Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography[1]

This standard is issued under the fixed designation D 4735; 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 refined benzene in the range from 0.5 mg/kg to 5.0 mg/kg. The range of the test method may be extended by modifying the sample injection volume, split ratios, calibration range, or sample dilution with thiophene-free solvent.

1.2 This test method has been found applicable to benzene characteristic of the type described in Specifications D 2359 and D 4734 and may be applicable to other types or grades of benzene only after the user has demonstrated that the procedure can completely resolve thiophene from the other organic contaminants contained in the sample.

1.3 The following applies to all specified limits in this test method: for purposes of determining conformance to applicable specification using this test method, 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.

1.4 *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 1685 Test Method for Traces of Thiophene in Benzene by Spectrophotometry[3]
D 2359 Specification for Refined Benzene-535[3]
D 3437 Practice for Sampling and Handling Liquid Cyclic Products[3]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]
D 4307 Practice for the Preparation of Liquid Blends for Use as Analytical Standards[4]
D 4734 Specification for Refined Benzene 545[3]
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]
E 260 Practice for Packed Column Gas Chromatography[5]
E 355 Practice for Gas Chromatography Terms and Relationships[6]
E 840 Practice for Using Flame Photometric Detectors in Gas Chromatography[5]
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[6]

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200[7]

3. Summary of Test Method

3.1 The thiophene concentration in refined benzene is determined at the milligram thiophene per kilogram sample level using conventional gas-liquid chromatography with a flame photometric detector (FPD) or pulsed flame photometric detector (PFPD). A reproducible volume of sample is injected. Quantitative results are obtained by the external standard technique using the measured peak area of thiophene.

4. Significance and Use

4.1 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.

4.2 This test method was found applicable for determining thiophene in refined benzene conforming to the specifications described in Specification D 2359 and may be applicable toward other grades of benzene if the user has taken the necessary precautions as described in the text.

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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 D16.04 on Instrumental Analysis.

Current edition approved July 10, 2002. Published September 2002. Originally published as D 4735 – 87. Last previous edition D 4735 – 96 (2000).

[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 05.02.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

[6] *Annual Book of ASTM Standards*, Vol 03.06.

[7] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

4.3 This test method was developed as an alternative technique to Test Method D 1685.

5. Apparatus

5.1 *Gas Chromatograph*—Any chromatograph having a flame photometric detector (FPD or PFPD) may be used which can operate at the typical conditions described in Table 1. The user is referred to Practices E 260 and E 355 for additional information about gas chromatography principles and procedures. An automatic sampler is recommended. The GC should have the following performance characteristics:

5.1.1 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation over a range sufficient for the separation of the compounds of interest. The programming shall be sufficiently reproducible to obtain retention time repeatability throughout the scope of the analysis.

5.1.2 *Sample Inlet System*—The sample inlet system shall have variable temperature control capable of operating continuously at a temperature up to the maximum column temperature employed. The sample inlet system shall allow a constant volume of sample to be injected by means of a syringe. For the PFPD a heated flash vaporizing injector designed to provide a linear sample split injection (that is, 50:1) is required for proper sample introduction. The associated carrier gas flow controls shall be of sufficient precision to provide reproducible column flows and split ratios in order to maintain analytical integrity.

5.2 *Column*—The column shall provide complete resolution of thiophene from benzene and any other hydrocarbon impurities because of potential quenching effects by hydrocarbons on the light emissions from the thiophene. The columns described in Table 1 have been judged satisfactory. The user is referred to Practice E 1510 for assistance on installing fused silica capillary columns into the gas chromatograph.

5.3 *Detector*—Any flame photometric detector (FPD or PFPD) can be used, provided it has sufficient sensitivity to produce a minimum peak height twice that of the base noise for a 4-µL injection on the FPD, or a 1.0-µL injection for the PFPD of 0.5 mg/kg thiophene in benzene. The user is referred to Practice E 840 for assistance in optimizing the operation and performance of the FPD.

5.4 *Data Acquisition System*—The use of an electronic integrating device or computer data system is recommended for determining the detector response. The device and software shall have the following capabilities: a) graphic presentation of the chromatogram, b) digital display of chromatographic peak areas, c) identification of peaks by retention time or relative retention time, or both, d) calculation and use of response factors, and e) internal standardization, external standardization, and data presentation.

5.5 *Microsyringe*, 5 or 10-µL capacity.

5.6 *Volumetric Flasks*, 50, 100 and 500-mL capacity.

5.7 *Separatory Funnel*, 1-L capacity.

6. Reagents and Materials

6.1 *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.[8] 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.

TABLE 1 Thiophene in Benzene Instrumental Conditions

Column	A	B	C	D
Tubing	6 ft 3⅛ in. Ni	15 ft by ⅛ in. stainless steel	10 ft by ⅛ in. stainless steel	30 meter, Fused Silica, 0.25 (or 0.32) mm ID
Phase	TCEEP[A]	SP-1000	OV-351	Bonded Polyethylene Glycol (PEG/CW)
Concentration, weight %	7	10	10	0.5 (or 1.0) micron film thickness
Support	Chromosorb P-AW[B]	Supelcoport	Chromosorb P-AW	N/A
Mesh	100/120	60/80	80/100	N/A
Gas chromatographic conditions				
Inlet	150	170	180	200
Carrier Gas	helium	helium	helium	helium
Carrier Flow, mL/min	30	30	30	1.0–1.5
Split Ratio	N/A	N/A	N/A	50:1
Column Temperature, °C	70	90	70	50°C for 1 mi., 10°C/min to 200°C, hold for 1 min
Detector (optimize flows per manufacturer's instructions)	FPD	FPD	FPD	PFPD (tuned for Sulfur) BG-12 Filter 2 mm combustor
H_2, mL/min	140	140	140	11.5 flow optimized for S mode
Air I, mL/min	80	80	80	12.0 flow optimized for S mode
Air 2, mL/min	70	70	70	10.0 flow optimized for S mode
Temperature (°C)	220	220	250	250

[A] Tetracyanoethylated pentaerythritol or pentrile.

[B] Chromosorb P is a registered trademark of the Manville Corp.

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[8] *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.

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

6.3 *Carrier Gas*, nitrogen, helium, or hydrogen, chromatographic grade, or shall have a purity of 99.999 % (V/V) or better.

6.4 *Hydrogen*, zero grade, or shall have a purity of 99.999 % (V/V) or better. (**Warning—**Hydrogen is an extremely flammable gas under high pressure.)

6.5 *Compressed Air*, hydrocarbon-free, or shall have a purity of 99.999 % (V/V) or better. (**Warning—**Compressed air and oxygen are gases under high pressure and they support combustion.)

6.6 *Cadmium Chloride Solution* (20 g/L)—Dissolve 20 g of anhydrous cadmium chloride $CdCl_2$ into 200 mL of water and dilute to 1 L.

6.7 *Isatin Solution*—Add 0.5 g of isatin to 200 mL of chloroform. Heat under a fume hood to a temperature just below the boiling point of chloroform (61°C) and maintain for 5 min with stirring. Filter the hot solution through hardened rapid-filter paper into a 250-mL volumetric flask and dilute to volume.

6.8 *Benzene, Thiophene-Free*—Wash 700 mL of benzene in a 1000-mL separatory funnel to which has been added 5 mL of isatin solution, with successive 100-mL portions of concentrated sulfuric acid until the H_2SO_4 layer is light yellow or colorless. Wash the benzene with 100 mL of water, then twice with 100 mL of cadmium chloride solution ($CdCl_2$). Finally, wash with another 100-mL portion of water and filter the benzene through medium filter paper into a storage bottle, stopper the bottle tightly and save for future use. Commercial sources of thiophene-free benzene are available and can be used as an alternative to this cleanup procedure.

6.9 *Sulfuric Acid*—Concentrated H_2SO_4.

6.10 *Thiophene*.

6.11 Stock solutions of thiophene in benzene are commercially available and can be used for preparation of calibration standards.

7. Hazards

7.1 Benzene is considered a hazardous material. Consult current OSHA regulations and supplier's Material Safety Data Sheets, and local regulations for all materials used in this method.

8. Sampling and Handling

8.1 Sampling of benzene should follow safe rules in order to adhere to all safety precautions as outlined in the latest OSHA regulations. Refer to Practices D 3437, D 4057, and D 4177 for proper sampling and handling of benzene.

9. Preparation of the Apparatus

9.1 The chromatographic separation of trace level sulfur compounds can be complicated by absorption of the sulfur compounds by the gas chromatographic system. Therefore, care should be taken to properly free the system of active sites where absorption or reactions could take place.

9.2 Follow the manufacturer's instructions for mounting and conditioning the column into the gas chromatograph and adjusting the instrument to conditions described in Table 1. Allow the instrument and detector sufficient time to reach equilibrium.

10. Calibration Curve

10.1 Prepare a 500-mL stock solution of thiophene in benzene at approximately the 100 mg/kg level by adding 0.04 g (38.0 µL) of thiophene to 435 g (500 mL) of thiophene-free benzene.

10.2 Calculate the thiophene content of the stock solution according to the following equation:

$$\text{Thiophene, mg/kg} = (A \times 10^3)/B$$

where:

A = weight of thiophene, mg, and

B = weight of benzene, g.

10.3 Prepare five calibration blends ranging from 0.00 to 5.0 mg/kg of thiophene in benzene by diluting the appropriate

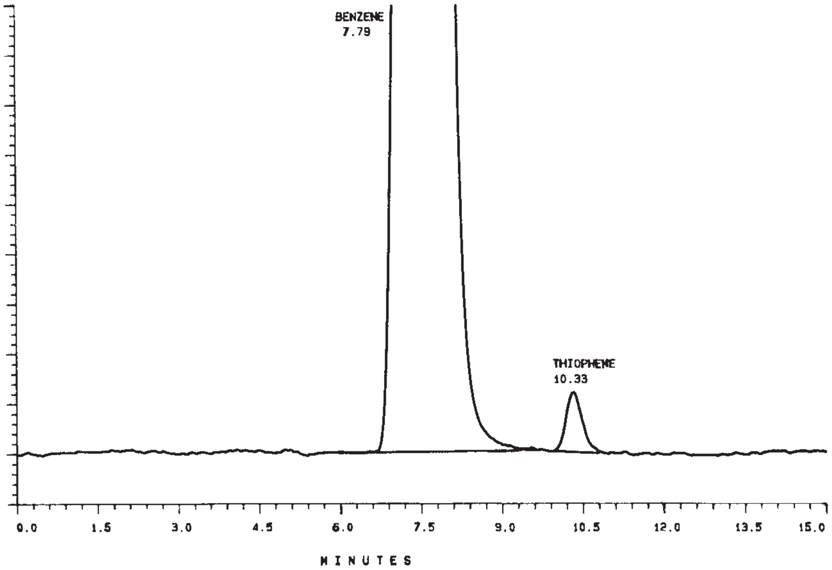

FIG. 1 Chromatogram Illustrating the Analysis of 1.10 mg/kg Thiophene in Benzene on an FPD

volume of stock solution into a known volume of thiophene-free benzene. The user is referred to Practice D 4307 for assistance preparation of liquid blends for use as analytical standards.

10.4 For example, an 87.0 mg/kg stock solution was prepared by dissolving 0.0378 g thiophene into 435 g of benzene. Aliquots of 0.00, 0.75, 1.0, 2.0, and 5.0 mL of stock solution were dissolved in 100 mL of thiophene-free benzene to produce 0.00, 0.65, 0.87, 1.75, and 4.35 mg/kg, respectively.

10.5 Inject an appropriate amount of each solution (4.0-µL for packed column or 1.0-µL for capillary column) into the gas chromatograph. Integrate the area under the thiophene peak. Each standard solution and the blank should be analyzed in triplicate. Injection volumes shall be consistent and reproducible.

10.6 Prepare a calibration curve by plotting the integrated peak area versus milligram per kilogram of thiophene.

Note 1—In the sulfur mode, the FPD will exhibit a response that is a nonlinear power law function. Please refer to Practice E 840 for additional information on the characteristics and usage of the FPD. A data system that can produce a quadratic curve fit for the calibration range can be utilized for quantification. The PFPD (and some FPD's) can produce a signal representing the square root of the detector response. This can result in a linearized output and a linear calibration curve which can also be used for quantitation.

11. Procedure

11.1 Inject an appropriate amount of each sample into the gas chromatograph (4.0-µL for packed columns and 1.0-µL for capillary columns).

11.2 Measure the area of the thiophene peak. The measurement of the sample peak should be consistent with the method for measuring peak areas in the calibration standards. A typical chromatogram is shown in Fig. 1 representing 1.10 mg/kg thiophene in benzene on the FPD. A typical chromatogram is shown in Fig. 2 representing 3.0 mg/kg thiophene in benzene using the capillary column and PFPD. A typical chromatogram is shown in Fig. 3 representing 0.5 mg/kg thiophene in benzene using the capillary column and PFPD.

12. Calculation

12.1 Determine the amount of thiophene directly from the calibration curve prepared in 10.6 or from the data processor results.

13. Report

13.1 Report the thiophene concentration to the nearest 0.01 mg/kg.

14. Precision and Bias

14.1 *Precision*:

14.1.1 The following criteria should be used to judge the acceptability of the 95 % probability level of the results obtained by this test method. The criteria were derived from a round robin between five laboratories. The data were obtained over 2 days using different operators. Data verifying performance of the PFPD capillary column method was shown to fall within the precision of the original round robin (single laboratory results) as shown in Table 2.

14.1.2 *Intermediate Precision (formerly called Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than the amount shown in Table 3.

14.1.3 *Reproducibility*—The results submitted by two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 3.

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

15. Keywords

15.1 benzene; capillary column; flame photometric detector; gas chromatography; pulsed flame photometric detector; split/splitless injector; thiophene

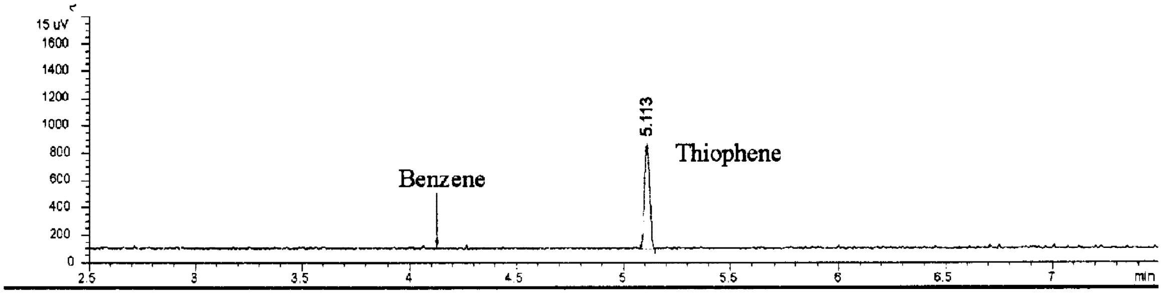

FIG. 2 Chromatogram Illustrating the Analysis of 3.00 mg/kg Thiophene in Benzene Using a Capillary Column and PFPD

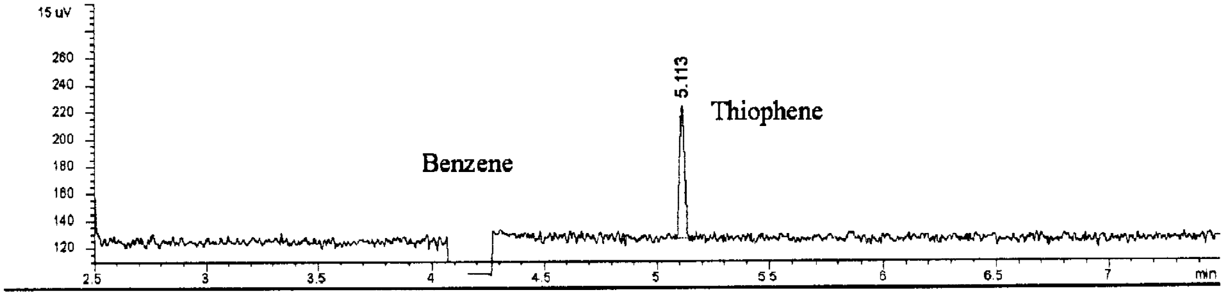

FIG. 3 Chromatogram Illustrating the Analysis of 0.50 mg/kg Thiophene in Benzene Using a Capillary Column and PFPD

TABLE 2 Intermediate Precision for the PFPD

Thiophene Concentration, mg/kg	Intermediate Precision, mg/kg
0.50	0.010
1.00	0.010
3.00	0.023
5.00	0.031

TABLE 3 Intermediate Precision and Reproducibility for the FPD

Thiophene Concentration, mg/kg	Intermediate Precision, mg/kg	Reproducibility, mg/kg
0.80	0.040	0.060
1.80	0.078	0.078

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