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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Phenols in Water by Gas-Liquid Chromatography[1]

This standard is issued under the fixed designation D 2580; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers a direct aqueous injection procedure for the gas-liquid chromatographic determination of phenols, cresols, and mono- and di-chlorophenols in water.[2]

1.2 The precision and bias of the test method has been calculated from the results of interlaboratory analyses of three master solutions, each containing phenol, *p*-cresol, *p*-chlorophenol, 3,5-dichlorophenol.

1.3 The test method may be applied to waste water or concentrates that contain more than 1 mg/L of phenolic compounds. Therefore, for a comparison with Test Methods D 1783, see Appendix X1.

1.4 The analyst should recognize that precision statements provided in 16.1 and 16.2 may not apply to waters of other matrices.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 1783 Test Methods for Phenolic Compounds in Water[4]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion Reporting Low-Level Data[3]

E 260 Practice for Packed Column Gas Chromatography[5]

E 355 Practice for Gas Chromatography Terms and Relationships[5]

3. Terminology

3.1 *Definitions*—Definitions and terms are presented in Practice E 355 and Terminology D1129.

3.1.1 The following terms used in this test method are defined in Terminology D1129 as follows:

3.1.2 *ghosting*— a gas-chromatographic interference, showing as a peak, which appears at the same elution time as a component from previous injection.

3.1.3 *internal standard*—a material present in or added to samples in known amount to serve as a reference measurement.

3.1.4 *noise*—an extraneous electronic signal that affects baseline stability.

3.1.5 *phenolic compounds*—hydroxy derivatives of benzene and its condensed nuclei.

3.1.6 *retention time*—the time that elapses from the introduction of the sample until the component peak maximum is reached.

4. Summary of Test Method

4.1 This test method uses a single gas-liquid chromatographic column for the separation of phenolic compounds and a flame-ionization detector for their measurement. The peak area of each component is measured and compared with that of a known standard to obtain quantitative results. A discussion of gas chromatography is presented in Practice E 260.

4.2 In this test method, elution of characteristic phenols occurs in the following order: (*1*) *o*-chlorophenol, (*2*) phenol and *o*-cresol, (*3*) *m*- and *p*-cresol, (*4*) 2,3-, 2,4-, 2,5- and 2,6-dichlorophenols, (*5*) *m*- and *p*-chlorophenol, and (*6*) 3,4-dichlorophenol.

4.2.1 For comparison purposes, see Appendix X1.

5. Significance and Use

5.1 Phenolic compounds are sometimes found in surface waters from natural and industrial sources. Chlorination of such waters may produce odoriferous, objectionable tasting chlorophenols. These compounds may include *o*-chlorophenol,

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Waterand is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] Baker, R. A., "Phenolic Analyses by Direct Aqueous Injection Gas Chromatography," *Journal American Water Works Association*, Vol 58, No. 6, 1966, pp. 751–760.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

p-chlorophenol, 2,6-dichlorophenol, and 2,4-dichlorophenol.[6]

6. Interferences

6.1 *Particulate Matter*—Particulate or suspended matter may, unless very finely subdivided, plug the needle used for sample injection. Such matter may be removed by centrifugation or filtration, provided it is ascertained that compounds of interest are not removed also. A colloid mill may be used, if necessary, to prepare a colloidal solution or suspension suitable for injection. Particulate matter may serve as condensation nuclei for samples; acid treatment may often dissolve such interfering solids.

6.2 *Nonphenolic Organics*—Compounds which have the same retention value as the phenolic compounds will interfere with the test. Such compounds may be eliminated by a suitable preliminary separation technique.

NOTE 1—Refer to Test Methods D 1783.

6.3 *Alkaline Compounds*—Under strongly alkaline conditions, some chlorophenols may form salts which reduce their volatility in the test. Also, some nonphenolic organics, for example, tar bases, may be more volatile in basic solution. Simple pH adjustment to near neutral or slightly acid will eliminate these interferences.

6.4 *Ghosts*—Elimination of ghosts or memory peaks is requisite before chromatographic analyses are possible. In this test method, ghosts are minimized or eliminated by injecting 3 µL of water between all sample injections. This water wash usually clears the injection port, column, and detector of artifacts; however, repeated wash injections may be necessary to clear the system. The electrometer should be set at maximum sensitivity during the wash injections to facilitate detection of ghosts.

NOTE 2—Glass injector inserts are recommended. Inserts are easy to clean or replace and minimize clean-up difficulties.

6.5 *Other Interferences*—It is beyond the scope of this test method to describe procedures for eliminating all possible interferences which might occur, particularly with highly contaminated industrial waste water.[7] In addition, the chromatographic resolution of this test method is insufficient to differentiate among some isomeric alkyl phenols.

7. Apparatus

7.1 *Chromatographic Columns*—Columns may be purchased or prepared by the analyst. Variations of column loading, length, diameter, support size, treatment, etc., are possible. Any column, for example, packed, wide bore (megabore) open tubular, analytical capillary, etc., may be used if it is shown to give precision and bias comparable to those obtained in the interlaboratory study of this test method. The three columns cited in this procedure may be modified with the understanding that the elution time and sensitivity may be altered.

7.1.1 *Carbowax 20-M*[8]—A 3-mm by 3-m (⅛-in. by 10-ft) stainless steel column packed with 60/80 mesh Chromosorb W [9] (acid washed and hexamethyldisilazane, (HMDS)-treated) coated with 20 weight % of Carbowax 20M-TPA (terephthalic acid).

7.1.2 *Free Fatty Acid Phase*, 1.5 m—A 3-mm by 1.5-m (⅛-in. by 5-ft) stainless steel column packed with 70/80 mesh Chromosorb W (acid washed) coated with 5 weight % free fatty acid phase.[10]

7.1.3 *Free Fatty Acid Phase*, 3-m—A 3-mm by 3-m (⅛-in. by 10-ft) stainless steel column packed with 60/80 mesh Chromosorb T coated with 10 % free fatty acid phase. Chromosorb T is a TFE-fluorocarbon 6 product which melts at 327°C and may begin to fuse above 250°C. It is available from suppliers of gas chromatographic materials.

7.2 *Gas Chromatograph*—A commercial or custom designed gas chromatograph with a column oven capable of isothermal temperature control to at least 210 ± 0.2°C. A unit equipped for temperature programming will facilitate elution of a mixture of phenolics of wide boiling-point range. This test method describes an isothermal analysis using a single column-type gas chromatograph. Temperature programming is an option of the analyst.

7.3 *Hydrogen Flame Ionization Detector*.

7.4 *Recorder*—To measure chromatographic output at a full-scale range of 1 mV with a response time of 1 s.

7.5 *Syringe*, 10-µL.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[11] 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 determinations.

8.2 Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as specified in Specification D 1193.

8.3 *Carrier Gases*— Research grade nitrogen or helium of highest purity are used as carrier gases.

8.4 *Hydrogen (H)*— For use with the flame ionization detector; may be obtained using a hydrogen generator, or from a high-purity tank supply.

8.5 *Phenolic Compounds*—Research grades of high purity are required. Highest purity compounds may be prepared by redistillation, recrystallization, or by using a preparatory gas chromatographic instrument.

[6] Burttschell, R. H., *et al.*, "Chlorine Derivatives of Phenol Causing Taste and Odor," *Journal American Water Works Association*, Vol 51, No. 2, 1959.

[7] Baker, Robert A., "Trace Organic Analyses by Aqueous Gas-Liquid Chromatography," *Air and Water Pollution Institute Journal*, Pergamon Press, Vol 10, 1966, pp. 591–602.

[8] Carbowax is a trademark of Union Carbide.

[9] Chromosorb is a trademark of Johns, Mansville.

[10] Available from Varian Aerograph, Walnut Creek, Calif.

[11] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

NOTE 3—**Warning**—Phenolic compounds are skin irritants. Appropriate safety measures should be taken to preclude contact with or inhalation of phenolic compounds.

The following phenolic compounds are suggested:
8.5.1 *o*-Chlorophenol,
8.5.2 *m*-Chlorophenol,
8.5.3 *p*-Chlorophenol,
8.5.4 *o*-Cresol,
8.5.5 *m*-Cresol,
8.5.6 *p*-Cresol,
8.5.7 2,3-Dichlorophenol,
8.5.8 2,4-Dichlorophenol,
8.5.9 2,5-Dichlorophenol,
8.5.10 2,6-Dichlorophenol,
8.5.11 3,4-Dichlorophenol, and
8.5.12 Phenol.

9. Sampling

9.1 Collect the sample in accordance with Practices D 3370.

9.2 Because of the possibility of oxidation or bacterial decomposition of phenols in the sample, the lapse of time before analyses should be kept to a minimum. In addition, keep the sample cool and protected from atmospheric oxygen.

10. Preparation of Chromatograph

10.1 Install the packed column in the chromatograph using suitable fittings. The use of antigalling thread lubricant is advisable.

10.2 Conduct a leak test at approximately 103 kPa (15 psi) above the operating pressure by shutting off the downstream end of the system and pressurizing from the carrier gas supply. Shut off the cylinder valve and observe the pressure gage. If no drop is noted in 10 to 15 min, the system may be considered tight. Aqueous soap solutions may be used to locate minor leaks but this should be done with caution. If soap solution enters the system, it may prove difficult to eliminate extraneous peaks or stabilize the system. Do not use the soap method for leak testing near the ionization detector.

10.3 *Column Conditioning*:

10.3.1 Condition columns for at least 24 h at temperatures 30 to 50°C above the expected operating temperature before use. Exercise caution to avoid exceeding the maximum allowable temperature for both the packing and substrate.

10.3.2 Disconnect the column at the end near the detector base to avoid deposition of volatiles on the detector during conditioning.

10.3.3 Adjust carrier gas flow to about 20 to 40 mL/min for a 3-mm (⅛-in.) diameter column.

10.3.4 Occasional injection of 3 to 5 µL of water during conditioning facilitates elution of impurities.

10.3.5 After conditioning, connect the column to the flame ionization detector.

10.3.6 Adjust the hydrogen flow to the detector to about 25 mL/min for a 3-mm (⅛-in.) diameter column. Adjust the air flow as specified in the instrument being used. Ignite the detector.

10.3.7 Adjust the column temperature to the desired level.

10.3.8 Adjust the carrier gas flow rate to 20 to 40 mL/min.

10.3.9 Observe the recorder base line. When a base line drift is no longer apparent, the column is ready for use.

10.3.10 When the series of analyses are completed and the column is to be moved and stored, it is advisable to seal or cap the ends.

11. Operating Conditions for Analysis

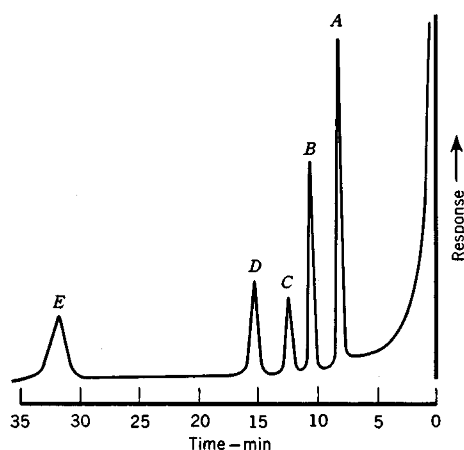
11.1 Typical operating conditions are summarized in Table 1. These operating parameters may be varied but analytical and calibration test variations must be reconciled in calculating results. For example, either nitrogen or helium may be used as the carrier gas; recorder chart speeds of approximately 30 in./h are commonly employed; sample sizes of 3 to 5 µL are usually injected (see Figs. 1-5).

12. Method of Compound Identification

12.1 Compound identification is based upon the retention time. The retention times of the sample peaks are matched with those of known standards obtained under the same operating conditions. Several related materials may elute at the same time. It is then necessary for complete resolution of these peaks to reanalyze the sample with a column of different type that effects such separation or to supplement the chromatographic procedure with spectrographic analyses.[7]

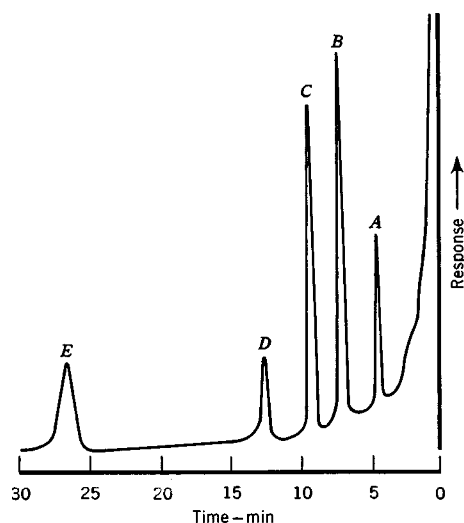
TABLE 1 Typical Operating Conditions for Chromatographic Columns

	Column Number		
Column and Packing	1 (see 7.1.1) 3-m by 3-mm (10-ft by ⅛-in.) SS, 20 % Carbowax 20M-TPA, 60/80 Chromosorb W-HMDS	2 (see 7.1.2) 1.5-m by 3-mm (5-ft by ⅛-in.) SS, 5 % FFAP, 70/80 Chromosorb W	3 (see 7.1.3) 3-m by 3-mm (10-ft by ⅛-in.) SS, 10 % FFAP Chromosorb T
Carrier gas	helium	helium	nitrogen
Carrier gas flow, mL/min	25	35	60
Temperature, °C:			
Injection port	250	205	250
Column	210	147	188
Hydrogen for detector, mL/min	25	25	30
Chart speed, in. (mm)/h	12 (305)	12	12
Sensitivity, mV	1	1	1
Electrometer range	1	0.1	1
Attenuation	1	1	1
Sample vol,µ L	1	1	1
Figure reference	Figs. 1 and 2	Fig. 5	Figs. 3 and 4



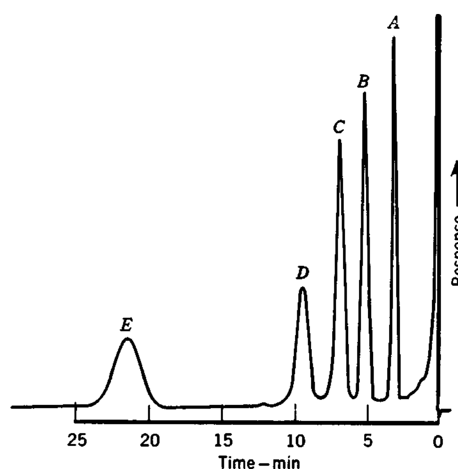
NOTE 1—Analyses were made with 3-m by 3-mm (10-ft by ⅛-in.) stainless steel column coated with 20 % Carbowax-terephthalic acid on 60/80-mesh diatomite, HMDS treated. Column temperature was 210°C, and injection temperature, 250°C. Hydrogen and helium flow rates were each 20 mL/min, at electrometer range 1 and attenuation 1, with chart speed at 305 mm (12 in.)/h, 1-mV full-scale response, and 1-µL sample of approximately 100-mg/L solutions of each phenolic. Peak A is for *o*-chlorophenol; B, phenol; C, *m*-cresol; D, 2,4-dichlorophenol; E, *p*-chlorophenol.

FIG. 1 Phenolic Analyses



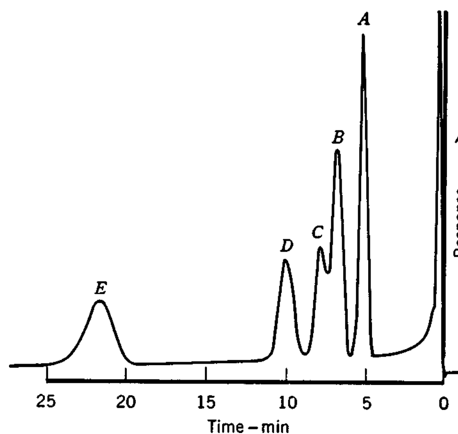
NOTE 1—Analyses were made with 3-m by 3-mm (10-ft by ⅛-in.) stainless steel column coated with 20 % Carbowax-terephthalic acid on 60/80-mesh diatomite, HMDS treated. Column temperature was 210°C, and injection temperature, 250°C. Hydrogen and helium flow rates were each 20 mL/min, at electrometer range 1 and attenuation 1, with chart speed at 305 mm (12 in.)/h, 1-mV full-scale response, and 1-µL sample of approximately 100-mL/L solutions of each phenolic. Peak A is for *o*-cresol; B, *p*-cresol; C, 2,6-dichlorophenol; D, 2,3-dichlorophenol; E, *m*-chlorophenol.

FIG. 2 Phenolic Analysis



NOTE 1—Analyses were made with 3-m by 3-mm (10-ft by ⅛-in.) stainless steel column coated with 10 % FFAP on 60/80-mesh fluorocarbon resin medium. Column temperature was 188°C, and injection temperature, 250°C. Flow rates for nitrogen were 60 mL/min, for hydrogen, 30 mL/min, at electrometer range 1 and attenuation 1, with chart speed at 305 mm (12 in.)/hL 1-mV full-scale response, and 1-µL sample for approximately 100-mg/L solutions of each phenolic. Peak A is for *o*-chlorophenol; B, phenol; C, *m*-cresol; D, 2,4-dichlorophenol; E, *p*-chlorophenol.

FIG. 3 Chromatographic Analysis of Phenolics in Aqueous Solution



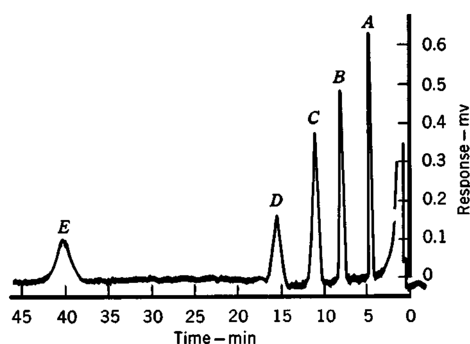
NOTE 1—Analyses were made with 3-m by 3-mm (10-ft by ⅛-in.) stainless steel column coated with 10 % FFAP on 60/80-mesh fluorocarbon resin medium. Column temperature was 188°C, and injection temperature, 250°C. Flow rates for nitrogen were 60 mL/min for hydrogen, 30 mL/min, at electrometer range 1 and attenuation 1, with chart speed at 12 in. (305 mm)/hL 1-mV full-scale response, and 1-µL sample of approximately 100-mg/L solutions of each phenolic. Peak A is for *o*-cresol; B, *p*-cresol; C, 2,6-dichlorophenol; D, 2,3-dichlorophenol; E, *m*-chlorophenol.

FIG. 4 Chromatographic Analysis of Phenolics in Aqueous Solution

12.2 Other methods of compound identification are by trapping the various sample components as they emerge from the system and analyzing them by mass, ultraviolet, or infrared spectroscopy, chemical analysis, etc.

12.3 To determine the retention time of phenol, cresols, mono- and dichlorophenols, the following procedure is recommended.

12.3.1 With the column at operating conditions, inject in turn a 1-µL sample of a 100-mg/L aqueous solution of the phenolic compound. Use a 10-µL syringe. Adjust the instrument attenuation so that the peak height is preferably to 50 % of full scale.



NOTE 1—Analyses were made with 1.5-m by 3-mm (5-ft by ⅛-in.) stainless steel column coated with 5 % FFAP on acid-washed 70/80-mesh diatomite. Column temperature was 147°C. Flow rates for helium were 35 mL/min, for hydrogen, 25 mL/min, at electrometer range 0.1 and attenuation 1, with chart speed 305 mm (12 in.)/hL 1-mV full-scale response; for 1-λ sample. Peak A is for *o*-chlorophenol; 10.4 mg/L; B, phenol, 9.3 mg/L; C, *m*-cresol; 10.7 mg/L; D, 2,4-dichlorophenol, 10.7 mg/L; E, *p*-chlorophenol, 11.2 mg/L.

FIG. 5 Chromatographic Analysis of Phenolics in Aqueous Solution

12.3.2 Mark the injection point on the recorder chart.

12.3.3 Measure the retention time in minutes to at least two significant figures.

12.3.4 To eliminate errors induced by ghosting, injections of water only are made after each phenolic sample. Electrometer range and attenuation should be set at maximum sensitivity during water washing. Inject the same volume of water as that used for the sample. Repeat water injections until a steady base line free of ghosts has been attained, after which the next sample injection may be made.

12.3.5 Make triplicate determinations for each phenolic compound and record the average retention value. Mixtures of phenols having different retention intervals may be injected simultaneously to expedite the standardizations.

NOTE 4—**Caution—**The injection syringe used for calibration should be flushed with water at least three times with each new sample before injecting into the chromatograph.

12.3.6 Calculate the retentions of all the phenolic compounds relative to phenol. The relative retention times with approximate chromatograph calibration factors are shown in Table 2 for two columns. These calibration values are presented only for information. The analyst must determine and regularly recheck calibration values for each column and phenolic material used.

13. Calibration and Standardization

13.1 Take the area under the peak of the chromatogram as a quantitative measure of the amount of the corresponding compound.

13.2 To make calibrations, select the phenolic concentration range desired, for example: 1 or 10 mg/L and prepare fresh solutions of each compound in Type II reagent water.

13.3 With the column at equilibrium operating conditions, inject measured volumes of the standard solutions using the previously described procedure and observing all precautions. Continue until at least three peaks are obtained which deviate by no more than ±1 % in area at the same attenuation. Three microlitres is a convenient sample size. Adjust the attenuation in all cases to keep the peak on-scale and preferably with a height of 50 % of full-scale recorder range.

13.4 Measure the peak area for each standard. This may be done by triangulation: however, accuracy will be improved by mechanical or electronic integration, or by weighing the peak cut-outs.

13.5 Prepared mixtures of the standards, depending on the phenolic compounds expected in the sample to be analyzed, may then be injected into the column.

13.6 Measure the peak areas as for the pure compounds. Express the results as nanograms per unit area.

13.7 Typical calibration factors are shown in Table 2. These must not be used in quantitative analysis and are presented only as a guide.

14. Procedure for a Sample

14.1 With the column at operating conditions, inject 1 to 3 μL of sample into the injection port.

TABLE 2 Chromatographic Phenolic Retention Time

Phenolic Compound	Boiling Point, °C	3-m by 3-mm (10-ft × ⅛-in.) SS, 20 % Carbowax 20 MM-TPA, 60/80 Chromosorb W-HMDS		3-m by 3-mm (10-ft × ⅛-in.) SS, 10 % FFAP, 60/80, Chromosorb T	
		Relative Retention	Calibration,[A,B] ng/in.^{2}	Relative Retention	Calibration,[A,C] ng/in.^{2}
Phenol	182	1.0	45.2	1.0	28.8
o-Cresol	192	1.0	51.0	1.0	27.0
m-Cresol	203	1.3	51.9	1.3	30.5
p-Cresol	202	1.3	51.3	1.3	31.3
o-Chlorophenol	176	0.8	86.7	0.6	44.8
m-Chlorophenol	214	3.6	106	3.6	45.4[B]
p-Chlorophenol	217	3.6	124	3.6	46.5[B]
2,3-Dichlorophenol	...	1.8	76.5	1.9	46.8
2,4-Dichlorophenol	210	1.8	117	1.9	55.3
2,5-Dichlorophenol	210	1.8	113	1.9	50.4
2,6-Dichlorophenol	220	1.6	71.5	1.5	50.0
3,4-Dichlorophenol	254	...	...	11.5	43.0[B]

[A] Calibration in nanograms (10^{-9}g) in.^{2}atchart speed 2286 mm (90 in.)/h, l mV response, range 1, attenuation 1.
[B] Column at 210°C.
[C] Column at 187°C, except as noted.

TABLE 3 Recovery for Reagent Water

Compound	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Phenol	120.3	117.8	17	10.6	−2.5	−2.0	No
	24.1	22.4	18	3.03	−1.7	−7.1	Yes
	7.2	7.7	18	0.85	+ 0.5	+ 6.9	Yes
p-Cresol	120.5	116.9	18	15.1	−3.6	−3.0	No
	24.1	23.1	18	2.54	−1.0	−4.1	No
	7.2	6.8	18	1.25	−0.4	−5.6	No
p-Chlorophenol	120.5	115.4	18	13.1	−6.1	−4.2	No
	24.1	23.8	18	2.26	−0.3	−1.2	No
	7.2	7.5	18	1.96	+ 0.3	+ 4.2	No
2,5-Dichlorophenol	112.6	106.0	18	20.7	−6.6	−5.9	No
	22.7	21.0	18	4.85	−1.7	−7.5	No
	6.7	6.1	18	2.12	−0.5	−8.9	No

14.2 Determine the retention times of the phenols in the sample.

14.3 If necessary, adjust the attenuation to keep the highest peak on-scale for the major phenolic component in the sample.

14.4 Perform triplicate determinations at identical column and instrument conditions; flush as required to eliminate artifacts.

14.5 Characterize and measure the peak areas obtained. Average the results of the triplicate determinations.

15. Calculation

15.1 Each peak area should be characterized by retention time. If supplementary tests such as infrared, ultraviolet, etc., are used in the characterization of trapped fractions, this should be reported.

15.2 For these peak areas representing two or more phenolic compounds, use an average value of the calibration obtained with the standard in the calculation; or measure the area as a given material with the notation in the results that other components have comparable elution intervals and may be represented.

15.3 Calculate each peak area as follows:

Phenolic compound(s), mg/L

$$= \frac{\text{sample area, in.}^2 \times \text{standard, ng/in.}^2 \times 10^{-6}\ \text{mg/ng}}{\text{sample used, } \mu L \times 10^{-6}\ \text{L}/\mu\text{L}}$$

16. Precision and Bias [12]

16.1 The precision of this test method was calculated for the analysis of three master solutions, each containing four phenolic compounds. The composition of the master solutions was as follows:

Phenolic Compounds	Master Solution (mg/L) 1	2	3
Phenol	120	24	7.2
p-Cresol	24	7.2	120
p-Chlorophenol	7.2	120	24
2,5-Dichlorophenol	113	23	6.7

Master solutions were prepared by addition of spiking solutions to both reagent water and to matrix water of the laboratories' choice. Replicate analyses were performed on each of three successive days.

16.2 Based on the results of six operators in six laboratories performing the replicate analyses on three successive days, the overall and single operator precison of this test method within the designated range of each phenolic compound may be expressed as follows:

Phenol	reagent water	$S_t = 0.11x + 0.15$
		$S_o = 0.05x + 0.36$
	selected water matrices	$S_t = 0.10x + 0.27$
		$S_o = 0.06x + 0.09$
p-Cresol	reagent water	$S_t = 0.13x - 0.03$
		$S_o = 0.02x + 0.70$
	selected water matrices	$S_t = 0.11x - 0.21$
		$S_o = 0.04x + 0.20$
p-Cholorphenol	reagent water	$S_t = 0.10x + 0.55$
		$S_o = 0.05x + 0.44$
	selected water matrices	$S_t = 0.07x + 1.26$
		$S_o = 0.04x + 0.40$
2,5–Dichlorophenol	reagent water	$S_t = 0.18x + 0.91$
		$S_o = 0.09x + 0.28$
	selected water matrices	$S_t = 0.06x + 1.49$
		$S_o = 0.02x + 0.67$

where:

S_t = overall precision,
S_o = single-operator precision, and
x = phenolic concentration, mg/L.

16.3 The overall and single-operator precision of this test method within its designated range varies with concentration.

16.4 Recoveries of known amounts of the following standard phenols spiked into reagent water and matrix water of the analyst's choice are listed in Table 3 and Table 4, respectively.

16.5 It should be recognized that these data may not apply to water matrices other than those tested.

17. Quality Assurance/Quality Control

17.1 Before this test method is applied to the analysis of samples of unknown phenol concentration, the analyst must establish quality control by the procedures recommended in Practice D 4210 and Guide D 3856.

17.2 A duplicate sample and known standard must be run each day that an analysis is performed. The duplicate and standard shall meet satisfactory limits as established by the control chart before a determination is considered satisfactory.

17.3 A blank and spike sample shall be run each day that an analysis is performed. The spike shall be in accordance with that outlined in 11.11 of Guide D 3856. The blank shall be low enough that it will not unduly influence the data.

17.4 One standard must be run with every 10 samples or

[12] Supporting data are available from ASTM Headquarters. Request RR: D-19-1093.

TABLE 4 Recovery for Matrix Water

Compound	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Phenol	120.3	119.6	15	12.7	−0.7	−0.6	No
	24.1	23.1	15	2.85	−1.0	−4.1	No
	7.2	7.3	15	0.94	+ 0.1	+ 1.4	No
p-Cresol	120.5	120.0	15	13.7	−0.5	−0.4	No
	24.1	24.4	15	1.90	+ 0.3	−1.2	No
	7.2	7.1	15	1.17	−0.1	−1.4	No
p-Chlorophenol	120.5	113.8	15	9.9	−6.7	−5.6	No
	24.1	24.4	15	2.75	+ 0.3	+ 1.2	No
	7.2	7.7	14	1.97	−0.1	−1.4	No
2,5-Dichlorophenol	112.6	116.9	15	8.4	+ 4.3	+ 3.8	No
	22.7	22.7	14	3.13	0	0	No
	6.7	6.7	14	1.69	0	0	No

with each batch, whichever results in the greater frequency. The results must meet the limits established in Section 16 of this test method before the data for that batch or set of 10 samples are acceptable.

17.5 Other QA/QC portions of this test method have not been completely established at this time. Analysts performing this test method will be required to measure their performance against the performance level achieved in the interlaboratory study of the test method.

17.6 It is the intention of Subcommittee D19.06 to incorporate formal QA/QC procedures into the test method at such time as they have passed the consensus process and have been officially accepted by the Society.

18. Keywords

18.1 chlorophenols; cresols; flame ionization; free fatty acid phase; gas chromatography; ghosts; internal standard; phenolic compounds

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL INFORMATION

X1.1 The information in Table X1.1 and Table X1.2 are presented to aid the analyst.

TABLE X1.1 Comparison of Phenolic Analytical Procedures[A]

Phenolic Compound	Concentration, mg/L		
	By Weight	4-Amino-Antipyrine [B]	GLC
Phenol	1.06	0.97	0.97
o-Cresol	1.04	0.64	1.03
m-Cresol	1.02	0.38	1.03
p-Cresol	1.00	0.00	1.00
Composite	4.12 [C]	2.40	3.94 [D] 4.11 [E]

[A] Baker, R.A., "Phenolic Analysis by Direct Aqueous Injection Gas Chromatography", *Journal American Water Works Association*, No. 6, 1966, pp. 751–760.

[B] Reported as phenol; Test Methods D 1783, Test for Phenolic Compounds in Water, average of two analyses.

[C] Composite of the four phenolics.

[D] Based on *m*- and *p*-cresol of 2.01 plus *o*-cresol and phenol as phenol of 1.93; average of four analyses.

[E] Based on *m*- and *p*-cresol of 2.01 plus *o*-cresol and phenol equal concentrations with calibration factors averaged.

TABLE X1.2 Effect of pH in GLC Analyses of 2,4-Dichlorophenol[A]

pH	4.5	7.7	9.7	10.8	11.7
Peak area, in ^{2}	2.88	2.90	2.90	2.93	1.08

[A] Column and opening conditions: column, 1.5 m by 3 mm (5 ft by ⅛ in.), stainless steel; 5 % FFAP, 60/80 Chromosorb W. Flow rates and temperature: hydrogen—25 mL/min; nitrogen—25 mL/min. Tc = 176 C; Ti = 205 C. R = 0.1 x, 1; 3 samples in distilled water; chart, 2286 mm (90 in.)/h, pH adjusted by NaOH; 1 mV full scale. Initial dichlorophenolic concentration = 5 mg/L.

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