Designation: D1619 – 20

Standard Test Methods for Carbon Black—Sulfur Content[1]

This standard is issued under the fixed designation D1619; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the determination of the sulfur content of carbon black. The following test methods are included:

		Sections
Test Method A	High-Temperature Combustion With Infrared Absorption Detection Procedures	6 to 13
Test Method B	X-Ray Fluorescence	14 to 19

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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.*

1.4 *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]

D1509 Test Methods for Carbon Black—Heating Loss
D1799 Practice for Carbon Black—Sampling Packaged Shipments
D1900 Practice for Carbon Black—Sampling Bulk Shipments
D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Significance and Use

3.1 The total sulfur content of a carbon black is useful in determining whether a material meets a customer's specifications, providing data for performing a sulfur material balance around a process for environmental monitoring and reporting, and in calculations for reconstructing a rubber composition from analytical data.

4. Reagents

4.1 *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.

5. Sampling

5.1 Samples of packaged materials shall be taken in accordance with Practice D1799 or Practice D1900.

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

6. Summary of Test Method

6.1 The specimen is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to oxidize the sulfur. Moisture and particulates are removed from the gas by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared (IR) absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted. Thus, at

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[1] These test methods are under the jurisdiction of ASTM Committee D24 on Carbon Black and are 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.

[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 *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis. This test method is empirical. Therefore, the apparatus must be calibrated by the use of standard reference materials (SRM).

6.2 This test method is for use with commercially available sulfur analyzers equipped to carry out the preceding operations automatically and must be calibrated using standard reference material (carbon black) of known sulfur content based on the range of sulfur in each carbon black specimen analyzed.

7. Apparatus

7.1 *Measurement Apparatus,* equipped to automatically combust the specimen.

7.2 *Combustion Tube,* made of mullite, porcelain, or zircon, approximately 40- to 45-mm inside diameter with a 3-mm thick wall, at least 450-mm long with provisions for routing the gasses produced by combustion through the infrared cell.

7.3 *Boat Puller*—Rod of a heat-resistant material with a bent or disk end to insert and remove boats from the combustion tube.

7.4 *Gravity Convection Drying Oven,* capable of maintaining 125 ± 5°C.

8. Reagents

8.1 *Purity of Reagents*—See 4.1.

8.2 *Magnesium Perchlorate.*

9. Preparation of Apparatus

9.1 Assemble the apparatus according to the manufacturer's instructions. Make a minimum of two determinations (see 10.3) to condition the equipment prior to calibrating the system.

10. Calibration

10.1 Select standards having sulfur values of approximately 0.5, 1.0, and 1.5 % sulfur[4].

10.2 *Adjustment of Response of Measurement System*—Weigh out approximately 0.5 g of the 1.0 % sulfur standard. Analyze the specimen (see Section 11). Repeat this procedure. Adjust instrument as recommended by the manufacturer until the absence of drift is indicated.

10.3 *Calibration Procedure*—Weigh out four specimens of the 1.0 % sulfur standard. Follow the calibration procedure recommended by the manufacturer. Confirm the calibration by analyzing the 1.0 % sulfur standard. The value should be within the allowable limits of the known value. If not, repeat the procedure. Then weigh out and analyze two specimens, each of the other calibration standards. Record the results after each analysis. Compare the results obtained to the known sulfur values of the specimens. They should be within the allowable limits of the known value of the respective specimen. If not, refer to the manufacturer's instructions for checking linearity of the analyzer.

11. Procedure

11.1 *Sample Preparation*—Dry an adequate sample of the carbon black for at least 1 h in a gravity-convection oven set at 125 ± 5°C, in an open container of suitable dimensions, so that the depth of black is no more than 10 mm. Cool to room temperature in a desiccator before use.

11.2 Stabilize and calibrate the analyzer (see 10.1 through 10.3).

11.3 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C. Weigh the specimen not to exceed more than 0.5 g of carbon black. Spread the specimen evenly in a combustion boat and use a boat puller to position the specimen in the hot zone of the furnace for at least 2 min, or until completely combusted.

NOTE 1—The analytical cycle should begin automatically as soon as sulfur is detected.

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

12. Report

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

12.2 Report results to the nearest 0.01 %.

13. Precision and Bias

13.1 These precision statements have been prepared in accordance with Practice D4483-99. Refer to this practice for terminology and other statistical details.

13.2 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 programs described in Table 1. 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.

13.3 Type 1 inter-laboratory precision programs were conducted as detailed in Table 1. Both repeatability and reproducibility represent short term (daily) testing conditions. The testing was performed using two operators in each laboratory performing the test once 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. The between operator component of variation is included in the calculated values for r, (r), R, and (R).

13.4 The results of the precision calculations for this test are given in Table 1. The materials are arranged in ascending

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[4] Coal standards have been found to be suitable standards and are usually available from the instrument manufacturer or may be obtained from Alpha Products for Analysis, 3090 Johnson Road, Stevensville, MI 49127, www.alpharesources.com.

TABLE 1 Precision Parameters for Test Methods D1619, Sulfur Content of Carbon Black (Type 1 Precision), Method A: Combustion[A]

Units are percent

Material	Period	Number of Laboratories (M/H/L)[B]	Mean Level	Sr	**r**	(r)	SR	**R**	(R)
STRM-A (SRB-8G)	Aug 2017	14(0/1/0)	0.022	0.002	**0.007**	29.791	0.021	**0.060**	269.841
STRM-B (SRB-8F2)	Mar 2015	11(0/2/0)	0.357	0.008	**0.023**	6.580	0.023	**0.065**	18.357
STRM-C (SRB-8B2)	Mar/Apr 2014	12(1/0/1)	0.791	0.010	**0.029**	3.646	0.026	**0.074**	9.343
STRM-D (SRB-8E2)	Aug 2016	17(0/1/0)	1.248	0.012	**0.034**	2.760	0.057	**0.161**	12.879
STRM-E (SRB-8D)	Mar 2017	15(0/0/1)	1.850	0.020	**0.056**	3.009	0.133	**0.376**	20.298
Average			0.854						
Pooled Values				0.012	**0.034**	3.959	0.067	**0.190**	22.242

[A] Preferred precision shown in bold text. Statistically, relative precision is preferred. However, the increase in relative precision limits when dealing with a mean value near zero, such as the SRB-8G material, makes the use of absolute precision more practical, so it is the preferred precision.

[B] M = number of outliers for Laboratory Mean as identified by Mandel h-value; H = number of outliers for High Laboratory variation as identified by a 2-sided test using the Mandel k-value; L = number of outliers for Low Laboratory variation as identified by a 2-sided test using the Mandel k-value. Low variation laboratories have variation that is less than expected based on the statistical evaluation of the data set.

"mean level" order. The preferred precision estimates are absolute (see bolded values in Table 1).

13.5 *Repeatability*—The pooled absolute repeatability, r, of this test has been established as 0.034 %. 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 2—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.

13.6 *Reproducibility*—The pooled absolute reproducibility, R, of this test has been established as 0.19 %. 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 two 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 or technical/commercial action taken.

13.7 *Bias*—Bias is the difference between a test value and a reference value. However, for this test method, bias has not been determined.

TEST METHOD B X-RAY FLUORESCENCE

14. Summary of Test Method

14.1 X-ray fluorescence may be used to determine sulfur in carbon black. Each element has an 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.

15. Apparatus

15.1 *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.

15.2 *Gravity Convection Drying Oven,* capable of maintaining 125 ± 5°C.

15.3 *Desiccator.*

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 X-ray fluorescence is not a primary test, but work by ASTM International Committee D24 on Carbon Black has shown that only carbon black with suitable levels of sulfur naturally occurring (that is, coming from the carbon black manufacturing process) can be used to properly calibrate the technique. It has been determined that a standard material cannot be made by adding elemental sulfur to carbon black.

16.3 Calibrate the instrument according to the manufacturer's instructions.