Designation: D2580 – 06 (Reapproved 2012)

Standard Test Method for Phenols in Water by Gas-Liquid Chromatography[1]

This standard is issued under the fixed designation D2580; 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 D1783, 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:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1783 Test Methods for Phenolic Compounds in Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[4]
E260 Practice for Packed Column Gas Chromatography
E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions:*

3.1.1 Definitions and terms are presented in Practice E355 and Terminology D1129.

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

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

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

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

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

3.1.7 *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 E260.

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.

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and 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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

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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, *p*-chlorophenol, 2,6-dichlorophenol, and 2,4-dichlorophenol.[5]

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 D1783.

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.[6] 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*[7]—A 3-mm by 3-m (⅛-in. by 10-ft) stainless steel column packed with 60/80 mesh Chromosorb W[7,8] (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.

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.[9] 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 reagent water that meets the purity specifications of Type I or Type II water presented in Specification D1193.

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

[6] 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.

[7] The sole source of Carbowax known to the committee at this time is Union Carbide, P.O. Box 4393, Houston, TX 77210. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] The sole source of supply of Chromosorb known to the committee at this time is Johns Manville, P.O. Box 5108, Denver, CO 80217.

[9] *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.

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.

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 D3370.

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

TABLE 1 Typical Operating Conditions for Chromatographic Columns

Column and Packing	Column Number		
	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