87-65-0		D076
3,4-Dichlorophenol	95-77-2		CP07
3,5-Dichlorophenol	591-35-5		D077
Pentachlorophenol	87-86-5		P022
2,3,4,5-Tetrachlorophenol	4901-51-3		T036
2,3,4,6-Tetrachlorophenol	58-90-2		T037
2,3,5,6-Tetrachlorophenol	935-95-5		T038
2,3,4-Trichlorophenol	15950-66-0		T033

2,3,5-Trichlorophenol	933-78-8	T034
2,3,6-Trichlorophenol	933-75-5	T035
2,4,5-Trichlorophenol	95-95-4	T043
2,4,6-Trichlorophenol	88-06-2	T042
3,4,5-Trichlorophenol	609-19-8	T044
Miscellaneous Phenols		
3-Aminophenol	591-27-5	n/a
4-Aminophenol	123-30-8	n/a
4-Chloro-3-methyl phenol	59-50-7	n/a
Dinitro-o-cyclohexyl phenol, 4,6-	131-89-5	n/a
2-Phenylphenol	90-43-7	n/a
Surrogates		
2,4-Dibromophenol	615-58-7	n/a
2,4,6-Tribromophenol	118-79-6	n/a

EMS Method Code(s)

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

Matrix

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

Interferences and Precautions

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

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

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

d) Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of some analytes.

Sample Handling and Preservation

Container: Glass Jars with Teflon-lined lids.

Preservation: Store at ≤ 6°C.

Stability

Holding Time:

Samples: Extract within 14 days of collection.

Extracts: May be held up to 40 days before instrumental analysis if stored at ≤ 6°C.

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

Procedure

Reagents:

a) Organics-free reagent water.

b) Solvents, distilled in glass, pesticide quality, or equivalent.

- Acetone.
- Dichloromethane (DCM).
- Hexane
- Isooctane.

c) Sodium Sulfate (Na_2SO_4), anhydrous, purified by heating at 400°C for four hours.

Extraction: The following instructions apply to Soxhlet extraction with DCM/acetone or

hexane/acetone. Microwave and Microscale extraction and other solvents are acceptable alternatives provided the data quality objectives described in the Performance Requirements and Quality Control sections are met.

a) Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Prepare sufficient sample to yield approximately 10 g after homogenization.

b) Blend 10 g of sample with 10 g or a suitable amount of heat-treated sodium sulfate until the moisture is absorbed and the sample is free-flowing.

c) Place the mixture in an extraction thimble or between two layers of glass wool in the Soxhlet extractor.

d) Add surrogate to the samples and spike solution to the sample selected for the matrix spike.

e) If recovery corrections are required to meet Data Quality Objectives (e.g., for hydroxyphenols, phenol, or 2,4-dimethylphenol), spike each sample with deuterated isomers of each compound for purposes of isotope dilution recovery corrections.

f) Add extraction solvent (either DCM/Acetone or Hexane/Acetone) to an extraction flask, attach the flask to the Soxhlet extractor and extract the sample for approximately 16 hours.

g) Allow the extract to cool.

h) Dry the extract by passing through a drying column containing anhydrous sodium sulfate and rinse the column and flask with extract solvent to complete the quantitative transfer.

i) Add 2 mL of iso-octane to the combined extracts and concentrate using an appropriate solvent concentration apparatus (e.g. rotary evaporator or KD).

j) If derivatization is required, a number of derivatization techniques may be used, e.g., acetylation, methylation.

k) Analyze the extracts for target analytes by GC/MS (or GC-ECD for nitrophenols).

Instrumental Analysis:

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

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

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

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

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

Performance Requirements

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

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

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Average accuracy must be between 50-130% for nitrophenols and 70-130% for all chlorinated phenols and all listed non-chlorinated phenols (after isotope dilution corrections where applicable).

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

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

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	50-140% except 30-130% for difficult compounds such as 2,4-dimethylphenol, 2,4-dinitrophenol
Lab Duplicates (DUP)	One per batch (max 20 samples)	50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	50-140% except 30-130% for difficult compounds such as 2,4-dimethylphenol, 2,4-dinitrophenol
Isotope Dilution Standards	All samples	Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%.
Surrogate Compounds	All samples	50-140%
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50-200% of the initial calibration CVS.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80-120%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	80-120%

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

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

Lab Duplicates: Required.

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

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

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

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

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

Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by GC/MS or GC-ECD for nitrophenols. For GC/MS at least one qualifier ion per analyte must be monitored (two recommended where possible). Initial calibrations must include at least 4 points.
2. All Performance Requirements and Quality Control requirements must be met.
3. Isotope dilution recovery correction must be used for any listed parameters where the stated DQOs cannot routinely be met, or where the stated Accuracy Requirements cannot be met (Accuracy Requirements reflect the long term average performance of the method). For typical solvent-extraction methods, isotope dilution is recommended for hydroxyphenols, phenol, and 2,4-dimethylphenol.
4. If an alternative to the Soxhlet extraction technique with DCM/acetone or hexane/acetone is utilized for extractions, laboratories must conduct and document a validation of phenolic compound extraction efficiency for the alternate method, either by a minimum of triplicate evaluations of at least one Certified Reference Material (certified for at least a representative sub-set of the test analytes), or by evaluation of at least 5 natural soil Matrix Spike samples that have been mixed and equilibrated with all test analytes (spiked in acetone) for at least 1 hour prior to extraction. All test samples (CRMs or Matrix Spikes) must contain at least 20% moisture content to be representative of typical soil samples. Accuracy DQOs from the Performance Requirements section must be met.

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

References

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

   US EPA Method 3540C, “Soxhlet Extraction”, SW-846 Revision 3, December 1996.
2. US EPA Method 3541, “Automated Soxhlet Extraction”, SW-846 Update II, September 1994.

   US EPA Method 3546, “Microwave Extraction”, SW-846 Revision 0, February 2007.

   US EPA Method 3550C, “Ultrasonic Extraction”, SW-846 Revision 3, February 2007.

   US EPA Method 3570, “Microscale Solvent Extraction (MSE)”, SW-846 Revision 0, November 2002.
3. US EPA Chapter 4, “Organic Analytes”, SW-846 Update V Revision 5, July 2014.

Revision History

March 7, 2017	Consolidates and replaces several existing methods in PBM format. Updated to include additional phenolic substances listed in the 2017 CSR. GC-ECD option added for nitrophenols for improved sensitivity and detection limits.