Designation: D 4961 – 99

Standard Test Methods for Gas Chromatographic Analysis of Major Organic Impurities in Phenol Produced by the Cumene Process[1]

This standard is issued under the fixed designation D 4961; 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.

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 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 Water[2]

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid[3]

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals[3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[4]

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, see Terminology D 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 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 1193.

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[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and are the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

Current edition approved Jan. 10, 1999. Published March 1999. Originally published as D 4961 – 89. Last previous edition D 4961 – 93.

[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.

7. Hazards

7.1 Consult the current OSHA regulations[6], 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 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 ±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.

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-µL 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.

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, µL	1

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 ± 3°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 residual impurity elutes with a known impurity, deduct the residual area obtained in 12.1 (adjusted to sample size) from the area of the impurity.

12.3 *Standardization Procedure*—Determine the relative response factors (RRF) of each impurity by adding known quantities of impurities and internal standard. Prepare standards with impurity levels that bracket the dynamic range of

[6] *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.

interest. Use the procedure in Section 13 for standardization. Determine the relative response factor, *F*, as follows:

$$F = [W_c \times A_I/(A_c - A_b)] \times W_I \quad (1)$$

where:
W_c = weight of impurity, g,
W_I = weight of internal standard, g,
A_I = peak area of internal standard,
A_c = peak area of impurity in calibration blend, and
A_b = peak area of impurity in phenol base stock.

Set the system sensitivity so that all impurity peaks are recorded at adequate levels for data acquisition. Normally, the minimum peak height will be twice that of the baseline noise.

NOTE 2—Phenol produced by processes other than the cumene process may have impurities that elute with tetradecane. Before using this test method, investigate this by analyzing the phenol without the internal standard. If interference exists, use other internal standards such as durene or *sec*-butyl alcohol.

12.4 See Table 2 for typical response factors and retention times.

13. Procedure

13.1 See Table 1 for chromatographic conditions.

13.2 Add an appropriate amount of internal standard to molten phenol and mix thoroughly.

13.3 Using a preheated chromatographic syringe (approximately 75°C), inject 1 µL of molten phenol specimen. Phenol is not diluted with water as in Test Method B, because water may cause ghost peaks.

13.4 Allow approximately 45 min for all components to elute from the column.

13.5 When phenol elutes, raise the column oven temperature to 235°C. The column should remain at 235°C for approximately 1 h. Before another chromatograph run is attempted, stabilize the oven at 180°C for at least 10 min.

14. Calculation and Report

14.1 *Calculation*—Determine the concentration of each impurity using the following formula:

$$M_C = (F_C \times A_C \times M_I)/A_I \quad (2)$$

TABLE 2 Component Relative Response Factors and Retention Times

Impurity	Typical Relative Response Factor	Typical Retention Time, min
Mesityl oxide (MO)	1.5	4.8
Cumene (CU)	1.0	6.0
α-methylstyrene (AMS)	1.0	9.5
Tetradecane (internal standard)	1.0	15.1
2-methylbenzofuran (2MBF)	1.2	19.4
Acetophenone (AP)	1.1	21.6
Dimethylbenzyl alcohol (DMBA)	1.1	25.0
Phenol		36

where:
M_C = concentration of impurity C, mg/kg,
F_C = relative response factor for impurity C versus the internal standard,
A_C = area of impurity C,
M_I = concentration of internal standard, mg/kg, and
A_I = area of internal standard.

14.2 Report the concentration of each impurity to the nearest milligram per kilogram.

15. Component Relative Response Factors and Retention Times

15.1 See Fig. 1 for a typical chromatogram.

16. Precision and Bias

16.1 *Precision*:

16.1.1 *Intermediate Precision (formerly called Repeatability)*—Results in the same laboratory should not be considered suspect (95 % confidence level) unless they differ by more than the concentrations listed in Table 3.

16.1.2 *Reproducibility*—Results submitted by two laboratories should not be considered suspect (95 % confidence level) unless they differ by more than the concentrations listed in Table 3.

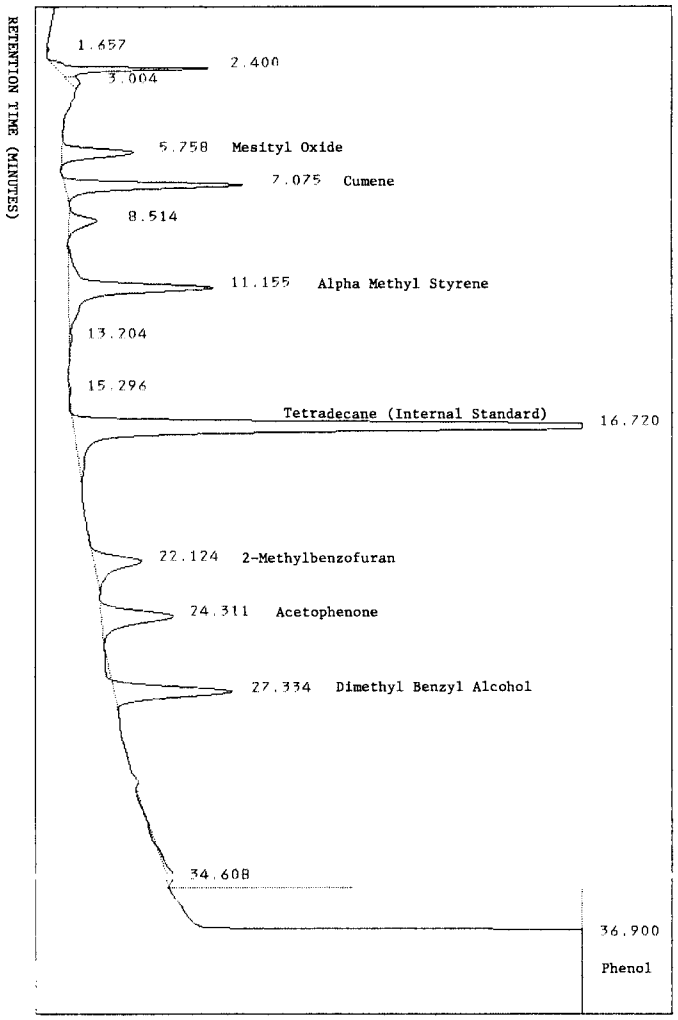

FIG. 1 Typical Chromatogram—Test Method A

TABLE 3 Repeatability and Reproducibility

Compound	Repeatability, mg/kg	Reproducibility, mg/kg
Mesityl oxide (MO)	15	36
Cumene (CU)	12	19
α-methylstyrene (AMS)	9	30
2-methylbenzofuran (2 MBF)	9	16
Acetophenone (AP)	8	21
Dimethylbenzyl alcohol (DMBA)	14	32

16.1.3 These values were determined by round-robin analyses conducted at approximately 50 and 100 mg/kg levels of mesityl oxide, cumene, α-methylstyrene, 2-methylbenzofuran, acetophenone, and dimethylbenzyl alcohol.

16.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has not been determined.

TEST METHOD B

17. Interferences

17.1 Hydroxyacetone will readily degrade; therefore, the following items are critical to the accuracy of this test method:

17.1.1 Column length of no greater than 0.61 m,

17.1.2 Injector temperature of 150 ± 2°C, and

17.1.3 On-column injector.

18. Apparatus

18.1 *Chromatograph*—See 9.1.

18.2 *Recorder*—See 9.2.

18.3 *Integrating Device*—See 9.3.

18.4 *Chromatograph Column*, glass, 2-mm inside diameter by 0.61-m length. Column lengths greater than 0.61 m should not be employed. Do not use metal columns.

18.5 *Syringe Adapter.*

19. Reagents and Materials

19.1 *Stationary Phase*—Porous polymer, 80 to 100 mesh.

19.2 *Acetol (Hydroxyacetone)*, 50 % purity. *Keep refrigerated*.

19.3 *Phenol*—High purity phenol containing less than 10 mg/kg of hydroxyacetone.

20. Preparation and Calibration of Standards

20.1 Add water to high purity phenol and make an aqueous solution of 90 weight % phenol and 10 weight % water. This solution will remain in the liquid state at room temperature.

20.2 Prepare standards that bracket the dynamic range of interest by adding hydroxyacetone to the 90 % aqueous phenol.

TABLE 4 Typical Conditions for Chromatographic Separation—Test Method B

Column temperature, °C	165
Injector temperature, °C	150 ± 2[A]
Detector temperature, °C	250
Carrier gas	nitrogen or helium
Carrier gas flow rate, cm^3/min	30
Hydrogen flow rate, cm^3/min	30
Air flow rate, cm^3/min	320
Specimen size, µL	1.0

[A] Critical.

Note that both the phenol and hydroxyacetone are aqueous solutions and must be corrected in the calculations.

20.3 Inject 1.0 µL (measured) of the standard hydroxyacetone solution and record the area generated by hydroxyacetone. Repeat this step at least two times or until repeated injections vary by no more than ±5 % relative. A syringe adapter may be used to enhance injection accuracy.

21. Procedure

21.1 See Table 4 for chromatograph conditions.

21.2 Add 1.0 g of water to 9.0 g of molten phenol.

21.3 Inject 1.0 µL (measured) of the specimen from 21.2 and record the area generated by the hydroxyacetone.

21.4 Wait until all the phenol has eluted from the column and the original baseline is established before the next injection.

22. Calculation

22.1 Determine the concentration of hydroxyacetone, using the following formula:

$$C_H = (A_s \times C_E)/A_E \quad (3)$$

where:

C_H = concentration of hydroxyacetone in the specimen, mg/kg,

A_s = area generated by the hydroxyacetone in the specimen,

C_E = concentration of hydroxyacetone in the external standard, mg/kg, and

A_E = area generated by the hydroxyacetone in the external standard.

22.2 A typical chromatogram is shown in Fig. 2.

23. Precision and Bias

23.1 *Precision*:

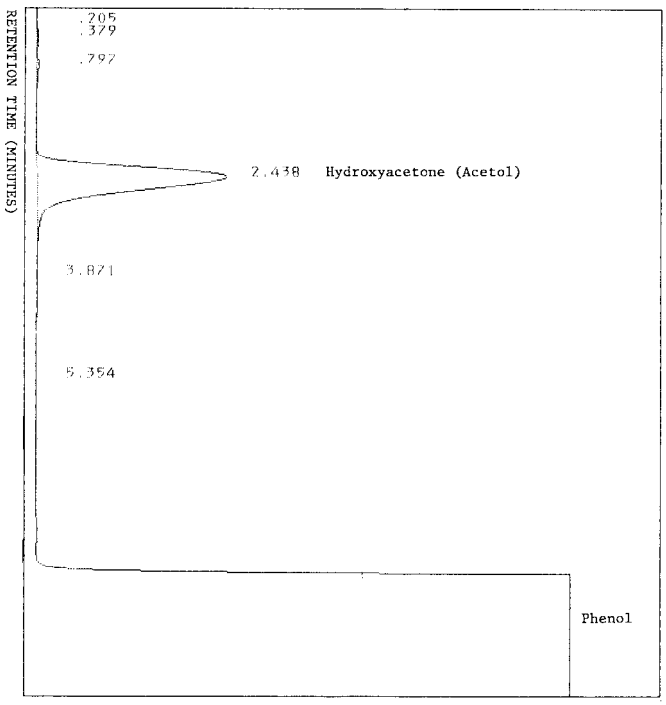

FIG. 2 Typical Chromatogram—Test Method B

23.1.1 *Intermediate Precision (formerly called Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than 30 % of the average value.

23.1.2 *Reproducibility*—Results submitted by 2 laboratories should not be considered suspect unless they differ by more than 34 % of the average concentrations.

23.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has not been determined.

24. Keywords

24.1 acetophenone; α–methylstyrene; cumene; dimethylbenzyl alcohol; hydroxyacetone; mesityl oxide; phenol; 2–methylbenzofuran