Chlorinated and Non-Chlorinated Phenols in Water - PBM

Parameter

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

Analytical Method

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

Introduction

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

Method Summary

Method Summary:

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

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

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

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL (µg/L)	EMS Analyte Code
Non-Chlorinated Phenols			
Catechol (2-Hydroxyphenol)	120-80-9	1- 5	n/a
2,4-Dimethylphenol	105-67-9	0.1 - 0.5	D048
2,6-Dimethylphenol	576-26-1	0.1 - 0.5	n/a
3,4-Dimethylphenol	95-65-8	0.1 - 0.5	n/a
Hydroquinone (4-Hydroxyphenol)	123-31-9	1- 5	n/a
2-Methylphenol (ortho-Cresol)	95-48-7	0.1 - 0.5	D084
3-Methylphenol (meta-Cresol)	108-39-4	0.1 - 0.5	D085
4-Methylphenol (para-Cresol)	106-44-5	0.1 - 0.5	D086
Phenol	108-95-2	0.1 - 0.5	0119
Resorcinol (3-Hydroxyphenol)	108-46-3	1- 5	n/a
Nitrophenols			
2,4-Dinitrophenol	51-28-5	1 - 10	D049
2-Methyl-4,6-Dinitrophenol	534-52-1	1 - 10	D047
2-Nitrophenol	88-75-5	1 - 10	N030
4-Nitrophenol	100-02-7	1 - 10	N031
Chlorinated Phenols			
2-Chlorophenol	95-57-8	0.1 - 0.5	C035
3-Chlorophenol	108-43-0	0.1 - 0.5	C054
4-Chlorophenol	106-48-9	0.1 - 0.5	C055
4-Chloro-3-Methylphenol	59-50-7	0.1 - 0.5	C036
2,3-Dichlorophenol	576-24-9	0.05 - 0.1	D073
2,4-Dichlorophenol	120-83-2	0.05 - 0.1	D050
2,5-Dichlorophenol	583-78-8	0.05 - 0.1	D075
2,6-Dichlorophenol	87-65-0	0.05 - 0.1	D076

3,4-Dichlorophenol	95-77-2	0.05 - 0.1	CP07
3,5-Dichlorophenol	591-35-5	0.05 - 0.1	D077
Pentachlorophenol	87-86-5	0.05 - 0.1	P022
2,3,4,5-Tetrachlorophenol	4901-51-3	0.05 - 0.1	T036
2,3,4,6-Tetrachlorophenol	58-90-2	0.05 - 0.1	T037
2,3,5,6-Tetrachlorophenol	935-95-5	0.05 - 0.1	T038
2,3,4-Trichlorophenol	15950-66-0	0.05 - 0.1	T033
2,3,5-Trichlorophenol	933-78-8	0.05 - 0.1	T034
2,3,6-Trichlorophenol	933-75-5	0.05 - 0.1	T035
2,4,5-Trichlorophenol	95-95-4	0.05 - 0.1	T043
2,4,6-Trichlorophenol	88-06-2	0.05 - 0.1	T042
3,4,5-Trichlorophenol	609-19-8	0.05 - 0.1	T044
Recommended Surrogates			
2,4-Dibromophenol	615-58-7	n/a	n/a
2,4,6-Tribromophenol	118-79-6	n/a	n/a

MDLs may vary substantially depending on analytical technique.

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

EMS Method Code(s)

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

Matrix

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

Interferences and Precautions

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

c) 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.

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

Sample Handling and Preservation

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

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

Stability

Holding Time:

Preserved Samples: Extract within 14 days of sample collection.

Unpreserved Samples: Extract within 7 days of sample collection.

Extracts: May be held up to 40 days from time of extraction prior to instrumental analysis.

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

Procedure

Reagents:

a) Organics-free reagent water

b) Solvents, distilled in glass, pesticide grade, or equivalent:
- Methyl-tert-butyl ether (MTBE),
- Dichloromethane (DCM)
- Iso-Octane.

c) Ascorbic acid

d) Sodium bisulfate or H_2SO_4

e) Sodium sulfate, anhydrous, reagent grade

f) Hydrochloric acid, reagent grade

g) Sodium chloride (NaCl), reagent grade

Extraction:

a) Measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials and any surface film.

b) Ensure sample pH is less than 2. If necessary, adjust pH using hydrochloric acid.

c) Add a small amount of NaCl into the sample (e.g. 10 g per 1000 mL of sample) to improve extraction efficiency of water-soluble phenolics. Use of larger quantities of NaCl may further improve extraction efficiency.

d) Spike the sample with deuterated phenolic surrogates. Refer to the Quality Control section.

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

f) Add 100 mL of MTBE to the sample bottle and rinse contents into the separatory funnel. Shake vigorously for a minimum of one minute with frequent venting. Allow layers to separate and drain the MTBE (top layer) through sodium sulfate into a round bottom flask.

g) Repeat extraction two more times with 100 mL of MTBE each time.

h) Repeat extraction one more time using 50 mL of DCM. Note, however, that the DCM solvent layer will be the bottom layer.

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

j) Transfer the concentrated extract to a test tube and evaporate under nitrogen to 1 mL.

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

Instrumental Analysis:

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

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

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

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

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

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

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

Performance Requirements

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

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

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

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

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

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

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Method Blank (MB)	One per batch (max. 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max. 20 samples)	All CPs and listed NCPs: 60-130% (isotope dilution correction may be required for some compounds, e.g. hydroxyphenols, phenol, and 2,4-DMP). Nitrophenols: 30-130% recovery
Field Duplicates	Recommended, One per batch (max 20 samples) Requires 2nd bottle	50% RPD [or within 2x reported DL for low level results]
Matrix Spike	Recommended, One per batch (max. 20 samples) Requires 2nd bottle	All CPs and listed NCPs: 50–140% Nitrophenols: 30–130%
Surrogate Compounds	All samples	See LCS recovery limits
Internal Standard	All samples	Peak area counts for all internal standards in all injections must be 50-200% of the initial calibration (average or mid-point) or initial CVS
Isotope Dilution Standards	All samples (if used)	Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%.
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	80-120%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	80-120%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. No corrective actions are required for field duplicate DQO exceedances.		

Method Blank: Required. Minimum one per batch.

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

Field Duplicates: Recommended.

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

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

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

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

Prescribed Elements

The following components of this method are mandatory:

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

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

References

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

Revision History

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