



Designation: ~~D 5016-07~~ Designation: D 5016 – 07a

~~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~~ Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption¹

This standard is issued under the fixed designation D 5016; 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 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 D1757.~~

~~1.3 The values stated in SI units (IEEE/ASTM SI 10) shall be regarded as the standard.~~

~~1.4~~

1.1 This test method describes a procedure using a high-temperature tube furnace and infrared detection for the determination of sulfur in coal and coke combustion residues, including lab ashes and residues from coal and coke combustion.

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 and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards:*²

~~D1757 Test Method for Sulfate Sulfur in Ash from Coal and Coke~~

~~D2795 Test Methods for Analysis of Coal and Coke Ash~~ 121 Terminology of Coal and Coke

~~D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal~~

~~D 3682 Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes~~ 016-07a

~~D 3683 Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption~~

~~D 4326 Test Method for Major and Minor Elements in Coal and Coke Ash By X-Ray Fluorescence~~

~~D 4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke~~

~~D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures~~

~~IEEE/ASTM SI 10 American National Standard for Use of the International System of Units (SI): The Modern Metric System~~

~~2.2 ISO Standard~~

~~ISO 5725-6 Accuracy of measurement methods and results-Part 6~~

~~D 6349 Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma Atomic Emission Spectrometry~~

~~D 6357 Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption~~

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~~

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

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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.

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 SO₂. 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. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology D 121.

4. Significance and Use

4.1 The purpose of this test method is to determine the percent sulfur trioxide (SO₃) portion of the major and minor elements in coal ash.

4.2 This test method may be used to determine the percent sulfur trioxide (SO₃) portion of ash determined by Test Methods D3174 or D5142 for coals containing high amounts of calcium. The ash may then be reported on a sulfur trioxide free basis. Summary of Test Method

4.1 A weighed test portion is mixed with a promoting agent and ignited in a tube furnace an operating temperature of 1450°C in a stream of oxygen. 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.

4.2 This test method is applicable for use with sulfur analyzers equipped to carry out the operations in 4.1 and must be calibrated using reference materials (RM's) covering the range of sulfur in the ash samples being analyzed.

5. Significance and Use

5.1 The percent sulfur content of the ash derived from coal or coke can be calculated to sulfur trioxide content. This information can be used in combination with results from the determination of major, minor and or trace elements in the same ash to calculate results on a sulfur trioxide free-basis or to calculate total recovered analyte.

6. Interferences

6.1 Known interferences in this test method are some alkaline earth metal ions, including barium and strontium, which form stable sulfate salts that are difficult to decompose. To minimize this interference a promoting agent shall be used to help decompose these salts. These promoting agents can have one or more of the following properties, (1) oxidizing agent, (2) reducing agent and (3) fluxing agent. Oxidizing and reducing agents help decompose the metal sulfates through the oxidation or reduction of the sulfate or metal ions, or both. The fluxing agent helps decompose the metal sulfates by fusing the salt, which leads to the decomposition of sulfates on further heating. Some promoting agents may contain sulfur, which needs to be addressed with their use.

7. Apparatus

5.1

7.1 Tube Furnace, electrically heated, capable of heating 150 to 165-mm length of the hot zone area of the combustion tube (see 5.27.2) to at least 1350°C. Specific dimensions can vary with manufacturer's design.

5.27.2 Combustion Tube, made of mullite, porcelain, or zircon, 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

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

5.4

7.4 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.

8. Reagents

6.1

8.1 *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.^{3,4} 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

8.2 *Magnesium Perchlorate (Mg(ClO₄)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

8.3 *Promotor*—Refer to the instrument manufacturer's recommended combustion accelerator. Suitable combustion accelerators include vanadium pentoxide, iron powder, and charcoal. —COM-CAT Combustion promoter⁵.

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 *1—COM-CAT⁵ is a promoting agent that is both a fluxing agent and oxidizing agent.*

8.4 *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 SO₃ determination to complement major elements in ash analysis, the sample is prepared in accordance with Test Method D2795, Test Method D3682, or Test Method D4326. Pure oxygen vigorously accelerates combustion. All regulators, lines, and valves shall be free of grease and oil.

9. Hazards

9.1 The user shall ensure acceptable documented safety procedures are in place for the handling of all reagents and test materials and for the operation of laboratory equipment specified for this test method.

10. Calibration Materials and Test Samples

10.1 *Calibration Materials*—Employ reference materials (RMs) for calibration and control. Reference material coal, coke and ash samples can be used for calibration. A reference material (RM) shall be a Certified Reference Material (CRM) from recognized certifying agencies such as the National Institute for Science and Technology (NIST) or the South African Bureau of Standards (SABS), an External Reference Material (ERM) available from suppliers that provide details of traceability to a recognized CRM with a similar matrix and composition, or an Internal Reference Material (IRM) that has been validated to use through intercomparison with one or more CRMs or ERMs traceable to a CRM.

10.2 For total sulfur in ash determination to complement major and minor elements in ash analysis, the ash sample is prepared in accordance with Test Methods D 3682, D 4326, or D 6349.

7.2 For SO₃ correction of ash as determined by Test Methods D3174 or D5142

10.3 For total sulfur in ash determination to calculate total recovered analyte in conjunction with the determination of trace elements, the ash sample is prepared in accordance with Test Methods D 3683 or D 6357.

10.4 For sulfur 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 2**—Ashing temperature, heating rate, and furnace ventilation have an important influence on SO₃ sulfur 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 3**—This test method can require up to 300 mg of ash per determination of percent SO₃ sulfur with reference to Test Method D2795, Test Method D 3174, Test Method D 3682, Test Method D 4326 or Test Method D5142, Test Method D 5142, or Test Method D 6349; therefore, it can be necessary to ash additional coal or coke.

³ Available from International Organization for Standardization (ISO), 1 rue de Varembe, Case postale 56, CH-1211, Geneva 20, Switzerland, <http://www.iso.ch>.

³ Interested parties are invited to submit information regarding the identification of alternatives to ASTM international Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

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.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1033.

⁵ The sole source of supply of COM—CAT known to the committee at this time is LECO Corporation, 3000 Lakeview Ave. St Joseph, MI 49085 USA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

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:

11. 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 D4621

11.1 *Instrument Preparation/Verification*—Use of COM-CAT⁵ requires the instrument to meet the parameters listed in Table 1. Verify the instrument meets these specifications before conducting instrument calibration or analysis.

11.2 *Calibration of the Infrared Detection System* —Select Reference Materials (RMs) with known 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 RMs are recommended for each range of sulfur values to be determined. Two of the RMs should bracket the range of sulfur values to be tested and the third should be near the mid-point of the expected range. Records for all calibrations will be maintained in accordance with Guide D 4621.

8.2.1 *11.2.1 Calibration Procedure*—Make a minimum of two six 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 RM’s used for calibration shall not be tested. Calibrate the instrument according to the manufacturer’s instructions using results degree of five determinations on the CRM that are within the certified uncertainty limits of that CRM. Verify calibration curve plus two. Table 2 summarizes these requirements.

11.2.2 *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 *11.2.3 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 or an RM 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 *11.2.1* 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)*

11.3 *Analysis Procedure:*

11.3.1 *Stabilize and calibrate the analyzer (see 11.2).*

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% SO₃ and 140 mg to the nearest 0.1 mg for test samples containing over 5.0% SO₃. Carefully blend the weighed test portion with a promoting*

TABLE 1 Concentration Range and Limits for Repeatability and Reproducibility for Total Sulfur in Ash from Coal, Coke, and Residues from Coal Combustion

Range %	Re 1450 °C
Furnace Temperature	1450 °C
Repeatability Limit (r) ^A	Reproducibility Limit (R) ^A
Comparator Level	0.3
Lance Delay	0.06X + 0.06
Minimum Run Time	10
Maximum Run Time	0.2 X + 0.2 seconds
	120 seconds
	300 seconds

^Awhere \bar{x} is the average of two single test results.