



Designation: D7679 – 16 (Reapproved 2020)

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	Sections 4 – 10
Test Method B: X-Ray Fluorescence	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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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.*

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 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

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.

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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.

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.

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.

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.

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.

11.2 Report results to the nearest 0.01 %.

12. Precision and Bias

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.

12.3 A type 1 inter-laboratory precision program was conducted. Both repeatability and reproducibility represent short-term (daily) testing conditions. The testing was performed in each laboratory performing the test twice on each of two days (total of four tests). A test result is the value obtained from a single determination. Acceptable difference values were not measured.

12.4 The results of the precision calculations for this test are given in Table 1 for the High Temperature Combustion Method A. The materials are arranged in ascending "mean level" order.

12.5 *Repeatability*—The pooled relative repeatability, (*r*), of this test has been established as 5.72 %. Any other value in Table 1 may be used as an estimate of repeatability, as appropriate. The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for this test will exceed the repeatability on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results that differ by more than the appropriate value from Table 1 must be suspected of being from different populations and some appropriate action taken.

NOTE 3—Appropriate action may be an investigation of the test method procedure or apparatus for faulty operation or the declaration of a significant difference in the two materials, samples, etc., which generated the two test results.

12.6 *Reproducibility*—The pooled relative reproducibility, (*R*) of this test has been established as 11.85 %. Any other value in Table 1 may be used as an estimate of reproducibility, as appropriate. The difference between two single and independent test results found by operators working under the prescribed reproducibility conditions in different laboratories on identical test material will exceed the reproducibility on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results produced in different laboratories that differ by more than the appropriate value from Table 1 must be suspected of being from different populations and some appropriate investigative action taken.

12.7 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by the test method. Bias, therefore, cannot be determined.

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

Material	Number of Laboratories	Units Percent	Sr	r	(r)	SR	R	(R)
		Mean Level						
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

TABLE 2 Precision Parameters for Test Method D7679, Type 1 Precision, CHNS, Sulfur Content of Feedstock

Material	Number of Laboratories	Units Percent	Sr	r	(r)	SR	R	(R)
		Mean Level						
9. Ethylene Cracker Residue	5	0.1140	0.0170	0.0482	42.27	0.0312	0.0884	77.54
10. NIST 1621e (0.95 % S)	6	0.9279	0.0295	0.0834	8.99	0.1219	0.3451	37.19
11. NIST 1622e (2.1 % S)	6	2.0917	0.0560	0.1585	7.58	0.1531	0.4331	20.71
12. NIST 2717a (3.0 % S)	6	2.9788	0.0513	0.1453	4.88	0.0970	0.2745	9.22
13. NIST 1620c (4.6 % S)	6	4.5825	0.0539	0.1524	3.33	0.1686	0.4772	10.41
Average		2.1390						
Pooled Values			0.0443	0.1255	5.87	0.1242	0.3515	16.43

TABLE 3 Precision Parameters for Test Method D7679, Type 1 Precision, X-ray fluorescence, Sulfur Content of Feedstock

Material	Number of Laboratories	Units Percent	Sr	r	(r)	SR	R	(R)
		Mean Level						
9. Ethylene Cracker Residue	2	0.151	0.0019	0.0055	3.65	0.0127	0.0358	23.71
10. NIST 1621e (0.95 % S)	2	0.975	0.0038	0.0107	1.09	0.0387	0.1095	11.23
11. NIST 1622e (2.1 % S)	2	2.155	0.0130	0.0367	1.70	0.0134	0.0378	1.75
12. NIST 2717a (3.0 % S)	2	3.063	0.0187	0.0530	1.73	0.0166	0.0469	1.53
13. NIST 1620c (4.6 % S)	2	4.627	0.0325	0.0919	1.99	0.0973	0.2754	5.95
Average		2.194						
Pooled Values			0.0178	0.051	2.30	0.0481	0.136	6.21

TEST METHOD B: X-RAY FLUORESCENCE

13. Summary of Test Method

13.1 X-ray fluorescence may be used to determine sulfur in carbon black feedstock oils. Each element has a unique energy response (fluorescence) when exposed to x-ray energy that can be used to identify the element. An x-ray source excites the sulfur atoms in the sample material. The instrument detects the excited sulfur atoms and produces a numeric value.

13.2 The sulfur analyzer shall be calibrated using appropriate calibration standards (see 16.3).

14. Apparatus

14.1 *X-ray Fluorescence Instrument*, designed specifically for the test of trace amounts of sulfur, with x-ray source (radioisotope or x-ray tube), detection, and numeric display. X-ray fluorescence instruments are either wavelength dispersive or energy dispersive. Energy dispersive instruments have a lower detectable limit of 15 ppm while wavelength dispersive instruments have a lower detectable limit of less than 1 ppm. Since the sulfur in oil furnace type carbon blacks is usually present in percent levels, either instrument type is suitable.

15. Sampling

15.1 Collect feedstock oil as specified in Practices D4057 or D4177.

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

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

16. Calibration

16.1 The ability of the instrument to detect an element's energy signature is strongly influenced by the sample matrix.

Therefore, the materials used to calibrate the instrument need to be as similar as possible to the unknown sample to be tested. If the unknown sample is a liquid, slurry, powder, or solid, the calibration materials need to be a similar liquid, slurry, powder, or solid. The preferred calibration materials will be made by (or come from) the same process as the unknown sample.

16.2 Calibrate the instrument according to the manufacturer's instructions using appropriate calibration standards.⁴

16.3 The following Sulfur Standards in Residual Fuel Oil are available from NIST:

SRM	Description
1620c	Sulfur in Residual Fuel Oil (4.0 %)
1623e	Sulfur in Residual Fuel Oil (0.3 %)
1622e	Sulfur in Residual Fuel Oil (2.0 %)
1621e	Sulfur in Residual Fuel Oil (1.0 %)
1619b	Sulfur in Residual Fuel Oil (0.7 %)

17. Procedure

17.1 Follow manufacturer's instructions for operation of the test equipment.

18. Report

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

19. Precision and Bias

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

19.2 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 3**.

19.3 A type 1 inter-laboratory precision program was conducted. Both repeatability and reproducibility represent short-term (daily) testing conditions. The testing was performed in each laboratory performing the test twice on each of two days (total of four tests). A test result is the value obtained from a single determination. Acceptable difference values were not measured.

19.4 The results of the precision calculations for this test are given in **Table 3** for the X-ray Fluorescence Method B. The materials are arranged in ascending “mean level” order.

19.5 *Repeatability*—The pooled absolute repeatability, r , of this test has been established as 0.05 %. Any other value in **Table 3** may be used as an estimate of repeatability, as appropriate. The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for this test will exceed the repeatability on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results that differ by more than the appropriate value from **Table 3** must be suspected of being from different populations and some appropriate action taken.

NOTE 4—Appropriate action may be an investigation of the test method

procedure or apparatus for faulty operation or the declaration of a significant difference in the two materials, samples, etc., which generated the two test results.

19.6 *Reproducibility*—The pooled absolute reproducibility, R , of this test has been established as 0.136 %. Any other value in **Table 3** may be used as an estimate of reproducibility, as appropriate. The difference between two single and independent test results found by operators working under the prescribed reproducibility conditions in different laboratories on identical test material will exceed the reproducibility on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results produced in different laboratories that differ by more than the appropriate value from **Table 3** must be suspected of being from different populations and some appropriate investigative action taken.

19.7 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by the test method. Bias, therefore, cannot be determined.

20. Keywords

20.1 carbon black; combustion; feedstock; hydrocarbon oil; sulfur content; x-ray fluorescence

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