METHOD 8041A

PHENOLS BY GAS CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method describes open-tubular, capillary column gas chromatography procedures for the analysis of phenols, using either single-column or dual-column/dual-detector approaches. The following RCRA compounds have been determined by this method:

		Appropriate Preparation Technique[b]				
Compound Name	CAS No.[a]	3510	3520	3540	3550	3580
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
Dinoseb (2-*sec*-Butyl-4,6-dinitro phenol)	88-85-7	X	ND	ND	ND	X
2-Methyl-4,6-dinitrophenol	534-52-1	X	X	X	X	X
2-Methylphenol (*o*-Cresol)	95-48-7	X	ND	ND	ND	X
3-Methylphenol (*m*-Cresol)	108-39-4	X	ND	ND	ND	X
4-Methylphenol (*p*-Cresol)	106-44-5	X	ND	ND	ND	X
4-Nitrophenol	100-02-7	X	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Phenol	108-95-2	DC(28)	X	X	X	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

[a] Chemical Abstract Service Registry Number.
[b] Additional sample preparation methods not included here because of table space limitations, e.g., Methods 3535, 3545, and 3546, have also been shown to work for these compounds.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
ND = Not determined. X = Data have shown greater than 70 percent recovery by this technique.

1.2 The single-column approach involves the use of a fused-silica, open-tubular wide-bore column for analysis. The fused-silica, open-tubular wide-bore column offers improved resolution, better selectivity, increased sensitivity, and faster analysis when compared to packed columns.

1.3 The dual-column/dual-detector approach involves the use of two fused-silica, wide-bore open-tubular columns of different polarities. The columns are connected to an injection tee and two identical detectors.

1.4 Underivatized phenols may be analyzed by GC/FID. This method also includes procedures for the derivatization of the phenols using either diazomethane or α-bromo-2,3,4,5,6-penta-fluorotoluene (also known as pentafluorobenzyl bromide, PFBBr). The derivatized phenols are separated and identified as either the methylated phenols (anisoles) or the pentafluorobenzyl ethers.

NOTE: Three phenols failed to derivatize using the PFBBr procedure: 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, and Dinoseb. If these compounds are target analytes for a specific project, then analyses should be conducted using the diazomethane derivatization or the underivatized phenols, if sufficient sensitivity can be achieved.

1.5 The following analytes may also be analyzed by this method:

Compound	CAS No.
2-Chloro-5-methylphenol	615-74-7
4-Chloro-2-methylphenol	1570-64-5
3-Chlorophenol	108-43-0
4-Chlorophenol	106-48-9
2-Cyclohexyl-4,6-dinitrophenol	131-89-5
2,3-Dichlorophenol	576-24-9
2,5-Dichlorophenol	583-78-8
3,4-Dichlorophenol	95-77-2
3,5-Dichlorophenol	591-35-5
2,3-Dimethylphenol	526-75-0
2,5-Dimethylphenol	95-87-4
2,6-Dimethylphenol	576-26-1
3,4-Dimethylphenol	95-65-8
2,5-Dinitrophenol	329-71-5
2-Nitrophenol	88-75-5
3-Nitrophenol	554-84-7
2,3,4,5-Tetrachlorophenol	4901-51-3
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4-Trichlorophenol	15950-66-0
2,3,5-Trichlorophenol	933-78-8
2,3,6-Trichlorophenol	933-75-5

1.6 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.7 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Samples are extracted using an appropriate sample preparation method. Prior to analysis, the extracts are cleaned up, as necessary, and the solvent exchanged to one that is compatible with the GC detector to be used.

2.2 Underivatized phenols may be analyzed by GC/FID, using either the single-column or dual-column approach.

2.3 The target phenols also may be derivatized with diazomethane or pentafluorobenzyl bromide (PFBBr) and analyzed by GC/FID or GC/ECD, respectively.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 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. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware.

4.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the syringe used for injection must be thoroughly rinsed between samples with solvent. Whenever a highly concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross-contamination. Column blanks should be analyzed whenever the analysis of a solvent blank indicates cross-contamination.

4.3 Some compounds may coelute on one or more of the GC columns (see Secs. 4.5 and 4.6). As a result, if all the analytes listed in Sec. 1.1 are to be determined, then the analytes must be divided among two or more calibration standards (see Sec. 7.7). In addition, if a peak is present in a sample chromatogram that corresponds to a coeluting pair of compounds, then the results must be reported as the sum of the two coeluting compounds unless the sample extract has been reanalyzed by GC/MS or other spectral techniques (see Sec. 9.0 and Method 8270) that are capable of separating the mass or other spectra of the coeluting compounds.

4.4 Non-specific interferences may occur in the analysis of the underivatized phenols, reducing the sensitivity of the method.

4.5 The pentafluorobenzyl ethers of the phenols cannot all be chromatographically separated using the two GC columns listed in this method. Five compound pairs coelute on the DB-5 column and three compound pairs coelute on the DB-1701 column. The parent phenols are shown below, but it is the pentafluorobenzyl ether forms that actually coelute.

DB-5	DB-1701
2,6-dimethylphenol/2,5-dimethylphenol	3-chlorophenol/3,4-dimethylphenol
2,4-dimethylphenol/2-chlorophenol	2,4-dichlorophenol/3,5-dichlorophenol
2,6-dichlorophenol/4-chloro-2-methylphenol	2,4,5-trichlorophenol/2,3,5-trichlorophenol
2,4,5-trichlorophenol/2,3,5-trichlorophenol	
2,3,4,5-tetrachlorophenol/2,5-dinitrophenol	

In addition, 3-methylphenol is only partially resolved from 4-methylphenol on the two columns, and 2-chlorophenol is only partially resolved from 2,3-dimethylphenol on the DB-1701 column.

As noted above, the PFB derivatives of 2,3,5-trichlorophenol and 2,4,5-trichlorophenol coelute on both the DB-5 and DB-1701 columns. Therefore, if these compounds are of concern, the analyst should perform an analysis of the underivatized forms of these compounds (see Sec. 11.2) or employ a GC column with a different stationary phase which permits their separation.

4.6 The following underivatized phenols coelute on the RTx-50 or the DB-5 columns in the dual-column configuration described in Sec. 11.5.1.

RTx-50	DB-5
phenol/2-chlorophenol	3-methylphenol/4-methylphenol
3-methylphenol/4-methylphenol	
2,4,5-trichlorophenol/2,4,6-trichlorophenol	

4.7 The methylated derivatives of 2-nitrophenol and 3-nitrophenol coelute on the DB-5 column, when used in the single-column configuration described in Sec. 11.5.3. The methylated derivatives of 2,3,5-trichlorophenol and 2,4,5-trichlorophenol also coelute on that column in that configuration.

4.8 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Given the safety concerns associated with the use of diazomethane, the analyst should carefully consider the potential benefits of the derivatization, including a possible increase in sensitivity and a decrease in interferences, in light of the intended application of the results. For example, the regulatory limits associated with the RCRA toxicity characteristic (40 CFR 261.24) should be achievable through the analysis of the phenols without derivatization.

5.3 WARNING: Diazomethane is a carcinogen and can EXPLODE under certain conditions.

5.4 WARNING: PFBBr is a lacrimator.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph

Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all necessary accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended. An FID is typically used as the detector for the analysis of the underivatized phenols and either an FID or an ECD may be used as the detector for the analysis of the phenols derivatized with diazomethane or PFBBr, respectively.

6.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 11.8 describes how GC/MS confirmation techniques may be employed). The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. Both the single-column approach and the dual-column approaches employ wide-bore (0.53-mm ID) columns.

The columns listed in this section were the columns used to develop the method. Listing these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

This method contains example retention time data for the analysis of the derivatized phenols on Columns 1 and 2, and data for the analysis of the underivatized phenols on Columns 1 and 3. These data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

6.2.1 Column 1 -- 30-m x 0.53-mm ID fused-silica open-tubular column, cross-linked and chemically bonded with 95 percent dimethyl and 5 percent diphenyl-polysiloxane (DB-5, RT_x-5, SPB-5, or equivalent), 0.83-µm or 1.5-µm film thickness.

6.2.2 Column 2 -- 30-m x 0.53-mm ID fused-silica open-tubular column cross-linked and chemically bonded with 14 percent cyanopropylphenyl and 86 percent dimethyl-polysiloxane (DB-1701, RT_x-1701, or equivalent), 1.0-µm film thickness.

6.2.3 Column 3 -- 30-m x 0.53-mm ID fused-silica open-tubular column cross-linked and chemically bonded with 50 percent phenyl and 50 percent methylpolysiloxane (RTx-50, or equivalent), 1.0 µm film thickness.

6.3 Splitter -- When the dual-column approach is employed, the two columns must be connected with a splitter such as those listed below (or equivalent).

6.3.1 Press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

6.3.2 8-in glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

6.3.3 Y-shaped fused-silica connector (Restek, Catalog no. 20405).

6.4 Column rinsing kit -- Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

6.5 Diazomethane generators -- Refer to Sec. 11.3 to determine which method of diazomethane generation should be used for a particular application.

6.5.1 Diazald kit -- Recommended for the generation of diazomethane (Aldrich Chemical Co., Catalog no. 210,025-0, or equivalent).

6.5.2 As an alternative, assemble the generator assembly shown in Figure 1 from two 20-mm x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract.

6.6 PFBBr derivatization equipment -- 10-mL graduated concentrator tubes with screw caps, disposable pipets, beakers, and water bath.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at $\leq$6 °C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. All standard solutions must be replaced after six months or sooner if routine QC (see Sec. 9.0) indicates a problem.

7.3 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

7.3.1 Hexane, C_6H_{14}

7.3.2 Acetone, CH_3COCH_3

7.3.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

7.4 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.5 Stock standard solutions (1000 mg/L) -- May be prepared from pure standard materials or may be purchased as certified solutions.

7.5.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

7.5.2 Transfer the stock standard solutions into bottles equipped with PTFE-lined screw-caps or crimp tops. Store at $\leq$6 °C and protect from light. Stock standards must be replaced after one year or sooner if a comparison with check standards indicates a problem. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.5.3 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.6 Composite stock standard -- May be prepared from individual stock solutions. For composite stock standards containing less than 25 components, transfer 1.00 mL of each individual stock solution at 1000 mg/L, add solvent, mix the solutions and bring to volume in an appropriate volumetric flask. This composite solution may be further diluted to obtain the desired concentrations.

7.7 Calibration standards

These should be prepared at a minimum of five different concentrations by dilution of the composite stock standard with hexane or other appropriate solvent. The solvent or solvents used to dilute the standards should be the same as the final solvent mixture in the sample extracts to be analyzed. The standard concentrations should correspond to the expected range of concentrations present in the field samples and should bracket the linear range of the detector. Concentrations of the target analytes at 5, 25, 50, 100, and 200 mg/L (except for 2,4- and 2,5-dinitrophenol and 2-methyl-4,6-dinitrophenol at about twice the given values) have been used as calibration solutions in soil recovery studies, but other concentrations may be employed at the discretion of the analyst, provided that they are appropriate for the specific application.

All standards must be prepared from the target phenols. When derivatization is employed, the phenol standards must be prepared, and then derivatized in the same fashion as the sample extracts, prior to calibration.

A noted in Sec. 4.0, some of the target phenols coelute on the GC Columns listed in Sec. 6.2. If determining any of the analytes listed in Sec. 1.1 that may coelute (see Secs. 4.5 - 4.7), then the analytes must be divided among two or more calibration standards. The two mixtures suggested below are based on the example retention time data provided in Tables 1 through 4, and consider both the underivatized and derivatized phenols. The analyst should consider the form of the phenols that will be analyzed (underivatized, methylated, or pentafluorobenzylated), as well as the GC columns and conditions that will be used in the laboratory, and prepare mixtures of standards that are acceptable for those circumstances. The analytes are listed in alphabetical order in this table.

Mixture 1	Mixture 2
4-Chloro-3-methylphenol	2-Chlorophenol
2,4-Dimethylphenol	2-Cyclohexyl-4,6-dinitrophenol
Dinoseb	2,4-Dichlorophenol
2,4-Dinitrophenol	2,6-Dichlorophenol
3-Methylphenol	4-Methylphenol
2-Methyl-4,6-dinitrophenol	4-Nitrophenol
Phenol	Pentachlorophenol
2,4,5-Trichlorophenol	2,3,4,6-Tetrachlorophenol
	2,4,6-Trichlorophenol

In addition, some of the phenols listed in Sec. 1.5 also coelute. The two mixtures suggested below address the underivatized forms of those additional analytes that are known to coelute. As with the phenols listed in Sec. 1.1, analysts may employ other mixtures appropriate for the specific GC columns and conditions used in the laboratory. The analytes below may be included in the same numbered mixture as the phenols in Sec. 1.1 and listed above (i.e., mixture 1 below may be combined with mixture 1 above, etc.). If the additional analytes are to be analyzed as their methylated derivatives, then the analyst may wish to include the coeluting analytes found in Table 2 in different mixes than shown below.

Mixture 1	Mixture 2
3-Chlorophenol	2,5-Dimethylphenol
3,5-Dichlorophenol	3,4-Dimethylphenol
2,3-Dimethylphenol	2-Nitrophenol
2,6-Dimethylphenol	3-Nitrophenol
2,5-Dinitrophenol	2,3,5-Trichlorophenol
2,3,5,6-Tetrachlorophenol	2,3,6-Trichlorophenol

7.8 Internal standard -- When internal standard calibration is used, prepare a solution of 1000 mg/L of 2,5-dibromotoluene and 2,2',5,5'-tetrabromobiphenyl. For spiking, dilute this solution to 50 ng/µL. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards.

7.9 Surrogate standard -- The performance of this method should be monitored using surrogate compounds. Surrogates are added to all samples, method blanks, matrix spikes, and calibration standards. Prepare a solution of 1000 mg/L of 2,4-dibromophenol and dilute it to 1.6 ng/µL. Use a spiking volume of 100 µL for a 1-L aqueous sample. The compounds listed in Sec. 1.5 may also be used as surrogates, provided that they are not target analytes for a given project.

7.10 Reagents for derivatization

NOTE: Other derivatization techniques may be employed, provided that the analyst can demonstrate acceptable precision and accuracy for the target compounds (see Sec. 9.0) and for the particular application.

7.10.1 Diazomethane derivatization

7.10.1.1 *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) -- High purity (Aldrich Chemical Co., or equivalent).

7.10.1.2 Diethyl ether, $C_2H_5OC_2H_5$, stabilized with BHT -- Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. If ethanol stabilized diethyl ether is used, the methylation reaction may not proceed efficiently.

7.10.1.3 Silicic acid, H_2SiO_5. 100-mesh powder, store at 130 °C.

7.10.1.4 HPLC-grade hexane.

7.10.1.5 Carbitol (diethylene glycol).

7.10.1.6 37% potassium hydroxide, KOH.

7.10.2 PFBBr derivatization

7.10.2.1 Standards for the target phenols are purchased as phenols and derivatized prior to calibration.

7.10.2.2 α-Bromo-2,3,4,5,6-pentafluorotoluene (PFBBr reagent) -- Dissolve 0.500 g of PFBBr in 9.5 mL acetone. Store in the dark at ≤6 °C. Prepare fresh reagent biweekly.

7.10.2.3 Potassium carbonate solution, K_2CO_3 (10%) -- Dissolve 1 g of anhydrous potassium carbonate in water and adjust volume to 10 mL.

7.10.2.4 HPLC-grade acetone.

7.10.2.5 HPLC-grade hexane.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes," Sec. 4.1.

8.2 It is recommended that extracts to be methylated undergo derivatization within 48 hr after extraction and methylated extracts be analyzed immediately after derivatization to minimize other reactions that may occur.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 or 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 5000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation is found in Method 8000 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. If appropriate, it is suggested that the quality control (QC) reference sample concentrate contain each analyte of interest at 20 mg/L. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.0 for information on calibration and standardization.

11.0 PROCEDURE

The following sections provide the procedures for the extraction of samples, as well as the derivatization of the phenols, and their analysis by gas chromatography.

WARNING: Given the safety concerns associated with the use of diazomethane, the analyst should carefully consider the potential benefits of the derivatization, including a possible increase in sensitivity and a decrease in interferences, in light of the intended application of the results. For example, the regulatory limits associated with the RCRA toxicity characteristic (40 CFR 261.24) should be achievable through the analysis of the phenols *without* derivatization.

Whatever approach is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the concentrations of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

11.1 Extraction

11.1.1 Refer to Chapter Two and Method 3500 for guidance on choosing the appropriate extraction procedure.

11.1.1.1 Water samples may be extracted at a pH of less than or equal to 2 with methylene chloride, using Method 3510, 3520, or 3535.

11.1.1.2 Solid samples may be extracted using Methods 3540, 3545, 3546 or 3550, and non-aqueous liquid samples may be prepared using Method 3580. Acid-base partition cleanup using Method 3650 is suggested for extracts obtained from application of either Method 3540 or 3550.

11.1.1.3 Other aqueous liquid or solid 3500 series extraction techniques in this manual may be appropriate for this method.

11.1.2 If phenols are to be determined without derivatization, proceed to Sec. 11.2 (see the note in Sec. 11.0).

11.1.3 If the phenols are to be determined by derivatization, the extraction solvent should be concentrated down to 1 mL using an appropriate concentration technique. If the sample is to be analyzed by GC/ECD the extraction solvent (methylene chloride) will need to be exchanged to hexane or some other nonhalogenated solvent compatible with the detector. If methylation with diazomethane is being performed, the sample should be diluted to a final volume of 4 mL with diethyl ether. If PFBBr derivatization is being performed, the sample should be diluted to a final volume of 4 mL with acetone.

CAUTION: It is critical to ensure that the sample extract is dry when preparing it for methylation. Any moisture remaining in the extract will result in low methylated phenol recoveries. It may be appropriate to add approximately 10 g of acidified anhydrous sodium sulfate to the extract prior to concentration and, periodically, vigorously shake the extract and drying agent. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2-hr drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

11.1.3.1 If the phenols are to be determined by methylation derivatization using diazomethane, proceed to Sec. 11.3.

11.1.3.2 If the phenols are to be determined by PFBBr derivatization, proceed to Sec. 11.4.

NOTE: Other derivatization techniques may be employed, provided that the analyst can demonstrate acceptable precision and accuracy for the target compounds (see Sec. 9.0).

11.2 If the phenols are to be determined without derivatization, then, prior to gas chromatographic analysis, the extraction solvent must be exchanged to 2-propanol or other solvent compatible with the detector. The exchange is performed as follows:

11.2.1 Concentrate the extract to 1 mL using the macro-Snyder column and allow the apparatus to cool and drain for at least 10 min.

11.2.2 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small amount of 2-propanol. Adjust the extract volume to 1.0 mL.

11.2.3 Stopper the concentrator tube and store refrigerated at ≤6 °C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial equipped with a PTFE-lined screw-cap or crimp top.

11.2.4 Analyze by gas chromatography (GC/FID). Proceed to Sec. 11.5 for suggested GC operating conditions.

11.3 Methylation derivatization procedures

11.3.1 Diazomethane derivatization

Two methods may be used for the generation of diazomethane: The bubbler method, Sec. 11.3.3, or the Diazald kit method, Sec. 11.3.4. The methylation of phenolic compounds for this analysis procedure has been documented for the Diazald kit only (Table 2). However, the bubbler method should also be applicable.

WARNING: Diazomethane is a carcinogen and can EXPLODE under certain conditions.

The bubbler method is suggested when small batches of samples (10 - 15) need methylation. The bubbler method works well with samples that have low concentrations of phenols (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing methylation. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of phenols (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method).

WARNING: The diazomethane derivatization procedures described below will react efficiently with all of the phenols described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use.

11.3.2 The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- WARNING: Do not heat above 90 °C -- EXPLOSION may result.
- WARNING: Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers -- EXPLOSION may result.
- WARNING: Store away from alkali metals -- EXPLOSION may result. Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

11.3.3 Bubbler method -- Assemble the diazomethane bubbler (see Figure 1).

11.3.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 - 0.2 g of Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for methylation of approximately three sample extracts. An additional 0.1 - 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total methylation.

11.3.3.2 Remove the concentrator tube and seal it with a Neoprene or PTFE stopper. Store at room temperature in a hood for 20 min.

11.3.3.3 Destroy any unreacted diazomethane by adding 0.1 - 0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately.

11.3.3.4 Extracts should be stored at ≤6 °C away from light. It is recommended that the methylated extracts be analyzed immediately after derivatization to minimize other reactions that may occur.

11.3.3.5 Analyze by gas chromatography (GC/FID). Proceed to Sec. 11.5 for suggested GC operating conditions.

11.3.4 Diazald kit method

Instructions for preparing diazomethane are provided with the generator kit. If the instructions conflict with the discussion below, then follow the instructions that are provided with the kit.

11.3.4.1 Add 2 mL of diazomethane solution and let the sample stand for 10 min with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

11.3.4.2 Rinse the inside wall of the ampule with 700 µL of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

11.3.4.3 Dilute the sample to 10.0 mL with hexane. Store the extract under refrigeration if further processing will not be performed immediately.

11.3.4.4 Extracts should be stored at ≤6 °C away from light. It is recommended that the methylated extracts be analyzed immediately after derivatization to minimize other reactions that may occur.

11.3.4.5 Analyze by gas chromatography (GC/FID). Proceed to Sec. 11.5 for suggested GC operating conditions.

11.4 PFBBr derivatization procedure

11.4.1 Using the individual phenol stock solutions at 1000 mg/L, make a composite solution and dilute with hexane or other appropriate solvent to the appropriate concentrations for the calibration range of the analysis.

11.4.2 Sample extracts should be in hexane and diluted to 4 mL with acetone according to the procedure in Sec. 11.1.3. Other extract volumes may be employed if the analyst can demonstrate adequate sensitivity for the compounds of interest.

WARNING: PFBBr is a lacrimator.

11.4.3 Add 100 µL of calibration standards and sample extracts to 8 mL of acetone in a 10-mL graduated concentrator tube with screw caps. Add 100 µL of 5% PFBBr reagent and 100 µL of K_2CO_3 solution to the composite standard.

11.4.4 Cap the tubes tightly and gently shake the contents. Heat the tube in a water bath at 60 °C for 1 hr.

11.4.5 After the reaction is complete, cool the solution and concentrate it to 0.5 mL, using nitrogen evaporation.

11.4.6 Add 3 mL of hexane and concentrate the solution to a final volume of 0.5 mL. If cleanup is not to be performed, proceed to Sec. 11.5 for the analysis of samples by GC/ECD.

11.4.7 Cleanup (optional)

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. If cleanup is necessary, refer to Method 3630 (Silica Gel Cleanup) for specific instructions regarding the cleanup of derivatized phenols. Following column cleanup, proceed to Sec. 11.5 for analysis of the samples using GC/ECD.

11.5 Suggested GC operating conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use either the columns listed in this method or other columns or columns of other dimensions, provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that meet the data quality needs of the intended application.

11.5.1 Suggested conditions for the dual-column analysis of the underivatized phenols are as follows:

Column 1:	DB-5
Column 2:	RTx-50
Carrier gas:	Helium
Temperature program:	4 min hold
	50 °C to 220 °C at 8 °C/min
	10 min hold
Injector temperature:	235 °C
Detector temperature:	325 °C
Detector type:	Dual FID

11.5.2 Suggested conditions for the dual-column analysis of the PFB derivatives of the phenols are as follows:

Column 1:	DB-5
Column 2:	DB-1701
Carrier gas:	Helium

Flow rate:	6 mL/min
Makeup gas:	Nitrogen
Flow rate:	20 mL/min
Temperature program:	1 min hold
	150 °C to 275 °C at 3 °C/min
	2 min hold
Injector temperature:	250 °C
Detector temperature:	320 °C
Detector type:	Dual ECD

11.5.3 Suggested conditions for the single-column analysis of either the underivatized phenols or the methylated derivatives of phenols are as follows:

Column	DB-5
Carrier gas:	Nitrogen
Flow rate:	6 mL/min
Makeup gas:	Hydrogen
Flow rate:	30 mL/min
Temperature program:	1.5 min hold
	80 °C to 230 °C at 6 °C/min
	230 °C to 275 °C at 10 °C/min
	4.5 min hold
Injector temperature:	200 °C
Detector temperature:	300 °C
Detector type:	FID

11.6 Calibration

11.6.1 Prepare the calibration standards according to the guidance in Sec. 7.7. Calibration standards and sample extracts should be derivatized using the same procedures. External or internal calibration may be used for this procedure. Refer to Method 8000 for guidance on either external and internal calibration techniques.

11.6.2 Establish the GC operating conditions appropriate for the single-column or dual column approach (see Sec. 11.5). Optimize the instrumental conditions for resolution of the target analytes and sensitivity.

NOTE: Once established, the same operating conditions *must* be used for both calibrations and sample analyses.

11.6.3 A 2-µL injection volume of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

11.6.4 Calibration factors

Refer to Method 8000 for guidance on calculating calibration factors when external calibration is used or on calculating response factors when internal calibration is used.

11.6.5 Retention time windows

Refer to Method 8000 for guidance on the establishment of retention time windows.

11.6.6 Initial calibration acceptance criteria

Refer to Method 8000 for guidance on initial calibration linearity and acceptance criteria.

11.7 Gas chromatographic analysis of sample extracts

11.7.1 Inject a 2-µL aliquot of the concentrated sample extract. (Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the application.) Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units. The same GC operating conditions used for the initial calibration *must* be employed for samples analyses.

NOTE: When using internal standard calibration, add 10 µL of the internal standard solution to the sample extract prior to injection.

11.7.2 Calibration verification

Verify calibration by injecting a calibration verification standard (see Sec. 7.7) prior to conducting any sample analyses. Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. Each sample analysis must be bracketed with an acceptable initial calibration or calibration verification standard interspersed between the sample analyses. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

11.7.2.1 The calibration factor for each analyte to be quantitated must not exceed a ±15 percent difference when compared to the initial calibration curve. Refer to Method 8000 for guidance on the proper calculation of percent difference using either calibration factors or response factors.

11.7.2.2 If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

11.7.2.3 If routine maintenance does not return the instrument performance to meet the QC requirements (Sec. 11.9) based on the last initial calibration, then a new initial calibration must be performed.

11.7.3 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established in Sec. 11.6.5. As described in Method 8000, the center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

11.7.4 Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window. Each tentative identification must be confirmed, when necessary (See Sec. 11.8), using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS (see Sec. 11.8). When using the dual-column technique, additional confirmation is not necessary, provided that the analyte meets the identification criteria in both columns.

11.7.5 Refer to Method 8000 for calculation of results from either external or internal calibration. Both external and internal standard quantitation can be applied to the analysis of either the underivatized or derivatized phenols, provided that the initial calibration is performed on the same type of standards.

11.7.5.1 Proper quantitation necessitates the appropriate selection of a baseline from which the peak area or height can be determined.

11.7.5.2 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

11.7.5.3 If partially overlapping or coeluting peaks are found, change columns or try GC/MS quantitation, see Sec. 11.8 and Method 8270.

11.8 Confirmation

Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the sample composition is not well characterized. Confirmatory techniques such as gas chromatography with a dissimilar column or a mass spectrometer should be used. See Method 8000 for information on confirmation of tentative identifications.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

When the dual-column approach is employed, the target phenols are identified and confirmed when they meet the identification criteria on both columns.

11.9 Suggested chromatograph maintenance

Corrective measures may involve one or more of the following remedial actions.

11.9.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific, Restek, Supelco, or equivalent), clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off a few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

11.9.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Reduce the injection port temperature to room temperature. Inspect the injection port and remove any visible foreign material.

11.9.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene.

11.9.2.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the columns.

11.9.3 Column rinsing

The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a satisfactory final rinse and in some cases may be the only necessary solvent. The column should then be filled with methylene chloride and allowed to remain flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.0 for information of data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2 Table 1 lists example retention times and recovery data for the underivatized analytes extracted from sandy loam soil that may be determined by this method. These data are taken from Reference 3 and are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.3 Table 2 lists example retention times for some of the methylated analytes that may be determined by this method. These data are taken from Reference 3 and are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.4 Table 3 lists example retention times for the PFB derivatives of the analytes that may be determined by this method. These data are taken from Reference 2 and are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.5 Table 4 lists example retention times for the underivatized phenols in standards under the dual-column configuration described in Sec. 11.5.1. These data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.6 Table 5 provides example single-laboratory accuracy data for phenols extracted from a spiked real-world soil sample using the microwave extraction technique in Method 3546. The phenols were spiked at 2560 µg/kg. All samples were extracted using 1:1 hexane:acetone. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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2. V. Lopez-Avila, E. Baldin, J. Benedicto, J. Milanes, and W. F. Beckert, "Application of Open-Tubular Columns to SW-846 GC Methods," final report to the U.S. Environmental Protection Agency on Contract 68-03-3511, Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

3. S. Tsang, P. Marsden, and N. Chau, "Performance Data for Methods 8041, 8091, 8111, and 8121A," draft report to U.S. Environmental Protection Agency under Contract 68-W9-0011, Science Applications International Corporation, San Diego, CA, 1992.

4. K. Li, J. M. R. Bélanger, M. P. Llompart, R. D. Turpin, R. Singhvi, and J. R. J. Paré, "Evaluation of Rapid Solid Sample Extraction Using the Microwave-assisted Process (MAP™) under closed-vessel conditions," *Spectrosc. Int. J.* `997, 13, 1-14.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figure referenced by this method.

TABLE 1

EXAMPLE RETENTION TIMES AND RECOVERIES OF UNDERIVATIZED PHENOLS ON A DB-5 GC COLUMN (SINGLE-COLUMN CONFIGURATION)

Analyte	RT (min)	Mix Number	Spiking Conc. (mg/kg)	Recovery (%)	% RSD
Phenol	6.364	1	20	93	16.9
2-Chlorophenol	6.897	2	20	93	11.6
2-Methylphenol	8.167	1	20	95	13.6
4-Methylphenol	8.626[a]	2	20	96	3.4
3-Methylphenol	8.648[a]	1	20	98	10.3
2,4-Dimethylphenol	9.632	1	20	93	11.5
2,5-Dimethylphenol	10.417	2	20	101	2.6
2,6-Dimethylphenol	10.543	1	20	101	8.1
2-Nitrophenol	10.575	2	20	99	2.8
2,4-Dichlorophenol	11.288	2	20	102	2.5
2,3-Dimethylphenol	11.322	1	20	106	7.1
3-Chlorophenol	11.684	1	20	116	6.7
2,6-Dichlorophenol	12.177	2	20	104	2.8
4-Chloro-3-methylphenol	14.07	1	20	128	3.8
2,3,5-Trichlorophenol	15.466	2	20	136	4.1
2,4,6-Trichlorophenol	15.908	2	20	122	2.7
2,4,5-Trichlorophenol	16.053	1	20	139	3.0
2,3,6-Trichlorophenol	16.679	2	20	125	2.6
2,5-Dinitrophenol	18.373[a]	1	40	177	5.1
3-Nitrophenol	18.374[a]	2	20	124	4.0
2,4-Dinitrophenol	19.285	1	40	157	7.3
4-Nitrophenol	19.616	2	20	123	5.6
2,3,5,6-Tetrachlorophenol	20.417	1	20	236	3.5
2,3,4,6-Tetrachlorophenol	20.604	2	20	146	3.3
2-Methyl-4,6-dinitrophenol	21.717	1	40	201	3.8
Pentachlorophenol	24.849	2	20	168	5.0
Dinoseb	25.705	1	20	210	4.9

See the next page for notes related to this table.

TABLE 1 NOTES:

[a] Coeluting analytes. The analyst should consider the form of the phenols that will be analyzed (underivatized, methylated, or pentafluorobenzylated), as well as the GC columns and conditions that will be used in the laboratory, and prepare mixtures of standards that are appropriate for those circumstances.

Data taken from Reference 3.

Five 5-g aliquots of clean, sandy loam soil were spiked separately and extracted using Method 3540 (Soxhlet) with methylene chloride as a solvent.

These example retention times were generated using the GC conditions described in Sec. 11.5.3.

All data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 2

EXAMPLE RETENTION TIMES OF METHYLATED PHENOLS ON A DB-5 GC COLUMN (SINGLE-COLUMN CONFIGURATION)

Analyte (derivatized)	Mix Number	RT (min)
3-Chlorophenol	1	7.74
2-Chlorophenol	2	8.07
2,6-Dichlorophenol	2	10.013
4-Chloro-3-methylphenol	1	10.27
2,4-Dichlorophenol	2	12.064
2,4,6-Trichlorophenol	2	13.123
3-Nitrophenol	2	13.476[a]
2-Nitrophenol	2	13.476[a]
2,3,6-Trichlorophenol	2	14.148
4-Nitrophenol	2	14.64
2,4,5-Trichlorophenol	1	15.869[a]
2,3,5-Trichlorophenol	2	15.869[a]
2,3,5,6-Tetrachlorophenol	1	17.499
2,3,4,6-Tetrachlorophenol	2	17.554
2,5-Dinitrophenol	1	20.067
2-Methyl-4,6-dinitrophenol	1	20.912
Pentachlorophenol	2	21.538
2,4-Dinitrophenol	1	22.145
Dinoseb	1	23.867

[a] Coeluting analytes. The analyst should consider the form of the phenols that will be analyzed (underivatized, methylated, or pentafluorobenzylated), as well as the GC columns and conditions that will be used in the laboratory, and prepare mixtures of standards that are appropriate for those circumstances.

Data taken from Reference 3.

These example retention times were generated using the GC conditions described in Sec. 11.5.3.

All data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 3

EXAMPLE RETENTION TIMES OF PFB DERIVATIVES OF PHENOLS[a]
(DUAL-COLUMN CONFIGURATION)

	Retention Time (min)	
Analyte	DB-5	DB-1701
Phenol	4.69	6.36
2-Methylphenol	5.68	7.44
3-Methylphenol	6.05	7.99
4-Methylphenol	6.21	8.13
2,6-Dimethylphenol	7.08	8.83
2,5-Dimethylphenol	7.08	9.02
2,4-Dimethylphenol	7.34	9.27
2,3-Dimethylphenol	7.96	10.11
2-Chlorophenol	7.34	10.24
3-Chlorophenol	7.86	10.78
3,4-Dimethylphenol	8.46	10.78
4-Chlorophenol	8.19	11.31
2-Chloro-5-methylphenol	9.12	12.25
2,6-Dichlorophenol	9.73	12.52
4-Chloro-2-methylphenol	9.73	12.89
4-Chloro-3-methylphenol	10.18	13.31
2,5-Dichlorophenol	10.71	14.37
3,5-Dichlorophenol	11.02	14.75
2,4-Dichlorophenol	11.02	14.75
2,4,6-Trichlorophenol	12.85	15.76
2,3-Dichlorophenol	12.01	16.22
3,4-Dichlorophenol	12.51	16.67
2,3,6-Trichlorophenol	13.93	17.36
2-Nitrophenol	12.51	19.19
2,4,5-Trichlorophenol	15.02	19.35
2,3,5-Trichlorophenol	15.02	19.35
3-Nitrophenol	13.69	20.06
2,3,5,6-Tetrachlorophenol	17.71	21.18
2,3,4,6-Tetrachlorophenol	17.96	21.49
2,3,4-Trichlorophenol	16.81	21.76

TABLE 3
(continued)

	Retention Time (min)	
Analyte	DB-5	DB-1701
4-Nitrophenol	15.69	22.93
2,3,4,5-Tetrachlorophenol	20.51	25.52
Pentachlorophenol	22.96	26.81
2,5-Dinitrophenol	20.51	30.15
2,5-Dibromotoluene (IS)	3.16	3.18
2,2',5,5'-Tetrabromobiphenyl (IS)	25.16	28.68
2,4-Dibromophenol (Surr)	16.02	20.56

[a] Coeluting analytes. The analyst should consider the form of the phenols that will be analyzed (underivatized, methylated, or pentafluorobenzylated), as well as the GC columns and conditions that will be used in the laboratory, and prepare mixtures of standards that are appropriate for those circumstances.

Data taken from Reference 2.

IS = Internal Standard
Surr = Surrogate

These example retention times were generated using the GC conditions described in Sec. 11.5.2. The analytes are listed in the order in which they elute on the DB-1701 column.

All data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 4

EXAMPLE RETENTION TIMES OF UNDERIVATIZED PHENOLS
(DUAL-COLUMN CONFIGURATION)

	Retention Time (min)	
Analyte	RTx-50	DB-5
Phenol	11.7	10.17
2-Chlorophenol	11.7	10.45
2-Methylphenol	13.45	11.96
4-Methylphenol	13.92	12.41
3-Methylphenol	13.92	12.41
2-Nitrophenol	15.8	13.8
2,4-Dimethylphenol	15.41	14.06
2,4-Dichlorophenol	15.94	14.56
2,6-Dichlorophenol	16.97	15.28
4-Chloro-3-methylphenol	18.73	16.89
2,3,5-Trichlorophenol	19.29	17.89
2,4,6-Trichlorophenol	19.81	18.22
2,4,5-Trichlorophenol	19.81	18.35
2,3,4-Trichlorophenol	20.42	18.55
2,3,6-Trichlorophenol	20.72	18.81
2,4-Dinitrophenol	24.14	20.84
4-Nitrophenol	24.37	21.16
2,3,5,6-Tetrachlorophenol	23.56	21.63
2,3,4,6-Tetrachlorophenol	23.77	21.78
2-Methyl-4,6-dinitrophenol	25.46	22.64
Dinoseb	27.44	25.62
Pentachlorophenol	27.6	24.96

[a] Coeluting analytes. The analyst should consider the form of the phenols that will be analyzed (underivatized, methylated, or pentafluorobenzylated), as well as the GC columns and conditions that will be used in the laboratory, and prepare mixtures of standards that are appropriate for those circumstances.

These example retention times were generated using the GC conditions described in Sec. 11.5.1. The analytes are listed in the order in which they elute on the DB-5 column.

All data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 5

EXAMPLE SINGLE-LABORATORY PERFORMANCE DATA FOR PHENOLS EXTRACTED FROM A REAL-WORLD SOIL MATRIX SPIKED AT 2560 PPB USING MICROWAVE EXTRACTION (METHOD 3546)

Compound	Recovery (%)	RSD (%)
2-Chlorophenol	101	4.5
m-+*p*-Cresol	106	3.1
2,4-Dimethylphenol	98	2.9
2,6-Dichlorophenol	10	3.9
2,4,5-Trichlorophenol	108	3.8
2,4-Dinitrophenol	85	13.2
2,3,4,6-Tetrachlorophenol	112	4.7
Dinoseb	95	12.7

Data taken from Reference 4.
These data are provided for guidance purposes only.

FIGURE 1

DIAZOMETHANE GENERATOR