Designation: D7183 – 16

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

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 (ε) 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 from 0.5 to 10 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.

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.

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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**

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_2. The actual temperature should be recommended by specific instrument manufacturer.

7.2 *Quartz Combustion 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 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,[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 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 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.

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

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.

8.8 *Oxidation Reagent (as required)*—Tungsten trioxide, (WO_3), granular (typical particle size >2.0 mm), high purity, 99.75% minimum.

9. Hazards

9.1 Consult the current version OSHA regulations, supplier's Safety 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.

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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.

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 6—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 7—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 ±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.

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:

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

14.3 Measurement utilizing weight of sample:

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

where:

M = measured sulfur value, µg
B = blank measured sulfur value, µg
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 .1 for sample greater than 1 mg/kg.

16. Precision and Bias[5]

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.

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[5] 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 1 Sulfur in Aromatics (mg S/kg)

Material	Average[A]	Repeatability Limit r	Reproducibility Limit R
p-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
p-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
p-Xylene Level 2	7.80	0.27	0.93
Toluene Level 4	9.96	0.32	1.90

[A] The average of the laboratories' calculated averages.

17. Quality Assurance and Quality Control

17.1 Refer to Guide D6809 for suggested QA/QC activities that can be used as a part of this test method. It is recommended that the operator of this test method select and perform relevant QA/QC activities like the ones in Guide D6809 to help ensure the quality of data generated by this test method.

18. Keywords

18.1 aromatics; fluorescence; hydrocarbons; sulfur; ultraviolet

APPENDIX

(Nonmandatory Information)

X1. OPERATIONAL CONDITIONS FOR SUCCESSFUL TRACE SULFUR ANALYSIS

X1.1 This method may be used to successfully analyze concentrations below the current scope. Careful analytical technique and adherence to the instrument manufacturer's instructions and recommendations can yield analysis to trace levels down to ≤50 ppb sulfur. The following is provided as information on these important factors.

X1.2 Prepare the instrument according to the manufacturer's instructions. The sample flow path must be leak free when pressure tested in accordance with the manufacturer's recommended procedure.

X1.3 Trace analysis cannot be achieved if contamination is present in the supply gas, flow path, standards and/or samples. Contamination in supply gas(es) and/or flow path can be identified by performing an analysis in which no sample is injected while allowing the analyzer to through its analytical program. If found, identify the cause and eliminate.

X1.4 Calibration standards must be prepared with solvent materials that have minimal or no contamination. Contribution from solvent materials and impurity of source material must be corrected for by either using a blank correction procedure or by entering the corrected concentrations based on standard addition during the calibration.

X1.5 Trace amounts of sulfur may be changed by the slightest mistakes in sample handling. Extreme care must be taken not to contaminate the standards or samples. The sample may need to be refrigerated. Ensure that sample vial caps are properly seated. This will prevent evaporation and provide for accurate sampling.

X1.6 All glassware, syringes and any other apparatus used should be clean and free of sulfur compounds to avoid possible contamination. Do not touch any sample introduction device (that is, syringe needle, quartz sample boat, etc.). This may contaminate the device with sulfur.

X1.7 Prior to analysis, be certain that the detector baselines are stable and noise free. For a given gain factor, photomultiplier tube voltage may be adjusted to insure maximum sensitivity while maintaining a stable, noise-free baseline.

X1.8 Gas supplies to various points in the sample path must be consistently controlled to allow for smooth, complete combustion of the sample.

X1.9 Always ensure that the gas flows and temperatures are correct and stable before introducing sample materials into the system.

X1.10 Use of an autosampler is recommended to achieve maximum repeatability and reproducibility for trace level analysis.

X1.11 Direct Injection Systems:

X1.11.1 The position of the syringe needle tip in the pyrotube can have an effect on the combustion efficiency. Follow the manufacturer's recommendation for the proper positioning of the syringe and needle.

X1.11.2 The residence time of the needle in the furnace must be consistent following the injection of the sample. Example, for some apparatus types, it is recommended that the needle remain in the furnace until the instrument returns to baseline and the analysis of the injected material is complete. Follow the manufacturer's recommendation for determining proper injection needle residence time.

X1.12 For boat inlet systems, avoid removing the sample introduction device (that is, quartz sample boat, etc.) before the sample material is completely combusted.

X1.13 The filling of the syringe and sample introduction can affect the ability to measure trace sulfur levels. Refer to manufacturer's recommendation for the proper procedure for filling the syringe and sample introduction. Avoid integration of any baseline upset caused by the needle penetration of the septum or the combustion of any material on the syringe needle.

X1.14 A wait of at least two to three minutes between sample introductions is recommended. This will allow the membrane dryer to regenerate. For an apparatus that utilizes a desiccant as an indicator of dryness, replace the drying agent when color change (blue to pink) indicates.

X1.15 Ensure that at least two rinses are purged through the syringe assembly between analyses.

X1.16 Always operate within the calibrated range; extrapolation is not recommended.

X1.17 Confirm the validity of the calibration curve on a daily basis by analyzing at least one material of known concentration. The result should be within normal analytical error.

X1.18 When constructing a calibration curve, select instrument settings which will yield at least three times baseline noise for the lowest point on the calibration curve.

X1.19 Frequently inspect the inlet and exit portions of the pyrotube for any carbon residue. If residue is found, immediately clean the residue from the system and check for gas leaks, proper gas flows, correct sample introduction technique, and suitable sample size.

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7183–15) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Updated Section 1.2.
(2) Updated Sections 7.1, 7.2, and 7.7.
(3) Updated Sections 8.2 and 8.3.
(4) Added new Section 8.8.
(5) Updated Section 9.1.
(6) Updated Section 11.5.
(7) Updated Section 12.1.
(8) Updated Note 7.
(9) Removed Tables 1 and 2 and replaced with new Table 1.
(10) Updated Sections 16.1, 16.1.1 and 16.1.2.
(11) Deleted Section 16.1.3.
(12) Updated footnote 5.

Committee D16 has identified the location of selected changes to this standard since the last issue (D7183–12) that may impact the use of this standard. (Approved June 1, 2015.)

(1) Updated Section 1.2.
(2) Added Appendix X1.