Designation: D 5016 – 98

Standard Test Method for
Sulfur in Ash from Coal, Coke, and Residues from Coal Combustion Using High-Temperature Tube Furnace Combustion Method with Infrared Absorption[1]

1. Scope

1.1 This test method describes a procedure using a high-temperature tube furnace and infrared detection for the rapid determination of sulfur in ash from coal and coke.

1.2 This test method is an alternative for test methods described in Test Methods D 1757.

1.3 The values stated in SI units (Practice E 380) shall be regarded as the standard.

1.4 *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 1757 Test Methods for Sulfur in Ash from Coal and Coke[2]
D 2795 Test Methods for Analysis of Coal and Coke Ash[2]
D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]
D 3682 Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption[2]
D 4326 Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence[2]
D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]
D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]
E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)[3]

3. Summary of Test Method

3.1 A weighed test portion is mixed with a promoting agent and ignited in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen (see Note 1). The combustible sulfur contained in the test portion is oxidized to gaseous oxides of sulfur. Moisture and particulates are removed by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared 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. 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.

NOTE 1—The promoter aids in the quantitative release of all sulfur present in the test portion as SO_2. Refer to the instrument manufacturer's recommended procedure for using oxidizing agents or promoters commonly referred to as "combustion accelerators."

3.2 This test method is applicable for use with commercially available sulfur analyzers equipped to carry out the operations in 3.1 automatically, and must be calibrated using certified reference materials (CRM's) covering the range of sulfur in the ash samples being analyzed.

4. Significance and Use

4.1 The purpose of this test method is to determine the percent sulfur trioxide (SO_3) portion of the major and minor elements in coal ash.

4.2 This test method may be used to determine the percent sulfur trioxide (SO_3) portion of ash determined by Test Methods D 3174 or D 5142 for coals containing high amounts of calcium. The ash may then be reported on a sulfur trioxide free basis.

5. Apparatus

5.1 *Tube Furnace*, electrically heated, capable of heating 150 to 165-mm length of the hot zone area of the combustion tube (see 5.2) to at least 1350°C. Specific dimensions can vary with manufacturer's design.

5.2 *Combustion Tube*, made of mullite, porcelain, or zircon,

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[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

Current edition approved Sept. 10, 1998. Published December 1998. Originally published as D 5016 – 89. Last previous edition D 5016 – 95.

[2] *Annual Book of ASTM Standards*. Vol 05.05.

[3] *Annual Book of ASTM Standards*. Vol 14.02.

approximately 23-mm inside diameter with a 3-mm thick wall, at least 450 mm long with means to route the gases produced by combustion through the infrared cell.

5.3 *Sample Combustion Boats*, made of iron-free material and of a convenient size suitable for the instrument being used.

5.4 *Boat Puller*, rod of a heat resistant material with a bent or disk end used to insert and remove boats from the combustion tube.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used unless otherwise specified. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications exist.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without affecting the accuracy of the determination.

6.2 *Magnesium Perchlorate* ($Mg(ClO_4)_2$)—**Warning:** Magnesium perchlorate is a strong oxidizing agent. Do not attempt to regenerate the absorbent. Do not permit contact with organic materials or reducing agents.

6.3 *Promotor*—Refer to the instrument manufacturer's recommended combustion accelerator. Suitable combustion accelerators include vanadium pentoxide, iron powder, and charcoal.

NOTE 2—**Caution:** Some promoters may contain sulfur. The user shall determine the sulfur content of the promoter by analyzing it as a sample and make appropriate corrections in 9.1 based on the mass of the promoter and its sulfur content.

6.4 *Oxygen, 99.5 % Pure*—Compressed gas contained in a cylinder equipped with a suitable pressure regulator and needle valve to control gas flow. **Warning**—Pure oxygen vigorously accelerates combustion. All regulators, lines, and valves shall be free of grease and oil.

7. Sampling

7.1 For SO_3 determination to complement major elements in ash analysis, the sample is prepared in accordance with Test Method D 2795, Test Method D 3682, or Test Method D 4326.

7.2 For SO_3 correction of ash as determined by Test Methods D 3174 or D 5142, the sample shall consist of the combined ash from duplicate samples of coal or coke as determined in accordance with that test method.

NOTE 3—Ashing temperature, heating rate, and furnace ventilation have an important influence on SO_3 retention; thus, observing the prescribed ashing conditions is important. Sulfur in ash as determined by these methods cannot be strictly related to the sulfur oxides retained in ash produced under the conditions of combustion in boiler furnaces, or other commercial combustion processes.

NOTE 4—This test method can require up to 300 mg of ash per determination of percent SO_3 with reference to Test Method D 2795, Test Method D 3174, Test Method D 3682, Test Method D 4326 or Test Method D 5142; therefore, it can be necessary to ash additional coal or coke.

7.3 *Certified Reference Materials (CRMs):*

NIST Coal Fly Ash—SRM 1633b, 2689, 2690, 2691

NIST Cements—SRM 1880, 1881M, 1884, 1885, 1886, 1887, 1888, 1889

8. Procedure

8.1 *Instrument Preparation*—All instrument preparation is to be done in accordance with the manufacturer's instructions.

8.2 *Calibration of the Infrared Detection System*—Select Certified Reference Materials (CRM's) with known dry-basis sulfur values in the range of the samples to be analyzed. For the initial calibration and periodic verification of instrument linearity, at least three such CRM's are recommended for each range of sulfur values to be determined. Two of the CRM's should bracket the range of sulfur values to be tested and the third should be near the mid-point of the expected range. When performing a single point calibration use a CRM that has a sulfur value higher than the expected range of the samples to be analyzed. Records for all calibrations will be maintained in accordance with Guide D 4621.

8.2.1 *Calibration Procedure*—Make a minimum of two determinations to condition the equipment prior to beginning the calibration procedure. The as-determined sulfur value of the CRM shall be used for calibration of the system. This value must have been previously calculated from the certified dry-basis sulfur value and residual moisture determined using either Test Methods D 3173, D 5142, or the procedure recommended by the vendor of the CRM. Alternatively, a quantity of the CRM can be dried using the previously mentioned procedures for determining moisture, in which case the dry basis sulfur value can be used. That quantity of CRM dried for calibration of the system must be stored in a desiccator and any portion remaining at the end of the normal working period must be discarded. Weigh a minimum of five samples of the CRM chosen to represent the range of sulfur values to be tested. Calibrate the instrument according to the manufacturer's instructions using results of five determinations on the CRM that are within the certified uncertainty limits of that CRM. Verify proper calibration by analyzing CRM's that bracket the range of sulfur values to be tested. These results must also be within the CRM's certified uncertainty limits.

8.2.2 *Periodic Calibration Verification*—On a periodic basis, verify the stability of the instrument and its calibration by analyzing a control sample. This control sample may be a CRM used for calibration or any other reference material that is certified for its sulfur content. The results of this determination must be within the certified uncertainty limits of that CRM, or reference material. If the criteria for a successful verification of calibration in accordance with Guide D 4621 are not met, the calibration procedure of Section 8.2.1 shall be repeated.

8.3 *Analysis Procedure:*

8.3.1 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C.

8.3.2 Stabilize and calibrate the analyzer (see 8.2).

8.3.3 Weigh 300 mg of the test sample to the nearest 0.1 mg for ash and combustion residue containing up to 5 % SO_3 and 140 mg to the nearest 0.1 mg for test samples containing over 5.0 % SO_3. Carefully blend the weighed test portion with a promoting agent, then spread the mixture evenly in the

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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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

combustion boat. Position the combustion boat in the hot zone of the furnace until the release of sulfur dioxide is completed as indicated by the instrument's return to baseline.

8.3.4 When the analysis is complete, the instrument should indicate the percent sulfur trioxide (SO_3). Refer to the manufacturer's recommended procedure.

9. Calculation and Report

9.1 Report results as percent sulfur trioxide (SO_3) in the ash.

9.2 Calculate ash on sulfur trioxide free basis as follows:

$$B = \frac{A(100 - S)}{100} \tag{1}$$

where:

A = percent ash as determined by Test Method D 3174,
B = percent ash on a sulfur trioxide free basis, and
S = percent sulfur trioxide in ash.

10. Precision and Bias

10.1 This test method is highly dependent upon the calibration of the equipment and the closeness of the standards to the samples in sulfur content.

10.2 *Precision*—The relative precision of this test method for the determination of sulfur in coal ash covers the concentration range from 0.8 to 12.9 % as sulfur trioxide.

10.2.1 *Repeatability*—The difference in absolute value between two consecutive tests results, performed on the same sample, in the same laboratory, by the same operator, using the same apparatus should not exceed the repeatability interval I(r) more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both of the test results. The repeatability interval may be determined by use of the following equation:

$$I(r) = 0.02 + 0.06\bar{x} \tag{2}$$

where $\bar{x}$ is the average of the two test results.

NOTE 5—Eq 2 applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for sulfur gave values of 9.78 and 9.95 %. The average sulfur of the duplicate analysis is 9.86 % and the calculated repeatability interval I(r) is 0.61. The difference between the two sulfur values is 0.17 and does not exceed the I(r) of 0.61; therefore, these two values are acceptable at the 95 % confidence level.

10.2.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval I(R) more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval may be determined by use of the following equation:

$$I(R) = 0.14 + 0.08\bar{x} \tag{3}$$

where $\bar{x}$ is the average of the between-laboratory results.

NOTE 6—Eq 3 applies to the relative spread of a measurement as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* duplicate analysis for sulfur in one laboratory gave an average value of 3.65 % and a value of 3.43 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.54 %, the calculated I(R) interval is 0.42 %, and the difference between the different laboratory values is 0.22 %. Since this difference is less than the I(R), these two values are acceptable at the 95 % confidence level.

10.3 *Bias*—If the instrument is calibrated with standard reference materials (SRM), such as the SRM's from NIST, there should be no bias.

11. Keywords

11.1 coal ash; coke ash; sulfur