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

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 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:*[2]

D1193 Specification for Reagent Water
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[3]

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 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

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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.

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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, http://www.access.gpo.gov.

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

TABLE 1 Typical Chromatographic Conditions

Column	30 m length, 0.32 mm internal diameter, 1 µm 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 µL

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 Method 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 ±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 µL capacity (±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.

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,[4] 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.

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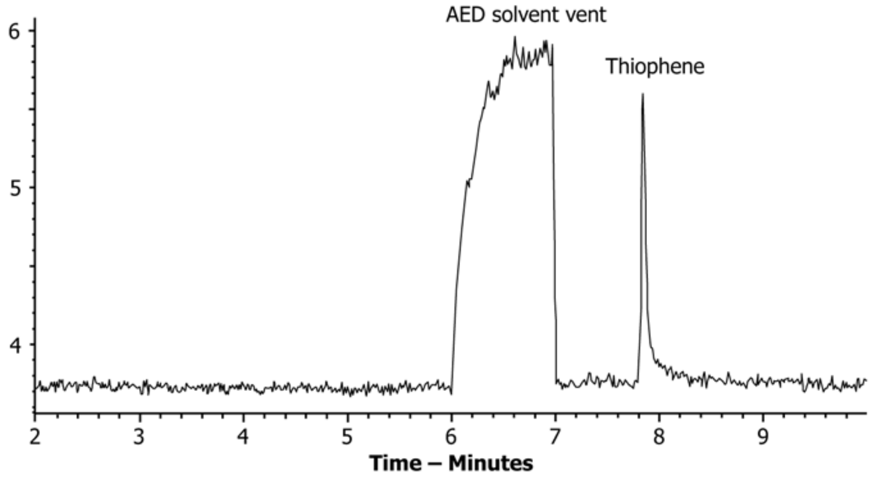
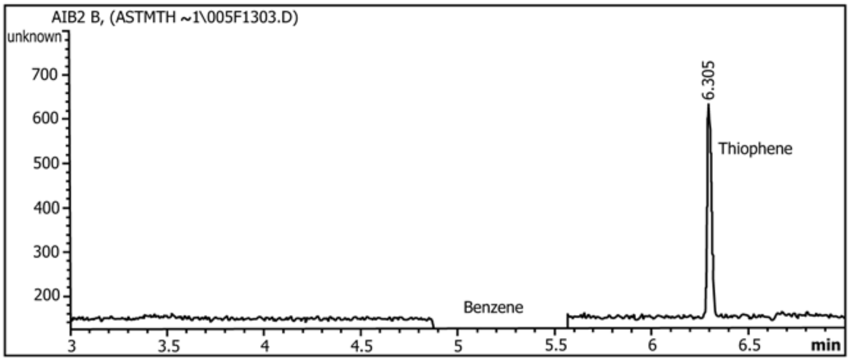
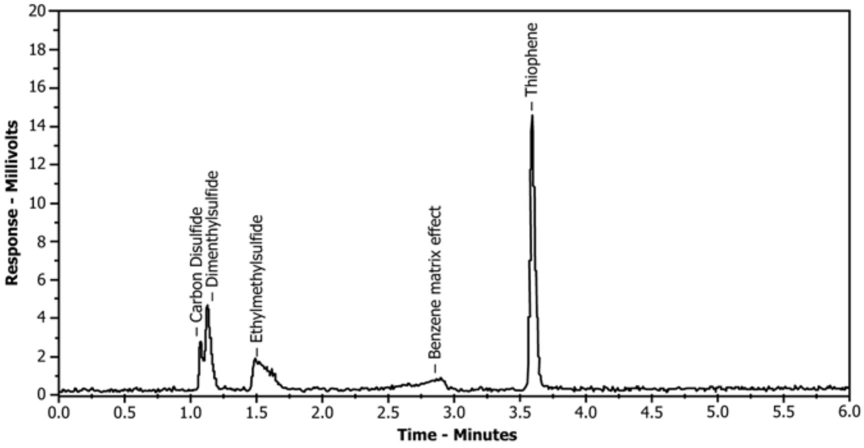
[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



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)

6.2 *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 ($CdCl_2$). 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 ($CdCl_2$) 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 H_2SO_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 supplier's 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.

9.3 The gas chromatograph and detector should be placed into service in accordance with the manufacturer's instructions.

10. Calibration

10.1 A manual or electronic calibration curve shall be prepared for the method of analysis. In some instances, for example when compliance with a certain specification is determined, it is sufficient to use a single point calibration according to user needs.

10.2 Prepare a stock solution of thiophene in benzene at the 100 mg/kg level by adding 0.1000 g of thiophene to 1000 g of thiophene-free benzene. Record actual measurements to 4 significant figures.

10.3 Prepare calibration blends covering the range of determination of thiophene in benzene. For example, use a microsyringe or volumetric pipette to dispense appropriate amounts of the stock solution into a volumetric flask containing thiophene-free benzene to prepare calibration blends containing nominally 0.02, 0.2, 0.5, 1, and 2 mg/kg thiophene in benzene.

10.4 Inject 1-2 µL of each solution and benzene blank into the chromatograph. Integrate the area under the thiophene peak. Each standard solution and the blank should be analyzed in duplicate. The data collected will be used for generation of the calibration curve (see 10.1). The benzene blank should contain less than 0.02 mg/kg thiophene. Higher levels warrant thiophene removal by 6.3.

10.5 *Quality Check*—A quality assurance check should be used to determine if the analysis is in control. If out of control, the cause shall be determined and corrective action taken to bring the analysis into control. The volume of the calibration blends injected for calibration shall be exactly the same as the sample volume injected for analysis.

10.6 *Thiophene Response Factor*—The thiophene response factor is determined according to Eq 1. Chromatographic data systems are capable of performing this calculation automatically.

$$R_f = C/A \tag{1}$$

where:

R_f = thiophene response factor,
C = thiophene concentration of standard, mg/kg, and
A = area (arbitrary units) of the thiophene calibration standard, after "blank" correction, if necessary (10.4).

11. Procedure

11.1 *Sample Analysis*—Introduce a representative aliquot of sample into the gas chromatograph. Exercise care that the amount of sample and standard injected does not cause detector saturation (indicated by flat-topped peaks). Inject the same sample size as used in 10.4. Obtain the chromatographic data by way of an integrator or computer based chromatographic data system. Examine the graphic display or digital data for any errors.

11.2 *Peak Measurement*—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 blends. Typical chromatograms of 0.2mg/kg thiophene in benzene obtained using the AED, PFPD and SCD are shown in Fig. 1.

12. Calculations

12.1 *Thiophene Concentration*—Determine the amount of thiophene in a sample using its measured area and response factor. Calculate the concentration of the thiophene peak according to Eq 2:

$$C_t = A_t \cdot R_f \tag{2}$$

where:

C_t = concentration of thiophene (mg/kg),
A_t = peak area of the thiophene in the sample, and
R_f = thiophene response factor.

12.2 *Report*—Report the thiophene concentration to the nearest 0.01 mg/kg.

13. Quality Control and Quality Assurance

13.1 Laboratories shall have a quality control system in place.

13.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

13.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

13.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

13.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

14. Precision and Bias[5]

14.1 The precision of this test method is based on an interlaboratory study (ILS) of Test Method D7011, Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection, conducted in 2008. The details of the ILS are given in ASTM Research Report No. RR:D16-1039. The ILS did not meet the minimum requirement of 6 laboratories for each detector as specified in Practice E691, but did include 8 laboratories overall. The ILS exceeded the minimum number of materials (four) and the minimum number of replicates (two) required by Practice E691.

14.1.1 AED: 2 laboratories analyzed 6 samples 3 times, for a total of 36 data points.

14.1.2 PFPD: 2 laboratories analyzed 5 samples 3 times, and 1 laboratory analyzed 4 samples 3 times, for a total of 42 data points.

14.1.3 SCD: 2 laboratories analyzed 6 samples 3 times, and 1 laboratory analyzed 5 samples 3 times, for a total of 51 data points.

14.2 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value of that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.2.1 Repeatability limits are listed in Tables 2-4.

14.3 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

14.3.1 Reproducibility limits are listed in Tables 2-4.

14.4 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

14.5 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made. To judge the equivalency of two test results, it is recommended to choose the material closest to characteristics to the test material.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1039. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability and Reproducibility for the AED (2 Laboratories)

Average Thiophene Concentration, mg/kg	Repeatability Limit mg/kg	Reproducibility Limit mg/kg	Number of Data Points Used in Calculations
0.02	0.01	0.01	6
0.53	0.04	0.10	6
0.70	0.04	0.04	6
1.13	0.07	0.20	6
1.84	0.10	0.31	6
2.18	0.08	0.25	6

TABLE 3 Repeatability and Reproducibility for the PFPD (3 Laboratories)

Average Thiophene Concentration, mg/kg	Repeatability Limit mg/kg	Reproducibility Limit mg/kg	Number of Data Points Used in Calculations
0.03	0.01	0.07	9
0.51	0.03	0.21	9
0.73	0.12	0.36	9
1.21	0.08	0.55	6
1.87	0.19	0.61	9

Note: Data from one sample were excluded from PFPD precision statics due to distribution difficulty.

TABLE 4 Repeatability and Reproducibility for the SCD (3 Laboratories)

Average Thiophene Concentration, mg/kg	Repeatability Limit mg/kg	Reproducibility Limit mg/kg	Number of Data Points Used in Calculations
0.03	0.01	0.05	9
0.60	0.03	0.24	9
0.81	0.05	0.29	9
1.24	0.04	0.45	9
1.83	0.04	0.48	9
2.11	0.06	0.44	6

15. Keywords

15.1 atomic emission detector; benzene; chemiluminescence detector; gas chromatography; pulsed flame photometric detector; sulfur; thiophene

APPENDIX

(Nonmandatory Information)

X1. RUGGEDNESS TEST INFORMATION AND RESULTS

X1.1 Scope

X1.1.1 A ruggedness test was conducted and used to produce the precision statement for this method. For the ruggedness test, thiophene free benzene, further purified to remove residual thiophene, was used to prepare five samples for analysis and two check samples. Concentrations of thiophene in the samples and check samples covered the scope of this method. Three manufacturers of sulfur selective detectors, around which this method was developed, participated in the ruggedness test. Participants were advised to use their own standards or the supplied check samples as standards, for which the thiophene concentrations were given.

X1.2 Summary of Results

X1.2.1 Results from the ruggedness test are shown in Table X1.1. The results were reviewed by a statistician. In the statistical analysis, estimates of repeatability were obtained by multiplying each standard deviation by the *t*-value with 2 degrees of freedom at the 0.05 significance level. It is assumed that the laboratories that ran this test are at least reasonably competent. Only similarly competent laboratories shall be assumed to generate similar results.

TABLE X1.1 Ruggedness Test Results

Thiophene Concentration (mg/kg)	0.02	0.08	0.2	0.8	1.92
Sample Designation	Sample E	Sample D	Sample B	Sample C	Sample A
Detector Technology			Test Results		
Atomic Emission Detector[A]					
Determination 1	0.020	0.075	0.173	0.787	2.04
Determination 2	0.019	0.084	0.222	0.797	1.93
Determination 3	0.021	0.076	0.209	0.787	1.98
Mean	0.0202	0.0784	0.201	0.790	1.983
Standard Deviation	0.0012	0.0047	0.025	0.006	0.054
Estimated Repeatability	0.007	0.029	0.154	0.036	0.327
Pulsed Flame Photometric Detector[B]					
Determination 1	0.019	0.069	0.204	0.857	1.96
Determination 2	0.018	0.074	0.205	0.861	1.94
Determination 3	0.021	0.068	0.228	0.857	1.84
Mean	0.0193	0.0706	0.212	0.858	1.913
Standard Deviation	0.0012	0.0033	0.013	0.002	0.067
Estimated Repeatability	0.007	0.02	0.082	0.013	0.405
Sulfur Chemiluminescence Detector[C]					
Determination 1	0.022	0.076	0.225	0.799	1.86
Determination 2	0.022	0.080	0.225	0.786	1.87
Determination 3	0.023	0.077	0.221	0.787	1.83
Mean	0.023	0.078	0.224	0.791	1.85
Standard Deviation	0.0004	0.0025	0.002	0.007	0.025
Estimated Repeatability	0.002	0.015	0.013	0.044	0.155

[A] Agilent Technologies used standards of 0.02, 0.2, 0.5, 1, and 2 mg/kg thiophene in benzene.

[B] O.I. Analytical used the provided 0.16 and 0.6 mg/kg thiophene in benzene check samples as standards.

[C] Ionics Instruments used the provided 0.16 and 0.6 mg/kg thiophene in benzene check samples as standards.

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7011–10a) that may impact the use of this standard. (Approved June 1, 2015.)

(1) Reference to inactive Test Method D1685 has been eliminated.