



Designation: **D 6142 – 9703**

Standard Test Method for Analysis of Phenol by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 6142; 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 This test method covers the determination of known impurities in phenol by gas chromatography (GC). It is generally meant for the analysis of phenol of 99.9 % or greater purity.

1.2 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or 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. Precision data is based on impurity concentrations of 15 to 70 mg/kg. Users of this test method believe it is linear over a wider range.

1.3 *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 9.

2. Referenced Documents

2.1 ASTM Standards:

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

Current edition approved June 10, 1997. Published August 1, 2003. Originally approved in 1997. Last previous edition approved in 1997 as D 6142 - 97.

*A Summary of Changes section appears at the end of this standard.

D 3852 Practice for Sampling and ~~h~~ Handling Phenol, Cresols, and Cresylic Acid²

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specific Specifications³

E 355 Practice for Gas Chromatography Terms and Relationships⁴

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs⁴

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁵

3. Terminology

3.1 See Terminology D 4790 for definition of terms used in this method.

4. Summary of Test Method

4.1 A known amount of an internal standard is added to a sample of phenol. The prepared sample is mixed and analyzed by a gas chromatograph equipped with a flame ionization detector (FID). The peak area of each impurity and the internal standard is measured. The amount of each impurity is calculated from the ratio of the peak area of the internal standard versus the peak area of the impurity. Results are reported in milligrams per kilogram.

5. Significance and Use

5.1 This test method is suitable for setting specifications on phenol and for use as an internal quality control tool where phenol is produced or is used in a manufacturing process. It may also be used in development or research work involving phenol. It is generally applied to determining those commonly occurring impurities such as mesityl oxide, cumene, hydroxyacetone, acetone, alpha-methylstyrene, 2-methylbenzofuran, acetophenone, o-cresol, and acetophenone, m & p-cresol.

5.2 Purity is commonly reported by subtracting the determined expected impurities from 100.00. However, a gas chromatographic analysis cannot determine absolute purity if unknown components are contained within the material being examined.

6. Interferences

6.1 The internal standard chosen must be sufficiently resolved from any impurity and the phenol peak.

6.2 Any solvent used must also be sufficiently resolved from any impurity, the internal standard, and the phenol peak.

7. Apparatus

7.1 *Gas Chromatograph*—Any chromatograph having a flame ionization detector that can be operated at the conditions given in Table 1. The system should have sufficient sensitivity to obtain a minimum peak height response for a 2-mg/kg impurity twice the height of the signal background noise.

7.2 *Columns*—Different columns have been found satisfactory, depending on the impurities of interest.

7.2.1 The column must give satisfactory resolution of the internal standard from phenol and the impurity peaks. Table 1 contains a description of ~~two~~ columns that has have been found to be satisfactory, polyethylene glycol-acid modified for all impurities except cresols, and 5 % phenyl-methylpolysiloxane for all impurity species.

7.3 *Recorder*—Electronic integration is recommended.

8. Reagents

8.1 *Purity of Reagent*—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.⁵⁷ 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.

8.2 *High Purity Phenol*, (99.99 % or greater purity).

8.3 *Carrier Gas*, chromatographic grade nitrogen or helium.

8.4 *Pure Compounds for Calibration*, shall include mesityl oxide, cumene, hydroxyacetone, acetone, alpha-methylstyrene, 2-methylbenzofuran, and acetophenone. The purity of all reagents should be 99.9 % or greater. If the purity is less than 99 %, the concentration and identification of impurities must be known so that the composition of the standard can be adjusted for the presence of the impurities.

² Annual Book of ASTM Standards, Vol 06.04.

³ Annual Book of ASTM Standards, Vol 14.02.

⁴ Available from the Superintendent

⁴ Annual Book of Documents, U.S. Government Printing Office, Washington, DC 20402; ASTM Standards, Vol 03.06.

Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing

⁵ Available from U.S. Government Printing Office Superintendent of reagents not listed by the American Chemical Society, see *Analar Standards for laboratory Chemicals*; BDH Ltd., Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD; Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

TABLE 1 Instrument Conditions for Phenol Analysis

<i>Column:</i>	To use for identification of all but cresols	To use for identification of all components
Tubing	<u>fused-silica</u>	
Tubing	fused silica	<u>fused silica</u>
Stationary phase	<u>polyethylene glycol-acid modified</u>	
Stationary phase	polyethylene glycol-acid modified	<u>(5 % Phenyl)-methylpolysiloxane</u>
Solid support	<u>crosslinked</u>	
Solid support	crosslinked	<u>bonded and crosslinked</u>
Film thickness, μ	0.5	
Film thickness, μ	0.5	<u>1.0</u>
Length, m	50	
Length, m	50	<u>60</u>
Inside diameter, m	0.32	
Inside diameter, m	0.32	<u>0.32</u>
Flow rate mL/min	1-3	
Flow rate mL/min	1.3	<u>1.3</u>
Temperature, °C		
—Injector	180	
—Injector	180	<u>200</u>
—Detector	230	
—Detector	230	<u>220</u>
Oven		
—Initial, °C	110 for 6 min	
—Initial, °C	110 for 6 min	<u>165 for 10 min</u>
—Rate, °C	12 per min	
—Rate, °C	12 per min	<u>10 per min</u>
—Final, °C	210 for 90 min	
—Final, °C	210 for 90 min	<u>250 for 90 min</u>
Internal Standard	<u>sec-butyl alcohol</u>	<u>sec</u>

8.4.1 *Internal Standard*— *sec*-Butylalcohol is one possible internal standard. However, other compounds may be found acceptable provided they meet the criteria as defined in Section 6 and 8.4.

9. Hazards

9.1 Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

10. Sampling

10.1 Refer to Practice D 3852 for proper sampling and handling of phenol analyzed by this test method.

11. Preparation of Apparatus

11.1 Follow manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table 1. Allow sufficient time for the equipment to reach equilibrium. See Practices E 355 and E 1510 for additional information on gas chromatography practices and terminology.

12. Calibration

12.1 Prepare synthetic mixtures of phenol with representative impurities on a weight basis. Weigh each impurity to the nearest 0.0001 g.

NOTE 1—Phenol will freeze at room temperature. The sample and syringe must be kept warm to prevent freezing. An alternative is to add about 10 % by weight of a solvent such as methanol that will not be an interference in the chromatogram.

12.2 Using the exact weight, or alternatively exact volumes and densities (see Table 2), calculate the mg/kg concentration for each impurity in each calibration blend of 12.1.

12.3 To a known weight of synthetic mixture, add a measured weight of *sec*-butyl alcohol as the internal standard. Calculate the concentration of internal standard in mg/kg (25 to 50 mg/kg is reasonable). Mix well.

12.4 Inject the resulting solution from 12.3 into the chromatograph. A typical chromatogram for each column is illustrated in Fig. 1 and Fig. 2.

12.5 Determine the response factor for each impurity relative to *sec*-butyl alcohol by measuring the area under each peak and calculate as follows:

¹ Supporting data are available from ASTM Headquarters. Request RR:D16-1021.

² *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., Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Densities of Compounds

Component	Density at 25°C (unless otherwise noted)
Phenol	1.072 (at 45°C)
Acetone	0.791
Mesityl oxide	0.853
Cumene	0.862
Hydroxyacetone	1.082
α-Methylstyrene	0.909
2-Methylbenzofuran	1.057
Acetophenone	1.026
sec-Butanol	0.808
<i>o</i> -Cresol	1.047
<i>m</i> & <i>p</i> -Cresol	1.034-1.039

$$R_i = A_s C_i / C_s A_i \quad (1)$$

where:

R_i = response factor for impurity i relative to the internal standard,

A_i = peak area of impurity i ,

A_s = peak area of the internal standard,

C_s = concentration of the internal standard, mg/kg, and

C_i = concentration of impurity i , as calculated in 12.3, mg/kg.

12.6 Calculate the response factors to the nearest 0.001.

13. Procedure

13.1 See 12.3 for the addition of the internal standard.

13.2 Depending upon the actual chromatograph's operating conditions, charge an appropriate amount of sample into the instrument.

13.3 Measure the area of all peaks except phenol. Measurements on the sample must be consistent with those made on the calibration blend. A poorly resolved peak will often require a tangent skim from the neighboring peak. Make consistent measurements on the sample and calibration chromatograms for tangents or poorly resolved peaks. A typical chromatogram is shown in Fig. 1.

14. Calculation

14.1 Calculate the concentration of each impurity as follows:

$$C_i = \frac{(A_i) (R_i) (C_s)}{(A_s)} \quad (2)$$

15. Report

15.1 Report the following information:

15.1.1 Individual impurities to the nearest 1 mg/kg, and

15.1.2 For concentrations of impurities less than 2 mg/kg, report as < 2 mg/kg and consider as 0 in summation of impurities.

16. Precision and Bias

16.1 *Precision*—The following criteria should be used to judge the acceptability at the 95 % probability level of the results obtained by this test method. The criteria were derived from an interlaboratory study between 7 laboratories. The data were obtained over 1 day using the same operators. Each laboratory received one standard for calibration purposes plus 2 samples with 2 levels of impurities. Except for the use of only 2 materials, Practice E 691 was followed for the design and analysis of the data^{7, 8}.

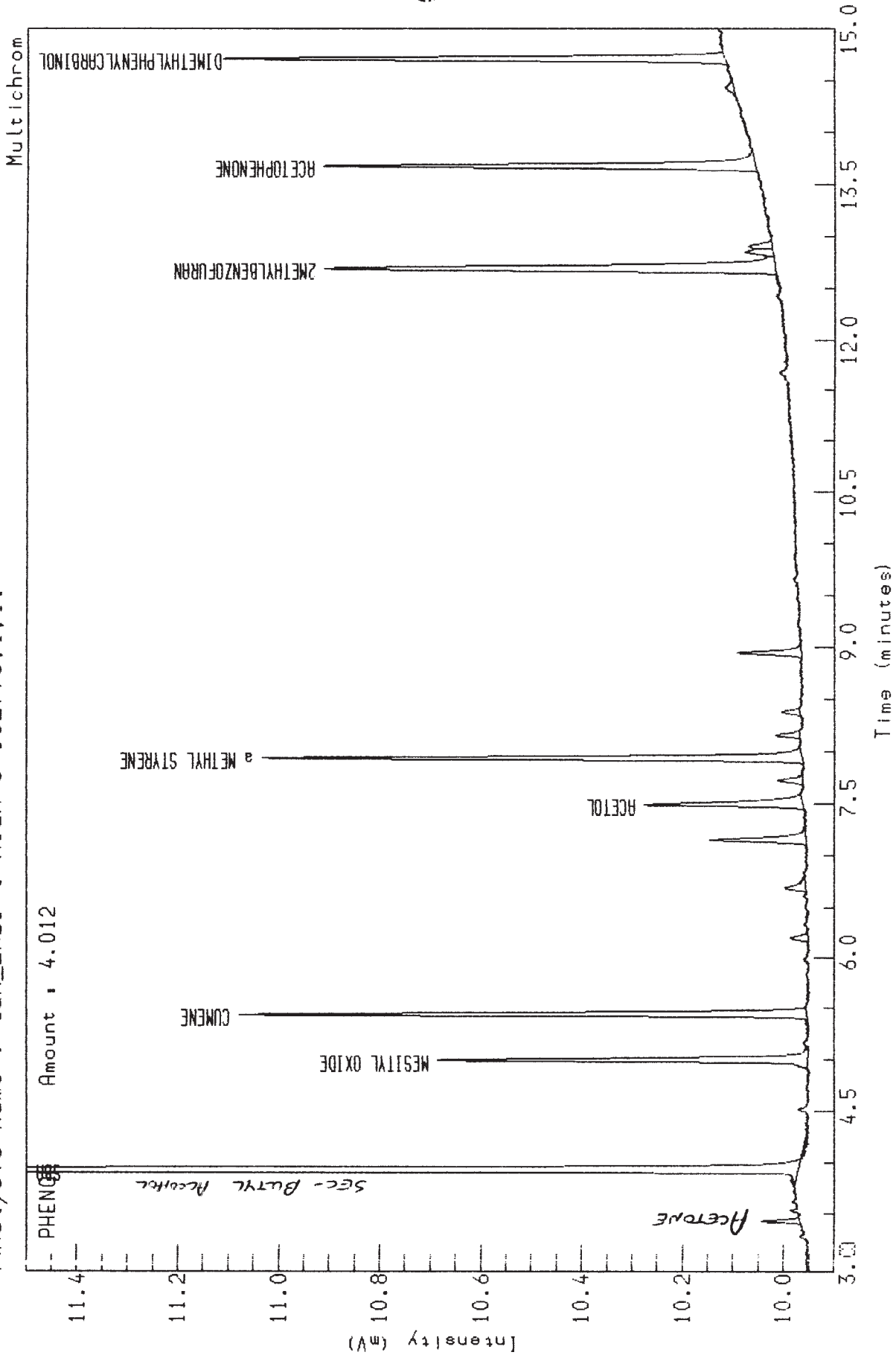
16.1.1 *Repeatability*—Results in the same laboratory should not be considered suspect unless they differ by more than the amount shown in Table 3-3, for the polyethylene glycol column, and Table 4 for the (5 %-Phenyl) methylpolysiloxane column.

16.1.2 *Reproducibility*—Results submitted by two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 3. Reproducibility from the (5 %-Phenyl) methylpolysiloxane column to be done at a later time with a round robin.

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

⁸ Supporting data are available from ASTM International Headquarters. Request RR:D16-1021.

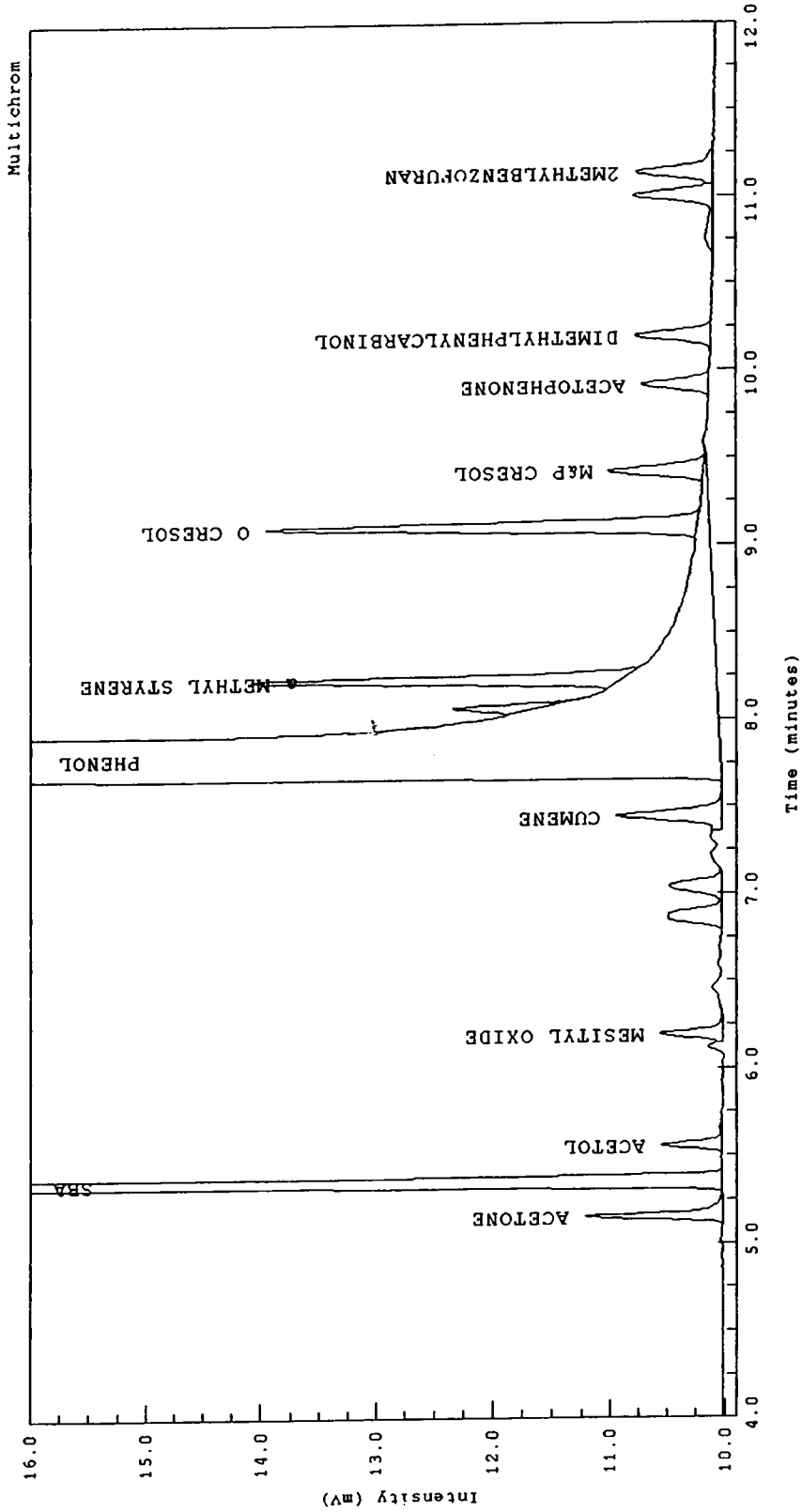
Analysis Name : [QA_LAB] 1 HIGH-5-052793.1,1.



Acquired on 27-MAY-1993 at 11.58 Reported on 27-MAY-1993 at 13.57

FIG. 1 Typical Phenol Chromatogram Polyethylene Glycol - Acid Modified Column, Phenol Method

Analysis Name : [PHENOL] 101 031003-STD,1,1.
 SAMPLE Amount : 4.000



Instrument : Method : PHENOL
 Channel Title : Channel #101 Calibration : ISPHENOL
 Lims ID : Run Sequence : PHENOL
 Acquired on 10-MAR-2003 at 07:37
 Reported on 20-MAR-2003 at 12:53

FIG. 2 Typical Phenol Chromatogram, (5 % Phenyl)-methylpolysiloxane Column, Phenol Method

TABLE 3 Repeatability and Reproducibility

Impurity	mg/kg	Repeatability	Reproducibility
Acetone	18	1.9	3.3
	73	3.7	10.3
Acetophenone	16	1.1	1.4
	70	3.2	18.9
α -Methylstyrene	20	1.5	4.3
	51	2.0	5.6
Cumene	17	4.0	4.0
	70	4.9	10.9
Hydroxyacetone	25	2.9	10.9
	70	4.0	6.3
Mesityl oxide	24	3.1	5.8
	77	5.3	16.4
2-Methylbenzofuran	17	1.9	4.9
	63	3.0	12.3

TABLE 4 Repeatability of Cresol Column

Impurity	mg/kg	Standard Deviation	Repeatability
Acetone	17.9	0.1	0.3
Acetophenone	7.1	0.2	0.5
α -Methylstyrene	33.5	2.2	6.2
Cumene	9.1	1.0	2.7
Hydroxyacetone	12.6	0.4	1.0
Mesityl oxide	5.8	0.2	0.6
2-Methylbenzofuran	9.9	0.6	1.6
<i>o</i> -Cresol	51.3	1.1	3.1
<i>m</i> & <i>p</i> -cresol	12.6	0.4	1.2

17. Keywords

17.1 2-methylbenzofuran; acetone; acetophenone; α -methylstyrene; cumene; gas chromatography; hydroxyacetone; mesityl oxide; 2-methylbenzofuran; phenol *m* & *p*-cresol; *o*-cresol; phenol; sec-butyl alcohol

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D 6142 - 97) that may impact the use of this standard.

- (1) A new column was added to Table 1 to identify cresols in phenol.
- (2) Table 1 includes the new column conditions.
- (3) The density of the cresols was included in Table 2.
- (4) A repeatability of the new column was included in Table 4.
- (5) Fig. 2, a chromatogram of the new column, was also included in the method.
- (6) A summary of changes was added to explain some of the changes and the purpose.

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