



Designation: D7183 – 23

# Standard Test Method for Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by Ultraviolet Fluorescence<sup>1</sup>

This standard is issued under the fixed designation D7183; 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 sulfur in aromatic hydrocarbons, their derivatives, and related chemicals.

1.2 This test method is applicable to samples with sulfur concentrations to 10 mg/kg. The limit of detection (LOD) is 0.03 mg/kg S and the limit of quantitation (LOQ) is 0.1 mg/kg S. With careful analytical technique, this method can be used to successfully analyze concentrations below the current scope (see [Appendix X1](#)).

NOTE 1—LOD and LOQ were calculated using data in ASTM Research Report RR:D16-1060.

1.3 The following applies for the purposes of determining the conformance of the test results using this test method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice [E29](#).

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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 [9](#).

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.*

<sup>1</sup> 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. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

[D1555](#) Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons and Cyclohexane

[D3437](#) Practice for Sampling and Handling Liquid Cyclic Products

[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

[E691](#) Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 2.2 Other Documents

[OSHA Regulations](#), [29 CFR](#) paragraphs [1910.1000](#) and [1910.1200](#)<sup>3</sup>

## 3. Terminology

3.1 *oxidative pyrolysis, n*—a process in which a sample is combusted in an oxygen-rich atmosphere at high temperature to break down the components of the sample into elemental oxides.

3.2 *ultraviolet fluorescence, n*—radiation in the region of the electromagnetic spectrum including wavelength from 100 to 3900A that excites SO<sub>2</sub> to (SO<sub>2</sub>)\*.

## 4. Summary of Test Method

4.1 A specimen is either directly injected or placed in a sample boat. The boat is then inserted into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO<sub>2</sub>) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed and the sample combustion

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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>.

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

gases are next exposed to ultraviolet (UV) light. The SO<sub>2</sub> absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO<sub>2</sub>\*). As it returns to a stable state, light is emitted and detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the specimen.

## 5. Significance and Use

5.1 Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur-bearing materials are contained in the feedstocks. This test method can be used to determine sulfur in process feeds, sulfur in finished products, and can also be used for purposes of regulatory control.

## 6. Interferences

6.1 Halogens present in the specimen in concentrations greater than 10 % and nitrogen concentrations of 1500 mg/kg or greater can interfere.

6.2 Moisture produced during the combustion step can interfere if not removed prior to the gas entering the detector cell.

## 7. Apparatus

7.1 *Combustion Furnace*—An electric furnace capable of maintaining a temperature sufficient to volatilize and combust all the sample and oxidize sulfur to SO<sub>2</sub>. The actual temperature should be recommended by specific instrument manufacturer.

7.2 *Quartz Combustion Tube*—Capable of withstanding 900 °C to 1200 °C. The tube should be recommended by the instrument manufacturer.

7.3 *Microlitre Syringe*—Capable of delivering from 5 µL to 250 µL of sample. Check with the instrument manufacturer for recommendations for specific sample requirements.

7.4 *Constant Rate Injector System*—If the sample is to be introduced into the pyrolysis furnace via syringe, use a constant rate injector or a liquid introduction module.

7.5 *Liquid Auto-Sampler*—Capable of injecting 5 µL to 250 µL of sample.

7.6 *Automatic Boat Drive System*—If the instrument is equipped with an inlet system, a device for driving the boat into the furnace at a controlled and repeatable rate is required.

7.7 *Flow Control*—The instrument must be equipped with a means of flow control capable of maintaining a constant supply of oxygen and carrier gas or air.

7.8 *Drier Tube*—The instrument must be equipped with a mechanism for removal of water vapor.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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, unless otherwise indicated. 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.

8.2 *Inert Gas or Air*—Either argon (Ar), helium (He) or air may be used. The purity should be no less than 99.99 %.

8.3 *Oxygen Gas (as required)*—The purity should be no less than 99.99 %.

8.4 *Solvent*—The solvent chosen should be capable of dissolving the sulfur compound. The solvent of choice should have a boiling point similar to the sample being analyzed. Suggested possibilities include, but not limited to methanol, iso-octane, and *p*-xylene (see **Note 2** and **Note 3**).

NOTE 2—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative area counts.

NOTE 3—All solvents should have known sulfur content or known to be less than what will interfere with results.

8.5 *Dibenzothiophene*—FW184.26, 17.399 % (m/m) Sulfur (see **Note 4**).

NOTE 4—A correction for chemical impurity is required. Normally 98 %.

8.6 *Quartz Wool*—If needed.

8.7 *Sulfur Stock Solution, approximately 870 µg to 1044 µg S/ml*—This standard may be purchased if desired. Prepare a stock solution by accurately weighing approximately 0.5 g to 0.6 g of dibenzothiophene to the nearest 0.1 mg into a tared 100 mL volumetric flask. Record the weight. Dilute to volume with the selected solvent. Use **Eq 1** to determine the concentration of stock solution. This stock solution can be further diluted to desired sulfur concentrations (see **Note 5** and **Note 6**). Alternate volumes of solutions may be prepared so long as the preparation meets the concentration specified.

$$\mu\text{g S/ml solvent} = \frac{(\text{g of DBT}) \times (.174) \times (\text{Purity of DBT}) \times (10^6)}{100 \text{ ml of Solvent}} \quad (1)$$

where:

*DBT* = dibenzothiophene  
*S in DBT* = 17.3994 %

NOTE 5—Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, stock solutions have a useful life of about 3 months.

NOTE 6—Check all new calibration standards against the previous standard.

8.8 *Oxidation Reagent (as required)*—Tungsten trioxide, (WO<sub>3</sub>), granular (typical particle size >2.0 mm), high purity, 99.75 % minimum.

## 9. Hazards

9.1 Consult the current version OSHA regulations, supplier's Data Sheets, and local regulations for all materials used in this test method.

<sup>4</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*. 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.

9.2 High temperature is employed in this test method. Extra care must be exercised when using flammable materials near the furnace.

9.3 **Warning**—Exposure to excessive quantities of ultraviolet light is injurious to health. The operator must avoid exposing any part of their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.

## 10. Sampling

10.1 Consult guidelines for taking samples from bulk containers in accordance with Practice [D3437](#).

## 11. Preparation of Apparatus

11.1 Set-up the instrument in accordance with manufacturer's instructions.

11.2 Adjust gas flows and pyrolysis temperature(s) to the operating conditions recommended by the manufacturer.

11.3 The actual operation of injecting a sample will vary depending upon the instrument manufacturer and the type of inlet system used.

11.4 An autosampler or a constant rate injector must be used when using an instrument equipped with a vertical furnace.

11.5 Prebake the sample boats to be used for the determination when using a horizontal furnace.

## 12. Calibration and Standardization

12.1 Using the sulfur standard stock solution (see [8.7](#)), make a series of calibrations standards covering the range of expected sulfur concentration.

NOTE 7—When looking for levels of sulfur below 1 mg/kg make a calibration curve using an autosampler or constant rate injector and standards, made from the sulfur stock solution, to cover the expected range of samples. Follow manufacturer's recommendations for constructing the curve.

NOTE 8—When looking for concentrations from 1 mg S/kg to 10 mg S/kg, follow manufacturer's recommendations for constructing the curve.

12.2 The sample size can be determined either volumetrically, by syringe or by mass.

12.3 Volumetric measurement can be utilized by filling the syringe with standard, carefully eliminating all bubbles, and pushing the plunger to a calibrated mark on the syringe, and recording the volume of liquid in the syringe. After injecting the standard, read the volume remaining in the syringe. The difference between the two volume readings is the volume of standard injected. This test method requires the known or measured density, to the third decimal place.

12.4 Alternatively, the syringe may be weighed before and after the injection to determine the weight of the sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of  $\pm 0.0001$  g is used.

12.5 Follow the instrument manufacturer's recommendation for introducing samples into the instrument.

12.6 If there are any problems with the calibration standards follow the instrument manufacturer's recommendations to correct.

12.7 Construct a linear regression curve ( $\mu\text{g S}$  versus Area) using as many points as recommended by the instrument manufacturer.

12.8 The linear regression curve should have a minimum of 0.99 correlation coefficient. If it does not, examine each point on the curve to determine which point or points are out. Correct the problem and run new standards.

## 13. Procedure

13.1 Obtain a test specimen using the procedure described in Section [10](#). The sulfur concentration in the test specimen must be less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration.

13.2 Follow the instrument manufacturer's recommendations for sample size.

13.3 Follow the instrument manufacturer's recommendations for introducing samples into the instrument.

13.4 Determine the sulfur concentration, by the average of three determinations, calculated by the instrument software. Make sure replicates are repeatable.

## 14. Calculation

14.1 All calculations are performed by the software, and results are displayed and printed out in ppm (mg/kg) as appropriate. The density is input during sample data entry and is used by the instrument to convert from wt./vol. to wt./wt.

14.2 Use Test Method [D1555](#) for measurements utilizing volume and known density in milligrams per kilograms as follows:

$$\text{Sulfur, mg/kg} = \frac{(M - B)}{V \times D} \quad (2)$$

14.3 Measurement utilizing weight of sample:

$$\text{sulfur, mg/kg} = \frac{(M - B)}{w} \quad (3)$$

where:

$M$  = measured sulfur value,  $\mu\text{g}$

$B$  = blank measured sulfur value,  $\mu\text{g}$

$V$  = sample injection volume, mL

$D$  = density of sample g/mL

$w$  = weight of sample, g

## 15. Report

15.1 Report the sulfur results as (mg/kg) of the sample to the nearest 0.01 mg/kg for samples less than 1 mg/kg. Report to the nearest 0.1 for samples greater than 1 mg/kg.

15.1.1 Results below 0.03 mg/kg should be reported as  $<0.03$  mg/kg.

**TABLE 1 Sulfur in Aromatics (mg S/kg)**

Material	Average <sup>A</sup>	Repeatability	Reproducibility
		Limit	Limit
		r	R
<i>p</i> -Xylene Level 1	0.02	0.01	0.05
Toluene Level 1	0.03	0.04	0.07
Benzene Level 1	0.05	0.03	0.08
Toluene Level 2	0.10	0.03	0.15
Benzene Level 2	0.25	0.05	0.20
<i>p</i> -Xylene Level 3	0.70	0.05	0.30
Toluene Level 3	1.96	0.25	0.48
Benzene Level 3	4.24	0.19	0.84
<i>p</i> -Xylene Level 2	7.80	0.27	0.93
Toluene Level 4	9.96	0.32	1.90

<sup>A</sup> The average of the laboratories' calculated averages.

## 16. Precision and Bias<sup>5</sup>

16.1 An ILS was conducted which included eleven laboratories analyzing ten samples two times. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1060.

16.1.1 *Repeatability Limit (r)*—Results should not be suspect unless they differ by more than shown in Table 1. Results differing by less than (*r*) have a 95 % probability of being correct.

16.1.2 *Reproducibility Limit (R)*—Results submitted by two laboratories should not be considered suspect unless they differ by more than shown in Table 1. Results differing by less than *R* have a 95 % probability of being correct.

16.2 *Bias*—At this time of the study, no accepted reference material suitable for determining the bias for this test method was utilized, therefore no statement on bias is being made.

### 16.3 Proficiency Testing Information:

16.3.1 The following information (Table 2) is included as general information. D16's Proficiency Testing Program sends a single sample of *p*-xylene to multiple laboratories. The sample is analyzed one time by each lab. The amount of sulfur in the sample is unknown. Different samples were used during this test period. Known amounts were added to some cycles. Each result below represents a different cycle.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1060. Contact ASTM Customer Service at service@astm.org.

**TABLE 2 Sulfur in *p*-xylene From D16 PTP Program (mg S/kg)**

Number of Labs	Average (mg S/kg)	Standard Deviation mg S/kg	Reproducibility	Amount S added
			R	(mg/kg)
9	0.06	0.03	0.08	0
11	0.10	0.08	0.22	0
7	0.04	0.02	0.06	0
13	0.19	0.09	0.25	0.12
9	0.48	0.19	0.53	0.12
7	0.25	0.11	0.31	0.12
6	0.10	0.05	0.14	0.12
12	0.28	0.06	0.17	0.24
8	0.22	0.05	0.14	0.24
8	0.15	0.14	0.39	0.24
8	0.60	0.14	0.39	0.48

## 17. Quality Guidelines

17.1 Laboratories shall have a quality control system in place.

17.1.1 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.

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

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

17.1.4 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.

### 17.2 Interlaboratory Testing:

17.2.1 A program that includes multiple laboratories analyzing the same samples is strongly encouraged. This program should allow labs to compare their results with other laboratories. This is particularly important when a plant is selling the product to customers or the laboratory is analyzing the product for acceptance. Producers and customers need to have confidence that results from different producers are comparable.

17.2.2 ASTM currently has a Proficiency Testing Program that sends a sample of mixed xylenes, *p*-xylene, and benzene to multiple labs twice a year for testing. Other programs are acceptable.

## 18. Keywords

18.1 aromatics; fluorescence; hydrocarbons; sulfur; ultra-violet