



Designation: ~~D7011-10~~ Designation: D7011 – 10a

## Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection<sup>1</sup>

This standard is issued under the fixed designation D7011; 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 ( $\epsilon$ ) 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 using gas chromatography and sulfur selective detection. The test method is applicable to the determination of thiophene at levels of 0.02 to 2.18 mg thiophene per kg in benzene (mg/kg) on the AED, 0.03 to 1.87 mg/kg on the PFPD, and 0.03 to 2.11 mg/kg on the SCD. 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 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 E29.

~~1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.~~

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

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:<sup>2</sup>

D1193 Specification for Reagent Water

D1685 Test Method for Traces of Thiophene in Benzene by Spectrophotometry

D2359 Specification for Refined Benzene-535

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4734 Specification for Refined Benzene-545

D4735 Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography

D5871 Specification for Benzene for Cyclohexane Feedstock

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

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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<sup>3</sup>

### 3. Summary of Test Method

3.1 The thiophene concentration in refined benzene is determined at the sub-mg/kg to low mg/kg level using conventional gas chromatography with a sulfur selective detector. A reproducible volume of sample is injected. Quantitative results are obtained by the use of the external standard calibration technique.

3.2 The method allows the use of a sulfur chemiluminescence detector, atomic emission detector, pulsed flame photometric detector, or any other sulfur selective detector provided that its performance meets requirements as set forth in 5.4. As sulfur

<sup>1</sup> 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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<sup>2</sup> 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.

<sup>3</sup> 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.

compounds elute from the gas chromatographic column, they are detected and quantified. While the benzene molecule does not contain any sulfur atoms, the possibility of matrix quenching and interference is a concern, especially for thiophene determination at levels less than about 0.5 mg/kg. The column and conditions specified in Table 1 yield acceptable results with minimal matrix quenching and interference. Employing the column and conditions listed in Table 1 is not a requirement to meet the needs of all users. For example, there is less concern of quenching and interference encountered with thiophene concentration levels greater than 0.5 mg/kg. Users of flame photometric detectors should refer to Test Method D4735.

#### 4. Significance and Use

4.1 Accurate gas chromatographic determination of trace levels of thiophene in benzene involves special analytical problems because of the difficulties of trace level analysis. These problems arise from the low concentration levels that need to be measured, the type of column and detector needed for analysis, and the potential interference from the benzene matrix.

4.2 This test method was found applicable for determining thiophene in refined benzene conforming to the specifications described in Specifications D2359, D4734, and D5871 and may be applicable toward other grades of benzene if the user has taken the necessary precautions as described in the text.

4.3 This test method was developed as an alternative technique to Test Methods D1685 and D4735.

#### 5. Apparatus

5.1 *Gas Chromatograph*—The gas chromatograph shall be capable of producing retention times for thiophene repeatable to within 0.05 min. The gas chromatograph shall be equipped with an appropriate sulfur selective detector, column for separation, and sample inlet system for repeatable injection of sample volume.

5.2 *Column*—Specifications and conditions described in Table 1 have been judged satisfactory for this analysis. The use of any column that permits separation and determination of thiophene in benzene at levels consistent with the scope of this method is allowed. Specific chromatographic results and conditions are illustrated in Fig. 1. The user is referred to Practice E1510 for information on installation of fused silica capillary columns.

5.3 *Sample Inlet System*—The sample inlet system shall be able to quantitatively transfer the sample to the analytical column. It shall be capable of introducing constant and repeatable volumes of sample and calibration standards. Use of a liquid autosampler or liquid sampling valve is permitted for the analysis of thiophene in benzene.

5.4 *Detector*—A sulfur selective detector is used and shall meet or exceed the following specifications: (1) linearity or compensated linearity of at least  $10^2$ , (2) minimum detectable level of less than 0.02 mg/kg thiophene in benzene, (3) selectivity of sulfur to carbon greater than  $10^5$ , and (4) absence of quenching that affect results under the conditions used for the analysis.

5.5 *Data Handling System*—Use of an electronic integrating device or computer is necessary. The device shall have the following capabilities: (1) graphic presentation of the chromatogram, (2) digital display of chromatographic peak areas, (3) identification of peaks by retention time, and (4) calculation and use of response factors.

##### 5.6 Gases:

5.6.1 *Carrier Gases*—Helium or nitrogen of high purity (99.995+ %). Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, hydrocarbons, and sulfur contaminants. Gases shall be regulated to ensure a constant carrier gas flow rate.

5.6.2 *Detector Gases*—Hydrogen and air are required as detector gases (99.995+ % purity). Additionally, oxygen (99.8+ %) may be substituted for air. These gases shall be free of interfering contaminants, especially sulfur compounds.

5.6.3 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical to optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictions or mass flow controllers capable of maintaining gas flow constant to  $\pm 1$  % at the required flow rates. The gas flow rate is measured by any appropriate means. The supply pressure of the gas delivered to the gas chromatograph shall be at least 70 kPa (10 psig) greater than the regulated gas at the instrument to compensate for the system back pressure of the flow controllers. In general, a supply pressure of 550 kPa (80 psig) is satisfactory.

5.7 *Microsyringes*—10, 50, 100, and 250  $\mu$ L capacity ( $\pm 1$  % accuracy).

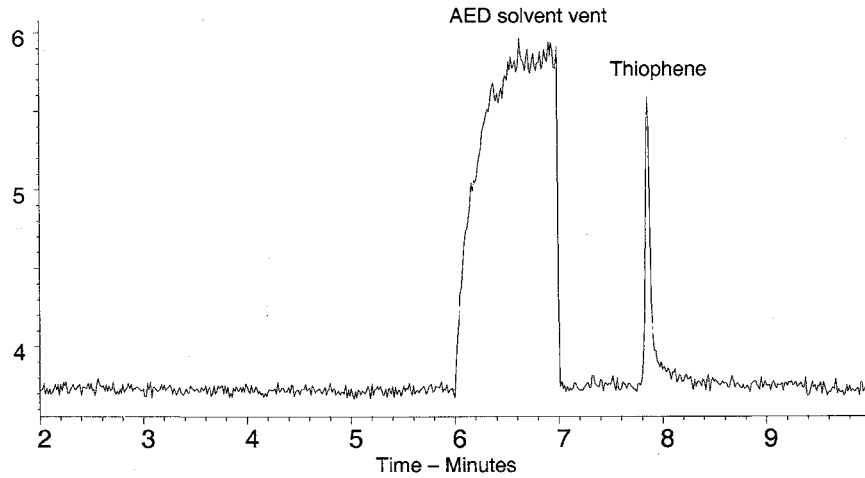
5.8 *Volumetric Pipettes*—0.5, 1.0, and 2.0 mL capacity (Class A).

5.9 *Volumetric Flasks*—10, 50, 100, and 500 mL capacity (class A).

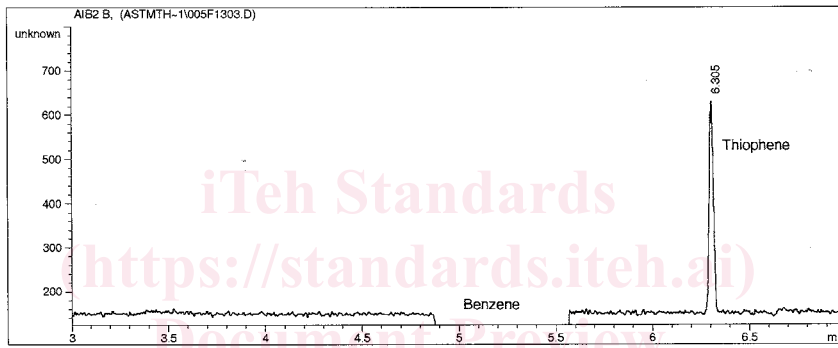
5.10 *Separatory Funnel*—1 L capacity.

**TABLE 1 Typical Chromatographic Conditions**

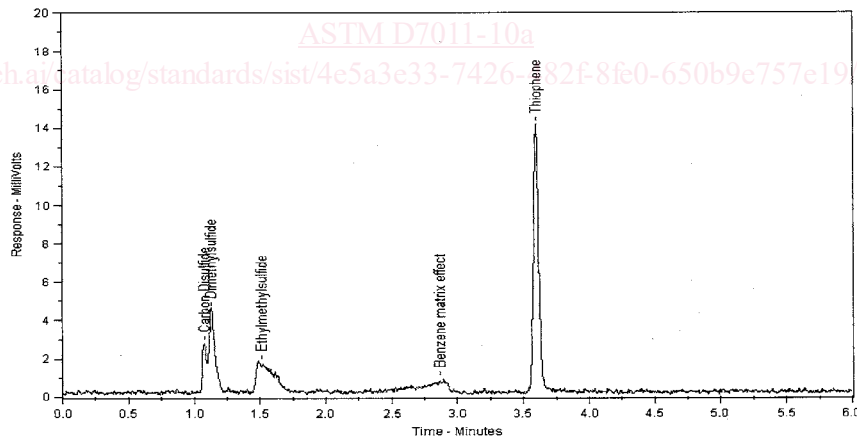
Column	30 m length, 0.32 mm internal diameter, 1 $\mu$ m thick film, cross-linked polyethylene glycol (wax-type)
Oven Temperature	40°C for 2 min; ramp to 100°C at 10°C/min, hold at 100°C for 1 min
Flow Rate	2 mL/min
Split Ratio	1:4 to 1:10
Injection Temperature	125°C
Injection Volume	1-2 $\mu$ L



**Atomic Emission Detector (AED)**



**Pulsed Flame Photometric Detector (PFPD)**



**Sulfur Chemiluminescence Detector (SCD)**

NOTE 1—The shorter retention time obtained with the SCD is primarily due to the column outlet being at sub-ambient pressure.

**FIG. 1 Chromatograms Illustrating the Analysis of a Sample Containing 0.2 mg/kg Thiophene in Benzene Using AED, PFPD and SCD (Upper, Middle, and Lower Chromatograms, Respectively)**

## 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,<sup>4</sup> where such specifications are available. 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.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type IV of Specification D1193.

6.3 *Benzene, Thiophene-free:*

6.3.1 In a fume hood, 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 acid layer is light yellow to colorless. Wash the benzene with 100 mL of water, then twice with 100 mL of cadmium chloride solution ( $\text{CdCl}_2$ ). 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.

6.3.2 Alternatively, thiophene-free benzene can be purchased commercially and used within this method, if its thiophene level meets the criteria within 10.4.

6.4 *Cadmium Chloride Solution (20 g/L)*—Dissolve 20 g of anhydrous cadmium chloride ( $\text{CdCl}_2$ ) into 200 mL of water and dilute to 1 L.

6.5 *Chloroform*—Reagent grade or better.

6.6 *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 with chloroform.

6.7 *Stock Solutions*—Commercially prepared stock solution of thiophene in benzene are available for use as calibration standards or for preparation of calibration standards.

6.8 *Sulfuric Acid*—Concentrated  $\text{H}_2\text{SO}_4$ .

6.9 *Thiophene*—Available from commercial sources for preparation of calibration standards, minimum 99 % purity.

## 7. Hazards

7.1 Benzene is listed as a known carcinogen and is considered a hazardous material. Consult current OSHA regulations and suppliers' Material Safety Data Sheets for all materials used in this method.

7.2 Helium and nitrogen are compressed gases under high pressure and can cause asphyxiation.

7.3 Hydrogen is an extremely flammable gas under high pressure.

7.4 Compressed air and oxygen are gases under high pressure and they support combustion.

7.5 Sulfur compounds are generally flammable, toxic, and produce noxious odors, and therefore shall be handled with appropriate precautions for safety.

7.6 Isatin is a toxic, cancer causing agent.

7.7 Chloroform is flammable, toxic and is a carcinogen.

7.8 Cadmium chloride is a highly toxic cancer causing agent.

## 8. Sample Handling

8.1 Collect the samples in accordance with Practice D3437.

8.2 To preserve sample integrity and prevent the loss of volatile compounds that may be in some samples, collect samples with a minimal head space and do not uncover samples any longer than necessary. Some headspace is necessary to prevent containers from rupturing if the possibility for thermal expansion exists. Sample containers shall be free of contaminants that could interfere with the analysis. Analyze the specimen as soon as possible after transferring it from the sample container to prevent loss of components or contamination.

8.3 Since this procedure is intended for trace level contamination, care shall be taken to ensure containers used for the sample, the specimen, and the working standard do not alter the sample results.

## 9. Preparation of Apparatus

9.1 The chromatographic separation of trace level sulfur compounds can be complicated by absorption onto active sites throughout the chromatographic system. This is less of a problem with thiophene, which is very stable relative to most sulfur compounds. The most likely cause of error in this method is presence of thiophene in matrix blanks (see 10.4).

9.2 Follow the manufacturer's instructions for mounting the column into the gas chromatograph and adjusting the instrument to typical conditions as described in Table 1. General guidelines for the installation of capillary columns can be found in Practice E1510.

<sup>4</sup> *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.