



Designation: ~~D7679~~—~~11~~ D7679 – 13

Standard Test Method for Sulfur Content in Carbon Black Feedstock Oils¹

This standard is issued under the fixed designation D7679; 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 instrumental determination of sulfur content in samples of carbon black feedstock oils. Values obtained represent the total sulfur content. Two analysis methods are available for use:

Test Method A: High-Temperature Combustion
With
Infrared Absorption Detection Procedures
~~Test Method B: X-Ray Fluorescence~~
Test Method B: X-Ray Fluorescence

Sections ~~4~~ – 10

Sections ~~11~~ – 15

Sections 13 – 17

1.2 This test method is applicable to carbon black feedstock oils derived from petroleum, coal, and other sources which include fuel oils, residues, tars, pitches, reclaimed oils, and similar materials that are normally handled as liquids. This test method is applicable to products typically containing 0 to 5 mass % sulfur.

1.3 The results of these tests can be expressed as mass % sulfur.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1619 Test Methods for Carbon Black—Sulfur Content](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries](#)

3. Significance and Use

3.1 Measuring the total sulfur content of feedstock oil is often a necessary component in calculations for sulfur dioxide emissions.

3.2 The carbon black industry measures sulfur content of feedstock oils along with sulfur content of carbon black products per Test Method [D1619](#) in calculations to determine sulfur dioxide emissions for compliance with governmental reporting requirements.

TEST METHOD A: HIGH-TEMPERATURE COMBUSTION WITH INFRARED ABSORPTION DETECTION PROCEDURES

4. Summary of Test Method

4.1 In this test method, a sample of feedstock oil is weighed in a combustion boat containing either a tungsten oxide based accelerator, sand or aluminum oxide absorbent, and the sulfur content is determined by placing the boat in a tube furnace at 1350°C in an air or oxygen-enriched atmosphere resulting in complete combustion. Sulfur in the sample is completely oxidized to sulfur

¹ This test method is under the jurisdiction of ASTM Committee [D24](#) on Carbon Black and is the direct responsibility of Subcommittee [D24.66](#) on Environment, Health, and Safety.

Current edition approved Nov. 1, 2011; Nov. 1, 2013. Published December 2011; December 2013. Originally approved in 2010. Last previous edition approved in 2010 as [D7679 – 10](#); [D7679 – 11](#). DOI: [10.1520/D7679-11](#); [10.1520/D7679-13](#).

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.

dioxide. Moisture and particulates are removed from the gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through a cell in which sulfur dioxide concentration is measured by an infrared (IR) absorption detector at a precise wavelength in the IR spectrum. The IR absorption detects sulfur dioxide throughout the entire combustion process. The integral of the detector signal is the basis for the total sulfur content of a sample.

4.2 This test method is for use with commercially available sulfur analyzers equipped to carry out the combustion and measurement operations automatically.

4.3 The sulfur analyzer shall be calibrated using appropriate calibration standards (see 6.7).

4.4 The instrument may be configured to analyze more than one element such as a carbon-sulfur analyzer. In this case, the analyzer has individual detectors for each element that are arranged in series.

5. Apparatus

5.1 There are a number of commercially available instruments designed to measure sulfur content in organic materials including sulfur and carbon-sulfur combustion analyzers. This test method makes no specifications regarding system designs.

5.2 Functionally, however, the following are specified for all instruments:

5.2.1 An analytical balance, or equivalent, that is capable of a weighing sensitivity of 0.1 mg or better resolution.

5.2.2 The combustion tube and boat are made of a suitable material such as mullite, porcelain, or zircon.

5.2.3 The sample is absorbed onto a solid which may include the following materials: (1) tungsten oxide based accelerator; (2) Sea sand; (3) Aluminum oxide. Refer to the instrument manufacturer's recommendations.

5.2.4 The sample is combusted at a temperature of $1350 \pm 15^\circ\text{C}$ in an air or oxygen-enriched atmosphere.

5.2.5 The combustion gas is passed through an absorbent (anhydrous magnesium perchlorate) to remove water vapor.

5.2.6 The detection system measures sulfur dioxide using an IR absorption detector at a wavelength suitable for linear responses with respect to the concentration over the full range of possible concentrations.

6. Reagents

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 where such specifications are available.³ 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 *Magnesium Perchlorate*.

6.3 *Oxygen*, high purity, 99.9 %.

6.4 *Tungsten (VI) Oxide Accelerator*, containing potassium dihydrogen-phosphate (optional).

6.5 *Sea Sand*, purified by acid and calcinated (optional).

6.6 *Aluminum Oxide*, optional.

6.7 *Calibration Standards*.⁴

7. Sampling

7.1 Collect feedstock oil as specified in Practices **D4057** or **D4177**.

7.2 *Sample*—This is the portion or aliquot of the feedstock oil for use in obtaining a result.

7.3 *Preparation*—Warm viscous samples until they are fluid and shake for 5 s.

7.4 *Transfer*—Use any convenient, clean syringe or pipet to transfer a sample to the combustion boat as described in Section 10.

8. Preparation of Apparatus

8.1 Assemble the apparatus according to the manufacturer's instructions.

8.2 Stabilize the furnace temperature at $1350 \pm 15^\circ\text{C}$.

8.3 Make a minimum of two determinations to condition the equipment or follow the manufacturer's recommendation to condition equipment before calibrating the instrument.

³ *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 *Annual 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.

⁴ Sulfur calibration and reference standards are typically available from the instrument manufacturer, National Institute of Standards and Technology's (NIST), <http://www.nist.gov>, and are also available from Alpha Resources, 3090 Johnson Road, Stevensville, MI 49127, www.alpharesources.com.

9. Calibration

9.1 Calibrate the instrument per the manufacturer’s recommendation using appropriate sulfur calibration standards.

9.2 *Adjustment of Response of Measurement System*—Weigh approximately 0.1 to 0.2 g of calibration standard or use the recommended mass per manufacturer. Analyze the sample (see Section 10). Repeat this procedure. Adjust the instrument as recommended by the manufacturer until the absence of drift is indicated. Insure the minimum analysis time is sufficient for complete combustion of the sample.

9.3 *Calibration Procedure*—Follow the calibration procedure recommended by the manufacturer. Confirm the calibration by analyzing a reference material of known sulfur concentration. Reference standards should be similar to feedstock oils with sulfur content in the range of approximately 0 to 5 %. The measured value should be within allowable limits of the known value. If not, repeat the procedure. If acceptable results are not obtained, refer to the manufacturer’s instructions for calibration.

10. Procedure

10.1 Stabilize and verify calibration of the analyzer (see Sections 8 and 9).

10.2 Confirm the furnace temperature is $1350 \pm 15^\circ\text{C}$.

10.3 Weigh an appropriate mass of accelerator or absorbent into the combustion boat.

NOTE 1—Use a material and mass recommended by the instrument manufacturer suitable for the combustion boat in use. Calibration standards and feedstock samples should be analyzed using a similar mass of accelerator or absorbent.

10.4 Weigh approximately 0.1 to 0.2 g of the sample into the combustion boat on top of the accelerator or absorbent.

10.5 Record the sample weight.

10.6 A portion of the accelerator or absorbent within the boat may be used to cover the sample, or alternatively, additional accelerator or absorbent may be weighed and added to cover the sample.

NOTE 2—When covering the sample use care to insure none of the sample is accidentally removed from the combustion boat due to contact with a spatula or other tool used to transfer or position the accelerator or absorbent.

10.7 Initiate the analysis and place the boat in the instrument using a boat puller or an auto-sampler mechanism.

10.8 When the analysis is complete, the instrument should indicate the sulfur value. Refer to the manufacturer’s recommended procedure.

11. Report

11.1 The percent sulfur value is obtained directly from the apparatus.

12. Precision and Bias⁵

12.1 These precision statements have been prepared in accordance with Practice D4483. Refer to this practice for terminology and other statistical details.

12.2 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials used in the particular interlaboratory program described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols of the test method. Any appropriate value may be used from Table 1 for the High Temperature Combustion Method A. An alternate combustion method for carbon content, CHNS, was included in the interlaboratory program used to generate this precision statement since a few labs use this instrumental method. Precision data specific to the CHNS method is found in Table 2.

⁵ A research report is pending.

TABLE 1 Precision Parameters for Test Method D7679, Type 1 Precision, High Temperature Combustion, Sulfur Content of Feedstock

Material	Number of Laboratories	Units Percent							
		Mean Level	Sr	r	(r)	SR	R	(R)	
9. Ethylene Cracker Residue	7	0.1378	0.0121	0.0343	24.92	0.0175	0.0494	35.88	
10. NIST 1621e (0.95 % S)	7	0.9739	0.0195	0.0552	5.67	0.0435	0.1232	12.65	
11. NIST 1622e (2.1 % S)	7	2.2038	0.0298	0.0843	3.83	0.1007	0.2851	12.93	
12. NIST 2717a (3.0 % S)	7	3.0525	0.0322	0.0911	2.98	0.0827	0.2341	7.67	
13. NIST 1620c (4.6 % S)	7	4.7190	0.0872	0.2467	5.23	0.1546	0.4376	9.27	
Average		2.2174							
Pooled Values			0.0448	0.127	5.72	0.093	0.263	11.85	