Designation: D 1685 – 05

Standard Test Method for Traces of Thiophene in Benzene by Spectrophotometry[1]

This standard is issued under the fixed designation D 1685; 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 thiophene in benzene in which the thiophene concentration is between 0.1 and 250 mg/kg.

1.2 Contaminating materials that are darkened by sulfuric acid interfere and must be compensated for by a sample blank determination. Neither carbon disulfide in concentrations as high as 100 mg/kg nor water as high as the level of saturation will interfere.

1.3 Contaminating materials may occasionally cause the color development in this test method to be time dependent and may also contribute to spectral interferences at 589 nm. Consequently, test results indicating substantial thiophene, that cannot be verified by total sulfur analysis, should be considered suspect.

1.4 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E 29.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 7.6, 8.1, and 9.1.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1193 Specification for Reagent Water

D 3437 Practice for Sampling and Handling Liquid Cyclic Products

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

D 6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

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

E 832 Specification for Laboratory Filter Papers

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definition of terms used in this test method see Terminology D 4790.

4. Summary of Test Method

4.1 Thiophene is reacted with isatin, under prescribed conditions, to form a colored compound. The compound is extracted into sulfuric acid, and the intensity of the color is measured spectrophotometrically. Thiophene concentration is obtained by correlation with knowns.

5. Significance and Use

5.1 This test method is suitable for setting specifications on benzene and for use as an internal quality control tool where benzene is either produced or used in a manufacturing process. It may also be used in development or research work involving benzene.

6. Apparatus

NOTE 1—Labware made from materials other than glass and is impervious to the materials used in this standard is allowed.

6.1 *Separatory Funnels*, 50, 250, 500, and 1000-mL, with stoppers.

6.2 *Spectrophotometer*—Any spectrophotometer may be used that is capable of repeatability of 0.005 absorbance units in the range from 0.1 to 1.4 absorbance and repeatability of wavelength of 1 nm in the region from 400 to 700 nm.

6.3 *Absorption Cells*, 1-cm, matched, glass or silica.

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[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 D16.01 on Benzene, Toluene, Xylene, Cyclohexane, and Their Derivatives.

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[2] 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.

[3] Available from U S. Government Printing Office Superintendent of Documents, 732 N Capitol St, NW, Mail Stop. SDE, Washington DC 20401.

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

6.4 *Analytical Balance*, capable of measuring 0.1 mg.

6.5 *Pipets*, 1, 2, 5, and 10-mL.

6.6 *Graduated Cylinders*, 250 and 1000-mL.

6.7 *Volumetric Flasks*, stoppered, 50, 100, 250, and 1000-mL.

6.8 *Filter Papers*:

6.8.1 Medium—Particle Retention: >11 μm; Porosity: Medium; Filtration Speed; Specification E 832, 40 seconds; Surface: Smooth.

6.8.2 Rapid hardened—Particle Retention: >20 to 25 μm; Porosity: Coarse; Filtration Speed: Specification E 832, 10 seconds; Surface: Smooth, hard.

7. Reagents [4]

7.1 *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.[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.

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

7.3 *Cadmium Chloride Solution (20 g/L)*—Dissolve 20 g of anhydrous cadmium chloride ($CdCl_2$) or 25 g of cadmium chloride hydrate ($CdCl_2 \cdot 2\frac{1}{2} H_2O$) in 200 mL of water and dilute to 1 L.

7.4 *Sulfuric Acid (sp gr 1.84)*—Concentrated H_2SO_4.

7.5 *Benzene, Thiophene-Free*:

7.5.1 Wash 700 mL of benzene in a 1000-mL separatory funnel with successive 100-mL portions of concentrated sulfuric acid (H_2SO_4) to which has been added 5 mL of isatin solution, until the H_2SO_4 layer is light yellow or colorless. Wash the benzene with 100 mL of water and then twice with 100 mL of cadmium chloride solution ($CdCl_2$). Finally, wash with another 100-mL portion of water. Filter the benzene through medium filter paper into a storage bottle and tightly stopper.

7.5.2 Prepare 1400 mL of thiophene-free benzene. Measure the absorbance of this material by the procedure outlined in 11.2 and 12.2. The absorbance should be no greater than 0.01.

7.6 *Ferric Sulfate, Sulfuric Acid Solution*—Add 0.2 g of ferric sulfate ($Fe_2(SO_4)_3 \cdot 9H_2O$) together with 38 mL of water to a 1-L volumetric flask. Swirl to dissolve. Cautiously add about 100 mL of H_2SO_4 and swirl. Allow time for the heat of reaction to subside and dilute to volume with H_2SO_4. (**Warning**—Appropriate personal protective equipment should be worn (for example, face shields, goggles, etc.) whenever concentrated sulfuric acid (H_2SO_4) is used.)

7.7 *Isatin, Chloroform, Benzene Solution*—Add 0.5 g of isatin to 200 mL of chloroform. Heat, in a fume hood, to a temperature just below the boiling point (61°C) of chloroform and maintain for 5 min with stirring. Filter into a 250-mL volumetric flask through hardened rapid filter paper. Wash the filter paper with two 20-mL portions of thiophene-free benzene (from 7.5) eluting the washings into the volumetric flask. Dilute to volume with thiophene-free benzene.

7.8 *Thiophene* — $\geq$99 %.

8. Hazards

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

9. Sampling

9.1 Sampling of benzene should follow safe rules in order to adhere to all safety precautions as outlined in the latest OSHA regulations. Refer to Practice D 3437 for proper sampling and handling of benzene.

10. Preparation of Reagent Blanks and Sample Blank [4]

10.1 *Reagent Blank 1*—To a 50-mL separatory funnel pipet 5 mL of isatin solution and 10 mL of ferric sulfate-sulfuric acid solution. Stopper and shake for 2 min ± 15 s. The shaking is accomplished by wrist action in a rocking motion through a 180° arc roughly once each second. Allow the two phases to separate and draw off the lower H_2SO_4 layer into a 50-mL volumetric flask. Add 10 mL of H_2SO_4 to the separatory funnel, stopper, and shake for 30 ± 5 s. Again draw off the lower H_2SO_4 layer into the 50-mL volumetric flask containing the first extract. Dilute to volume with H_2SO_4 and mix. This blank is stable for 8 h and need not be repeated with each analysis during this period.

10.2 *Reagent Blank 2*—Into a 50-mL volumetric flask, pipet 10 mL of ferric sulfate-sulfuric acid solution and dilute to volume with H_2SO_4. Stopper and mix. This blank is stable for 8 h and need not be repeated with each analysis during this period.

10.3 *Sample Blank*—Take a 100-mL portion of the $CdCl_2$ washed and filtered benzene sample (prepared in accordance with the procedure in 12.1). Transfer to a 250-mL separatory funnel. Add 10 mL of ferric sulfate-sulfuric acid solution, stopper, and shake for 2 min ± 15 s. Allow the two phases to separate and draw off the lower H_2SO_4 layer into a 50-mL volumetric flask. Add 10 mL of H_2SO_4 to the separatory funnel and shake for 30 ± 5 s. Again draw off the lower H_2SO_4 layer into the 50-mL volumetric flask containing the first extract. Dilute to volume and mix. Repeat with each specimen.

11. Preparation of Calibration Curves [4]

NOTE 2—The use of purchased solutions is allowed. The user of this standard assumes the responsibility of ensuring solutions or standards are prepared with materials that meet the requirements expressed in the Reagents section of this standard. Additionally, the user of this standard assumes the responsibility of ensuring any purchased solutions or standards are prepared as expressed in this standard.

11.1 Add approximately 0.2 g of thiophene, weighed to the nearest 0.0002 g to a 100-mL volumetric flask containing about

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[4] Alternate volumes of solutions may be prepared providing the specified concentrations are met and there is adequate volume to accurately perform the test.

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

TABLE 1 Calculation Factors

Designation of Equation of Section 12	Cell Solutions		
	Solution of Sample	Versus	Solution of Reference
A	$H_2SO_4 \cdot Fe_2(SO_4)_3$; isatin after contact with sample, (see 12.2)		reagent blank 1 (see 10.1)
B	sample blank (see 10.3)		reagent blank 2 (see 10.2)

50 mL of thiophene-free benzene. Dilute to volume with thiophene-free benzene and mix. This is Solution 1. Pipet 1 mL of Solution 1 into a 100-mL volumetric flask, dilute to volume with thiophene-free benzene, stopper, and mix. This is Solution 2 and will contain approximately 20 μg of thiophene per millilitre.

11.2 Pipet 0, 1, 2, 5, 7, and 10-mL of Solution 2 into 100-mL volumetric flasks and dilute to volume with thiophene-free benzene. Transfer to 500-mL separatory funnels and follow the procedure in 12.2 and 12.3 for each concentration. Plot absorbance versus concentration in micrograms per millilitre.

NOTE 3—The 7 mL of Solution 2 may be transferred using the 2 and 5 mL pippettes.

11.3 Prepare Solution 3 containing approximately 40 μg of thiophene per millilitre by pipetting 2 mL of Solution 1 into a 100-mL volumetric flask and diluting to volume with thiophene-free benzene. Follow the procedure in 11.2 to obtain the calibration curve for 50-mL specimens.

12. Procedure

12.1 To a 500-mL separatory funnel, add 250 mL of sample and 40 mL of cadmium chloride solution. Stopper and shake for approximately 30 s. Allow to settle and discard the aqueous layer. Filter the benzene layer through medium filter paper into a 250-mL graduated cylinder. Part of the filtered benzene is to be used for the sample blank. Proceed with preparation of the sample blank as described in 10.3. From the remaining filtered benzene, transfer 100 mL to 250-mL separatory funnel.

12.2 To the separatory funnel add 5 mL of isatin solution and 10 mL of ferric sulfate-sulfuric acid solution. Stopper and shake for 2 min ± 15 s. Allow the phases to separate and draw off the lower H_2SO_4 layer into a 50-mL volumetric flask. Add 10 mL of H_2SO_4 to the separatory funnel, stopper, and shake for 30± 5 s. Again draw off the lower H_2SO_4 layer into the 50-mL volumetric flask containing the first extract. Dilute to volume with H_2SO_4 and mix.

12.3 Measure the absorbance of this material at 589 nm in a 1-cm cell versus Reagent Blank 1 (10.1) in a matched 1-cm cell. Instrument conditions should be identical with those employed during calibration.

12.4 Determine the concentration of thiophene from the calibration curve (Section 11). If the absorbance is greater than 1.6, repeat the procedure using a 50-mL specimen instead of 100 mL. If the 50-mL specimen still gives absorbance above 1.6, then the specimen must be diluted with thiophene-free benzene before proceeding.

12.5 Determine the absorbance of the sample blank (10.3) at 589 nm using Reagent Blank 2 (10.2) as reference. Determine the apparent concentration of thiophene in the sample blank.

13. Calculation

13.1 Calculate the thiophene content of the sample in milligrams per kilogram as follows:

$$\text{Thiophene, mg/kg} = (A - B)F/d$$

where:

A = thiophene for sample determined from appropriate calibration curve (see Table 1), μg/mL,
B = apparent thiophene determined for sample blank from appropriate calibration curve (see Table 1), μg/mL,
F = dilution factor of sample, and
d = density of benzene at the temperature of the sample.

14. Precision and Bias

14.1 The data given in Table 2 should be used for judging the acceptability of results (95 % probability).

NOTE 4—The precision limits given in Table 2 are based on data published as Appendix III to Report of Committee D16, ASTM *Proceedings*, Am. Soc. Testing Mats., Vol 59, 1959, p. 514.

14.2 Repeatability is based on test results obtained by repetitive testing of a homogeneous sample by a single operator. Reproducibility is based on test results obtained by repetitive testing of different samples in different laboratories and different operators.

14.3 *Bias*—The bias of this test method has not been determined.

TABLE 2 Precision Limits

Thiophene Concentration, Range, mg/kg	Repeatability, Percent of Value	Reproducibility, Percent of Value
100 to 250	11.4	15
20 to 100	12.3	19
2 to 20	13.8	21
0 4 to 2	14.0	25
less than 0 4	less than 0 06 mg/kg	less than 0.15 mg/kg

15. Quality Guidelines

15.1 Refer to Guide D 6809 for suggested QA/QC activities that can be used as part of this method. It is recommended that the operator of this method select and perform relevant QA/QC activities like the ones in Guide D 6809 to help ensure the quality of data generated by this method.

16. Keywords

16.1 benzene; spectrophotometry; thiophene

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D 1685 – 00) that may impact the use of this standard.

(1) 1.4 – Replaced with language from Editorial Guidelines.
(2) Section 6 – Note 1 added to allow use of labware other than glass. Specifications added to Balance and Filter Papers.
(3) Section 7 – Precaution statement rephrased and renamed Warning statement and moved into text.
(4) Section 11 – Note 2 added allowing use of purchased solutions.
(5) Section 15 – Quality Guidelines section added.
(6) Added Footnote 4 allowing use of Alternate Volumes.

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