



Designation: D4735 – 19

Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography¹

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1. Scope*

1.1 This test method covers the determination of thiophene in refined benzene in the range from 0.80 to 1.80 mg/kg for the Flame Photometric Detector (FPD), and from 0.14 to 2.61 mg/kg for the Pulsed Flame Photometric Detector (PFPD). For the PFPD, the minimum level of quantitation (LOQ) is 0.14 mg/kg and the minimum level of detection (LOD) is 0.04 mg/kg, as described in ASTM Research Report RR:D16-1038.² 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 The values stated in SI units are to be regarded as standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section [7](#).

¹ This test method is under the jurisdiction of ASTM Committee [D16](#) on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee [D16.04](#) on Instrumental Analysis.

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² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1038. Contact ASTM Customer Service at service@astm.org.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:³

- [D1193](#) Specification for Reagent Water
- [D2359](#) Specification for Refined Benzene-535
- [D3437](#) Practice for Sampling and Handling Liquid Cyclic Products
- [D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products
- [D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products
- [D4307](#) Practice for Preparation of Liquid Blends for Use as Analytical Standards
- [D4734](#) Specification for Refined Benzene-545
- [D6809](#) Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
- [E29](#) Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- [E177](#) Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- [E260](#) Practice for Packed Column Gas Chromatography
- [E355](#) Practice for Gas Chromatography Terms and Relationships
- [E691](#) Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- [E840](#) Practice for Using Flame Photometric Detectors in Gas Chromatography
- [E1510](#) Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

³ 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.

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

TABLE 1 Thiophene in Benzene Instrumental Conditions

| Column | A | B | C | D |
|---|------------------------------|----------------------------------|----------------------------------|---|
| Tubing | 6 ft 3/8 in. Ni | 15 ft by 1/8 in. stainless steel | 10 ft by 1/8 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 1, 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 pentrite.

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

2.2 Other Document:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200⁴

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.

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 proce-

dures. 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- μ L injection on the FPD, or a 1.0- μ L injection for the PFPD of 0.5 mg/kg thiophene in benzene. The user is referred to

⁴ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.