



Designation: D 4961 – 99

Standard Test Methods for Gas Chromatographic Analysis of Major Organic Impurities in Phenol Produced by the Cumene Process¹

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1. Scope

1.1 These test methods cover the determination of major organic impurities in refined phenol manufactured by the cumene (isopropylbenzene) process. Two test methods are employed to determine the stated major impurities.

1.2 Test Method A determines the concentration of major impurities such as mesityl oxide, cumene, α -methylstyrene, 2-methylbenzofuran, acetophenone, and dimethylbenzyl alcohol.

1.3 Test Method B determines the hydroxyacetone content.

1.4 The following applies to all specified limits in this standard: for purposes of determining conformance with this standard, an observed value or a calculated value shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29E 29.

1.5 *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 Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid³

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals³

E 29 Practice for Using Significant Digits in Test Data to

Determine Conformance with Specifications⁴

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁵

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, see Terminology D 4790D 4790.

4. Summary of Test Methods

4.1 Two test methods are used to determine the major impurities in phenol:

4.1.1 *Test Method A, Major Impurity Determination*—A known amount of internal standard is added to the sample. A portion of the sample is analyzed by gas chromatography. The concentration of each impurity is calculated relative to the known amount of internal standard that is added.

4.1.2 *Test Method B, Hydroxyacetone Determination*—A measured amount of sample is analyzed by gas chromatography. The concentration of hydroxyacetone in the sample is determined by the ratio of the area of hydroxyacetone in the sample to the area in a standard sample containing a known amount of hydroxyacetone.

5. Significance and Use

5.1 This test method is useful in setting specifications for refined phenol manufactured by the cumene process and for process control. Test Method A is useful for individual impurities in the range from 10 to 100 mg/kg. Test Method B is useful for hydroxyacetone in the range from 5 to 500 mg/kg.

6. Purity of Reagents

6.1 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

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.04.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

Reagents of the American Chemical Society, where such specifications are available.⁵ 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193D 1193.

7. Hazards

7.1 Consult the current OSHA regulations⁶, supplier's Material Safety Data Sheets and local regulations for all materials used in these test methods.

7.2 The materials used in these test methods are highly toxic and flammable.

8. Sampling

8.1 Sample the material in accordance with Practice D 3852D 3852.

TEST METHOD A

9. Apparatus

9.1 *Chromatograph*, equipped with an on-column injector and flame ionization detector.

9.2 *Recorder*, with a full scale of 1 mV and a response time of 1 s or less.

9.3 *Integrating Device*—Any device capable of integrating chromatograph peak areas with a repeatability of $\pm 1\%$ relative.

9.4 *Chromatographic Column*, glass (2-mm inside diameter) or Nickel 200 (5.3-mm inside diameter by 3-m length). The column may be purchased or prepared as described in Section 11.

NOTE 1—**Caution:** Other nickel tubing may not be satisfactory because of the catalytic decomposition of compounds of interest that may occur in tubing other than Nickel 200.

10. Reagents and Materials

10.1 *Solid Support 100/120 Mesh*—Acid washed, dimethylchlorosilane (DMCS) treated diatomaceous earth.

10.2 *Stationary Phase*—A combination of 8 weight % acidified polyethylene glycol plus 4 weight % polyamide resin. A suitable solvent is 75 volume % methylene chloride plus 25 volume % toluene.

10.3 *Internal Standard*—Tetradecane.

10.4 *Pure Components for Calibration*—Mesityl oxide, cumene, α -methylstyrene, 2-methylbenzofuran, acetophenone, and dimethylbenzyl alcohol. The purity of each component should exceed 99 weight %.

10.5 *Phenol*—High purity phenol.

10.6 *Carrier Gas*—Helium or nitrogen.

⁵ *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 Pharmacopeial and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

11. Column Preparation

11.1 Either glass or nickel columns may be used. Glass columns are preferred because of their superior inertness. Nickel columns are preferred because of ease of handling. If nickel tubing is used, it must be cleaned with glacial acetic acid, followed by water rinsing.

11.1.1 Prepare the column packing as 12 weight % of the stationary mixed phase (see 10.2) to 88 weight % of the solid support. Dissolve the stationary phase in sufficient solvent so that the solution will cover the solid support completely in a flat, shallow, glass or porcelain vessel. Place the vessel in a ventilating hood and evaporate the solvent to a constant weight, with occasional gentle stirring. Add the free-flowing packing thus obtained to the column with the aid of a small funnel, and apply vacuum to draw the packing into place. Either tap or vibrate the column to ensure even distribution of the packing in the column. Place a glass-wool plug at the outlet end of the column before adding the packing, and one at the inlet end after the column is full. Do not pack the packing too tightly; evenly distribute it with no voids.

11.2 *Column Condition*—Install the column into the chromatograph and precondition it at the elevated temperature described in 11.2.1 through 11.2.4. Do not connect the column to the detector block until 11.2.2 has been completed.

11.2.1 Start the flow of helium or nitrogen carrier gas and allow the column to age for 30 min with no heat.

11.2.2 Increase the column temperature to 230°C at the rate of 2°C/min and hold that temperature for at least 24 h. Connect the column to the detector block after this step has been completed.

11.2.3 If a nickel column is used, reduce the temperature to 130°C and make fifteen 1- μ L injections of phenol.

11.2.4 Establish the conditions shown in Table 1 and make repetitive phenol injections until two or more injections exhibit the same peak configuration.

12. Preparation and Calibration of Standards

12.1 Use high purity phenol in preparing the calibration standards. Determine the residual impurities in the phenol by the procedure outlined in Section 13.

12.1.1 *Sample Preparation*—The sample must be handled in a molten state at $50 \pm 3^\circ\text{C}$. Higher temperatures will degrade the sample.

12.2 Prepare a calibration mixture of phenol containing mesityl oxide (MO), cumene (CU), α -methylstyrene (AMS), 2-methylbenzofuran (2MBF), acetophenone (AP), and dimethylbenzyl alcohol (DMBA). All the above impurity levels should be near the anticipated levels in the sample. If any

TABLE 1 Typical Conditions for Chromatographic Separation (Method A)

Column temperature, °C	180 isothermal
Injector temperature, °C	180
Detector temperature, °C	250
Carrier gas	nitrogen or helium
Gas flow rate, cm ³ /min	22
Hydrogen flow rate, cm ³ /min	30
Air flow rate, cm ³ /min	320
Specimen size, μ L	1

