Designation: D4735 – 02

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

This standard is issued under the fixed designation D4735; 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 D2359 and D4734 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 E29.

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:* [2]

D1193 Specification for Reagent Water [3]

D1685 Test Method for Traces of Thiophene in Benzene by Spectrophotometry [3]

D2359 Specification for Refined Benzene-535 [3]

D3437 Practice for Sampling and Handling Liquid Cyclic Products [4]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products [4]

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products [4]

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards [3]

D4734 Specification for Refined Benzene-545 [5]

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications [5]

E260 Practice for Packed Column Gas Chromatography [6]

E355 Practice for Gas Chromatography Terms and Relationships [5]

E840 Practice for Using Flame Photometric Detectors in Gas Chromatography [6]

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

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 D2359 and may be applicable toward other grades of benzene if the user has taken the necessary precautions as described in the text.

[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.

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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 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 D1685.

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 E260 and E355 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 E1510 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 E840 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,

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.