Designation: D 1619 – 99

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

This standard is issued under the fixed designation D 1619; 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 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

1.2 The values stated in SI units are to be regarded as 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter[2]

D 1193 Specification for Reagent Water[3]

D 1509 Test Methods for Carbon Black—Heating Loss[4]

D 1799 Practice for Carbon Black—Sampling Packaged Shipments[4]

D 1900 Practice for Carbon Black—Sampling Bulk Shipment[4]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[4]

E 1 Specification for ASTM Thermometers[5]

3. Significance and Use

3.1 The total sulfur content of a carbon black is useful 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.[6] 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.

4.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

5. Sampling

5.1 Samples shall be taken in accordance with Practice D 1799 or Practice D 1900.

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 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

[1] These test methods are under the jurisdiction of ASTM Committee D-24 on Carbon Black and are the direct responsibility of Subcommittee D24.31 on Non-Carbon-Black Components of Carbon Black.

Current edition approved Aug. 10, 1999. Published September 1999. Originally published as D 1619 – 58 T. Last previous edition D 1619–97.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 09.01.

[5] *Annual Book of ASTM Standards*, Vol 14.03.

[6] *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.

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.

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 black standard reference materials (SRM) containing known sulfur values of approximately 0.5, 1.0, and 1.5 % sulfur.

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

11.2 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.

11.3 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.

13. Precision and Bias

13.1 These precision statements have been prepared in accordance with Practice D 4483. 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 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

13.3 A type 1 inter-laboratory precision program was conducted as detailed in Table 2. 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 and R.

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

13.5 *Repeatability*—The pooled relative repeatability, (r), of this test has been established as 5.5 %. 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

TABLE 1 Precision Parameters for D 1619 Sulfur Content, Method B, (Type 1 Precision)

Units	Percent Sulfur				
Material	Mean Level	Sr	(r)	SR	(R)
IRB#6 (N330)	1.11395	0.01979	5.0	0.05440	13.8
SRB A5 (N135)	1.22003	0.02582	6.0	0.14246	33.0
SRB N762	1.39269	0.02105	4.3	0.07174	14.6
N550	1.70521	0.04220	7.0	0.12184	20.2
N650	1.92001	0.02888	4.3	0.13966	20.6
Average	1.47038				
Pooled Values		0.02869	5.5	0.11203	21.6

TABLE 2 Interlaboratory Precision Program

Nominal Test Period	Material	Number of Laboratories
March 1996	N650	27
October 1996	IRB#6 (N330)	22
March 1997	SRB N762	27
September 1997	SRB A5 (N135)	25
March 1998	N550	29

significant difference in the two materials, samples, etc., which generated the two test results.

13.6 *Reproducibility*—The pooled relative reproducibility, (R), of this test has been established as 21.6 %. 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*—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.

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. Since there are different types of instruments, no detail of testing can be given here. Follow manufacturer's instructions for operation of test.

14.2 X-ray fluorescence is not a primary test, but work by D24 has shown that only carbon black with suitable levels of sulfur naturally occuring can be used to properly calibrate the technique. Four carbon black standards have been identified[7] and their respective sulfur level determined by combustion methods following D 1619 calibration procedures. They are:

	% sulfur	std deviation
Standard A	0.00	0.00
Standard B	1.54	0.05
Standard C	1.93	0.06
Standard D	0.82	0.03

15. Keywords

15.1 carbon black; high temperature combustion; infrared titration; oxygen bomb calorimeter; sulfur content; sulfur dioxide

[7] Sulfur-in-carbon black standards A-D are available from Titan Industries, P.O. Box 2316, Pampa, TX 79065.