



# Standard Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption<sup>1</sup>

This standard is issued under the fixed designation D5016; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Table A1.1 was editorially revised in July 2009.

## 1. Scope

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:<sup>2</sup>

[D121 Terminology of Coal and Coke](#)

[D3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal](#)

[D3682 Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes](#)

[D3683 Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption](#)

[D4326 Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence](#)

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[D4621 Guide for Quality Management in an Organization That Samples or Tests Coal and Coke](#)

[D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures](#)

[D6349 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](#)

[D6357 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 Ab](#)

## 3. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology [D121](#).

3.2 Throughout this test method the term ash is used to describe the sample being analyzed. The term ash is to be interpreted as a combustion residue.

## 4. Summary of Test Method

4.1 A weighed test portion is mixed with a promoting agent and ignited in a tube furnace at 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 (RMs) 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. In order to have an accurate analysis of the material all mineral sulfates must be decomposed to yield sulfur dioxide, which is then presented to the IR detection system for measurement. To minimize interferences 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

7.1 *Tube Furnace*, electrically heated, capable of heating 150 to 165-mm length of the hot zone area of the combustion tube (see 7.2) to at least 1350°C. Specific dimensions can vary with design.

7.2 *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.

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

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.

## 8. Reagents

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.<sup>3,4</sup> 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.

8.2 *Magnesium Perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>)*—**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.

8.3 *Promotor*—COM-CAT Combustion promoter<sup>5</sup>.

NOTE 1—COM-CAT<sup>5</sup> 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.

## 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 RMs for calibration and control. Reference material coal, coke and ash samples can be used for calibration. A 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 D3682, D4326, or D6349.

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 D3683 or D6357.

10.4 For sulfur correction of ash as determined by Test Methods D3174 or D5142, the sample shall consist of the

<sup>3</sup> 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.

<sup>4</sup> *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.

<sup>5</sup> 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,<sup>1</sup> which you may attend.

**TABLE 1 Instrument Parameters**

Furnace Temperature	1450°C
Comparator Level	0.3
Lance Delay	10
Minimum Run Time	120 seconds
Maximum Run Time	300 seconds

**TABLE 2 Number of Reference Materials Needed for Calibration**

Curve Type	Degree	Minimum Number of RMs
Linear	1	3
Quadratic	2	4
Cubic	3	5

combined ash from duplicate samples of coal or coke as determined in accordance with that test method.

NOTE 2—Ashing temperature, heating rate, and furnace ventilation have an important influence on 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 3—This test method can require up to 300 mg of ash per determination of percent sulfur with reference to Test Method D3174, Test Method D3682, Test Method D4326, Test Method D5142, or Test Method D6349; therefore, it can be necessary to ash additional coal or coke.

## 11. Procedure

11.1 *Instrument Preparation/Verification*—Use of COM-CAT<sup>5</sup> requires the instrument to meet the parameters listed in Table 1. Verify the instrument meets these specifications before conducting instrument calibration or analysis (see Note 4).

11.2 *Calibration of the Infrared Detection System*—Calibration of the infrared detector system is accomplished when a measurable amount of sulfur dioxide is presented for detection using the conditions outlined in Table 1. 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 D4621.

NOTE 4—The use of a combustion promoter is required for the analysis of ash and combustion residues (6.1). Calibration of the sulfur analyzer may be done with coal or coke RMs. The use of a combustion promoter is not necessary for coal or coke RMs, since the materials themselves are excellent reducing agents that decompose mineral sulfates in the RMs.

11.2.1 *Calibration Procedure*—Make a minimum of six determinations to condition the equipment prior to beginning the calibration procedure. The as-determined sulfur value of the RM 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 D3174, D5142, or the procedure recommended by the vendor of the RM. Alternatively, a quantity of the RM 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 RM 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. The number of RMs used for calibration shall not be less than the degree of the calibration curve plus two. Table 2 summarizes these requirements.

11.2.2 Verify proper calibration by analyzing RMs that bracket the range of sulfur values to be tested. These results must also be within the RMs certified uncertainty limits.

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 an RM used for calibration or any other reference material that is certified for its sulfur content (see Note 5). The results of this determination must be within the certified uncertainty limits of that reference material. If the criteria for a successful verification of calibration in accordance with Guide D4621 are not met, the calibration procedure of 11.2.1 shall be repeated.

NOTE 5—Some RMs, especially ashes with very low sulfur contents, may not be acceptable for use as periodic calibration verifications. This is due to the difficulty of decomposing the mineral sulfates in the ash and the low sulfur contents. The infrared detection system only functions to measure the sulfur dioxide presented for measurement.

### 11.3 Analysis Procedure:

11.3.1 Stabilize and calibrate the analyzer (see 11.2).

11.3.2 Weigh 250 mg of the test sample to the nearest 0.1 mg (sample weight may have to be adjusted in order for the sulfur concentration to land within the calibration range). Carefully blend the weighed test portion with approximately 1.0 g COM-CAT<sup>5</sup>. Spread the mixture evenly in the 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.

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

NOTE 6—For instrumentation with a fixed furnace temperature (usually 1350°C), sulfur dioxide may not be completely released from the test sample. Annex A2 describes alternate procedures using extended analysis times and/or alternative promoting agents that can be employed under these conditions.

## 12. Calculations

12.1 Calculate percent sulfur trioxide (SO<sub>3</sub>) in the ash as follows:

$$SO_3 \text{ in ash, \%} = 2.5 \times S_T \quad (1)$$

where:

$S_T$  = sulfur % determined on the test sample.

12.2 Calculate ash on sulfur trioxide free-basis as follows:

$$B = A \times (100 - S)/100 \quad (2)$$

$A$  = percent ash as determined by Test Method D3174 or Test Method D5142

$B$  = percent ash on a sulfur trioxide-free basis

$S$  = percent sulfur trioxide in ash from 12.1

**TABLE 3 Concentration Range and Limits for Repeatability and Reproducibility for Total Sulfur in Coal and Coke Combustion Residues**

Range %	Repeatability Limit (r) <sup>A</sup>	Reproducibility Limit (R) <sup>A</sup>
0.7-3.8	0.06 $\bar{X}$ + 0.06	0.2 $\bar{X}$ + 0.2

<sup>A</sup>where  $\bar{X}$  is the average of two single test results.

**TABLE 4 Comparison of Certified Values for NIST 1633b with Interlaboratory Study Values for Total Sulfur in Coal and Coke Combustion Residues**

Reference CRM	RR value, %	CRM value, %	Bias, Relative %	Significant (95% Confidence Level)
NIST 1633b	0.1907	0.2075	-8.10	Yes

### 13. Precision and Bias

13.1 *Precision*—The precision of this test method for the determination of sulfur in the analysis sample of coal and coke combustion residues is shown in [Table 3](#). The precision characterized by the repeatability ( $S_r$ ,  $r$ ) and reproducibility ( $S_R$ ,  $R$ ) is described in [Table A1.1](#) in [Annex A1](#).

13.1.1 *Repeatability Limit (r)*—the value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95%.

13.1.2 *Reproducibility Limit (R)*— the value below which the absolute difference between two test results carried out in different laboratories using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95%.

13.2 *Bias*—Certified reference material NIST 1633b was included in the interlaboratory study to ascertain a possible bias between the reference material value and that determined by

this method. A comparison between the NIST value and the value obtained in the interlaboratory study is shown in [Table 4](#).

NOTE 7—The analysis of several reference materials, spanning the concentration range of interest, is the most meaningful way to investigate measurement bias. When a matrix match is possible, the uncertainty in sample measurements can be equated to that observed in measurement of the RM. When such a match is not possible, but a RM with a related matrix is available, the test sample uncertainty may be related to those observed when measuring the RM. Different methods of measurement of a property may not be capable of equal repeatability. Accordingly, instances could arise where the method of measurement has greater variability than that of those used in certification of the RM8.

13.3 An interlaboratory study, designed consistent with Practice E691, was conducted in 2003. Twelve laboratories participated. The details of the study and the supporting data are given in a Research Report filed at ASTM headquarters.<sup>6</sup>

### 14. Keywords

14.1 coal ash; coke ash; sulfur

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D05-1033.

## ANNEXES

### A1. PRECISION STATISTICS

A1.1 The precision of this test method, characterized by repeatability ( $S_r$ ,  $r$ ) and reproducibility ( $S_R$ ,  $R$ ) has been

determined for the following materials as listed in [Table A1.1](#).

**TABLE A1.1 Repeatability ( $S_r$ ,  $r$ ) and Reproducibility ( $S_R$ ,  $R$ ) Parameters Used for the Calculation of Precision Statement**

Materials	Average	$S_r$	$S_R$	$r$	$R$
1633b	0.19067 <sup>†</sup>	0.00921	0.01569	0.0258	0.04394
APBA	0.06919	0.00582	0.0144	0.01629	0.04032
BD	0.30605	0.01171	0.03036	0.03279	0.085
BHA	1.74675	0.04919	0.15276	0.13773	0.42773
ESP5	3.14143	0.14028	0.32076	0.39278	0.89811
LP1	1.4066	0.02739	0.06569	0.07668	0.18393
LP2	3.8102	0.07168	0.21425	0.2007	0.59989
SDA	2.3825	0.09103	0.15721	0.25488	0.4402
SFA	1.74825	0.0652	0.12927	0.18255	0.36195

<sup>†</sup> Editorially revised in July 2009.

**TABLE A2.1 Procedural Comparison for the Sulfur Analysis of Sample CA-18 Using COM-CAT**

Furnace Temperature Control	Analysis Temperature °C	T-Max s	Time Day 1-1	Time Day 1-21	Time Day 2-1	Time Day 2-2	Sulfur Day 1-1	Sulfur Day 1-2	Sulfur Day 2-1	Sulfur Day 2-2	Average S, %
Variable	1450	300	223	300	241	300	2.43	2.39	2.48	2.43	2.43
Fixed	1350	300	300	300	300	300	1.97	2.04	2.15	2.11	2.07
Fixed	1350	480	378	438	441	401	2.47	2.44	2.36	2.40	2.42

## A2. ALTERNATIVE PROCEDURES

A2.1 Sulfur analyzers with furnaces that are not able to attain an operating temperature of 1450 °C can be employed for the determination of sulfur in coal and coke combustion residues. When employing such a system (usually fixed at 1350 °C) the maximum analysis time (T-Max) shall be increased to allow for more complete SO<sub>2</sub> release. Increase the maximum analysis time in 60 second increments until the observed analysis time approaches, but does not exceed, the maximum allowed setting. For sample CA-18 below, T-Max was increased to 480 seconds.

A2.2 Following the Test Method D5016 procedure (Section

11) there is complete release of SO<sub>2</sub> using the higher furnace temperature, as shown in [Table A2.1](#). CA-18 is a fly ash that contains 1.57% (by wt.) barium oxide. Analyzing sample CA-18 using this procedure, except with a temperature of 1350 °C, resulted in incomplete sulfur recovery. This occurred even though the preset T-Max (300 seconds) was achieved in all replicates indicating longer analysis times are necessary. Analyzing sample CA-18 using the standard procedure and a temperature of 1350 °C with an adjusted T-Max (480 seconds), resulted in a more complete recovery of sulfur (2.42%)

## A3. ALTERNATIVE PROMOTER

A3.1 An alternative promoter, such as vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), can be used in place of COM-CAT<sup>5</sup>. Vanadium pentoxide may be more readily available, however, it is also a health hazard. **Warning**—V<sub>2</sub>O<sub>5</sub> is highly toxic, an irritant, and a possible mutagen.

A3.2 Three laboratories analyzed the WAL-1 combustion residue using both promoting agents at 1450 °C. The sample was run in duplicate on two different days. The average values for the four runs are listed in [Table A3.1](#). The combined averages of the three laboratories are also listed in the last column. The sulfur recovery for WAL-1 was similar for each laboratory at 1450 °C, regardless of which promoter was used.

A3.3 In a second experiment the combustion residue sample CA-18 was analyzed using both promoting agents at 1350 °C. The sample was run in duplicate on two different days. The average values for the four runs are listed in [Table A3.2](#). The combined averages of the three laboratories are also listed in the last column. The data in [Table A3.2](#) show complete sulfur recovery is not achieved with COM-CAT<sup>5</sup> for this sample under these conditions. Also, two of the three laboratories reach T-Max with COM-CAT<sup>5</sup>. By comparison analysis times are much shorter with V<sub>2</sub>O<sub>5</sub>, and a more complete sulfur recovery occurs. These data indicate V<sub>2</sub>O<sub>5</sub> is a more aggressive promoter and is recommended for difficult samples at 1350 °C.

**TABLE A3.1 Promoter Comparison for the Analysis of Sulfur in Ash Sample WAL-1 at 1450 °C**

Promoter	Analysis Temperature (°C)	Lab 1		Lab 2		Lab 3		Average of 3 Labs	
		Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur
COM -CCAT	1450	181	1.76	139	1.60	156	1.71	159	1.69
V <sub>2</sub> O <sub>5</sub>	1450	139	1.78	138	1.60	161	1.72	146	1.70

**TABLE A3.2 Promoter Comparison for the Analysis of Sulfur in Ash Sample CA-18 at 1350 °C**

Promoter	Lab 1		Lab 2		Lab 3		Average of 3 Labs	
	Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur	Avg Analysis Time (Sec)	Avg % Sulfur
COM -CCAT	300	2.11	244	2.27	300	2.38	281	2.25
V <sub>2</sub> O <sub>5</sub>	184	2.46	169	2.3	263	2.43	225	2.40

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