Designation: ~~D7183 – 12~~ D7183 – 15

Standard Test Method for
Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by Ultraviolet Fluorescence[1]

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 from 0.5 to 100 mg/kg. With careful analytical technique, this method can be used to successfully analyze concentrations below the current scope (see Appendix X1).

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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]
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 [3]

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_2 to (SO_2*).

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_2) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2*). 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.

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

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 *Pyrolysis Furnace*—An electric furnace capable of maintaining a temperature sufficient to volatilize and pyrolyze all the sample and oxidize sulfur to SO_2. The actual temperature should be recommended by specific instrument manufacturer.

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

7.3 *Microlitre Syringe*—Capable of delivering from 5 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 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 flow controllers capable of maintaining a constant supply of oxygen and carrier gas.

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,[4] 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*—Either argon (Ar) or helium (He) may be used. The purity should be no less than 99.99 mol %.

8.3 *Oxygen Gas*—The purity should be no less than 99.99 mol %.

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,~~iso-octane, and ~~p-xylene~~p-xylene (see Note 1 and Note 2).

NOTE 1—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative area counts.
NOTE 2—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 3).

NOTE 3—A correction for chemical impurity is required. Normally 98 %.

8.6 *Quartz Wool*—If needed.

8.7 *Sulfur Stock Solution, approximately 870 to 1044 µg S/ml*—This standard may be purchased if desired. Prepare a stock solution by accurately weighing approximately 0.5 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 4 and Note 5). Alternate volumes of solutions may be prepared so long as the preparation meets the concentration specified.

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

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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.

where:

DBT	=	dibenzothiophene
S in DBT	=	17.3994 %

where:

~~DBT~~	=	~~dibenzothiophene~~
~~S in DBT~~	=	~~17.3994 %~~

Note 4—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 5—Check all new calibration standards against the previous standard.

9. Hazards

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

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 ~~auto-sampler~~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.

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. If the expected levels include 0 to 1.0 mg/kg and 1 to 100 mg/kg, then two curves should be made to cover the entire range, one from 0 to 1.0 mg/kg (low curve) and one from 1.0 to 100 mg/kg (high curve).

Note 6—When looking for levels of sulfur below 1 mg/kg make a calibration curve using an ~~auto-sampler~~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 7—When looking for concentrations from 1 mgS/kg to 100 mgS/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 ±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 (µg 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.