



Designation: **D4239—12 D4239 – 13**

## Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High- Temperature Tube Furnace Combustion<sup>1</sup>

This standard is issued under the fixed designation D4239; 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.

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

### 1. Scope

1.1 This test method covers the determination of sulfur in samples of coal or coke by high-temperature tube furnace combustion.

1.1.1 Two analysis methods are described.

1.2 When automated equipment is used, either method can be classified as an instrumental method.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:*<sup>2</sup>

[D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis](#)

[D2013 Practice for Preparing Coal Samples for Analysis](#)

[D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke](#)

[D3176 Practice for Ultimate Analysis of Coal and Coke](#)

[D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases](#)

[D7448 Practice for Establishing the Competence of Laboratories Using ASTM Procedures in the Sampling and Analysis of Coal and Coke](#)

[D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

2.2 *ISO Standard:*<sup>3</sup>

[ISO 11722 Solid Mineral Fuels—Hard Coal – Determination of Moisture in the general analysis test sample by drying in nitrogen](#)

### 3. Summary of Test Method

3.1 *Combustion Method A (1350°C)*—A weighed test portion of sample is burned in a tube furnace at a minimum combustion tube operating temperature of 1350°C in a stream of oxygen. During combustion at temperatures above 1350 °C, the sulfur and sulfur compounds contained in the sample are decomposed and oxidized almost exclusively to gaseous sulfur dioxide, SO<sub>2</sub>. Moisture and particulates are removed from the gas by filters. 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.

3.1.1 One procedure for Method A uses coal or coke reference materials to calibrate the sulfur analyzer. A second procedure for Method A uses a pure substance, BBOT, to calibrate the sulfur analyzer.

<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 D05.21 on Methods of Analysis. Current edition approved Feb. 1, 2012. Oct. 1, 2013. Published February 2012. Originally approved in 1983. Last previous edition approved in 2011 as [D4239—11](#); [D4239 – 12](#). DOI: [10.1520/D4239-12.10.1520/D4239-13](#).

<sup>2</sup> 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.

<sup>3</sup> Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, [http://www.iso.ch](#).

3.2 *Combustion Method B (1150°C)*—A weighed test portion of sample is burned in a quartz combustion tube in a stream of oxygen with an equal or excess weight of tungsten trioxide ( $WO_3$ ). Sulfur is oxidized during the reaction of the sample and  $WO_3$ . The tube furnace is operated at a minimum combustion tube operating temperature of 1150°C and tin (Sn) sample boats are utilized. Moisture and particulates are removed from the combustion gas by filters. The gas stream is then 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.

4. Significance and Use

4.1 Sulfur is part of the ultimate analysis of coal and coke.

4.2 Results of the sulfur analysis are used for evaluation of coal preparation and cleaning, evaluation of potential sulfur emissions from coal and coke combustion or conversion processes, and evaluation of coal and coke quality in relation to contract specifications, as well as for scientific purposes.

4.3 The competency of laboratories with respect to use of this standard can be established through reference to Practice D7448.

5. Sample

5.1 Pulverize the sample to pass No. 60 (250- $\mu$ m) sieve and mix thoroughly in accordance with Practice D2013 or Practice D346.

5.2 Analyze a separate portion of the analysis sample for moisture content in accordance with Test Method D3173, or D7582 or ISO 11722 for calculations to other than the as-determined basis.

5.3 Procedures for calculating as-determined sulfur values obtained from the analysis sample to other bases are described in Practices D3176 and D3180.

6. Apparatus

Combustion Method A (1350°C)

6.1 *Measurement Apparatus*—Equipped to combust the sample as described in 3.1 (See Fig. 1).

6.2 *Tube Furnace*—Capable of heating the hot zone or outer surface of the combustion tube, or both (6.3) to at least 1350°C. It is normally heated electrically using resistance rods, a resistance wire, or molybdenum disilicide elements. Specific dimensions can vary with manufacturer’s design.

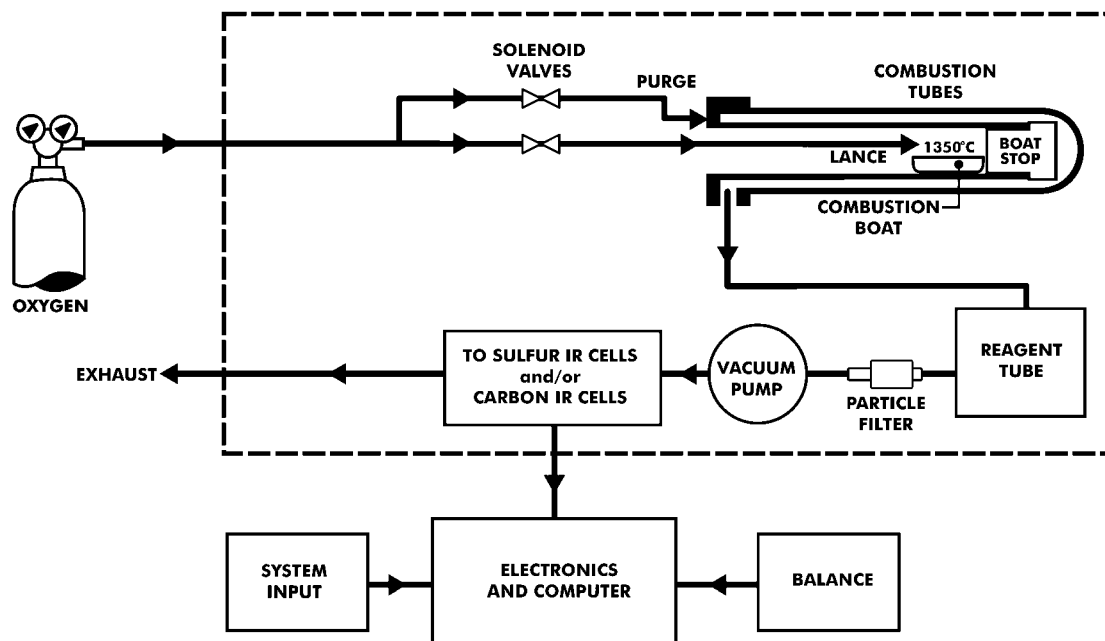


FIG. 1 Apparatus for the Determination of Sulfur by the Infrared Detection, Method A

6.3 *Combustion Tube*—Made of mullite, porcelain, or zircon with provisions for routing the gases produced by combustion through the infrared cell. The tube may have a boat stop made of reticulated ceramics heated to 1350°C that serves to complete the combustion of sulfur containing materials.

6.4 *Sample Combustion Boats*, made of iron-free material and of a convenient size suitable for the dimensions of the combustion tube.

6.5 *Boat Puller*—Where required, a rod of a heat-resistant material with a bent or disk end to insert and remove boats from the combustion tube.

### Combustion Method B (1150°C)

6.6 *Measurement Apparatus*—Equipped to combust the sample as described in 3.2 (See Fig. 2)

6.7 *Tube Furnace*—Capable of heating the hot zone or outer surface of the combustion tube, or both (6.8) to at least 1150°C. It is normally heated electrically using resistance wire. Specific dimensions can vary with manufacturer’s design.

6.8 *Combustion Tube*—Made of quartz with provisions for routing the gases produced by combustion through the infrared cell.

6.9 *Sample Combustion Boat*—Made of an iron-free tin material and of a convenient size suitable for the dimensions of the combustion tube.

## 7. Reagents

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Available Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Other grades can be used, provided it is first ascertained the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Magnesium Perchlorate*—(**Warning**—Magnesium perchlorate is a strong oxidizing agent. Do not regenerate the absorbent. Do not allow contact with organic materials or reducing agents.)

7.3 *Oxygen, 99.5 % Pure*—Compressed gas contained in a cylinder equipped with a suitable pressure regulator and a needle valve to control gas flow. (**Warning**—Pure oxygen vigorously accelerates combustion. Verify all regulators, lines, and valves are free of grease and oil.)

7.4 *Reference Materials, Reference Material (RM)*—that are coal(s) or coke(s) prepared by a national metrology body. Other materials that are coal(s) or coke(s) with documented traceability to reference material (CRM) coal(s) or coke(s) prepared by a national metrology body can also be used. Only use material(s) with an assigned value and assigned uncertainty for sulfur. The uncertainty expressed as the confidence interval of the assigned value shall be less than the repeatability specified in the appropriate section on Precision and Bias of this test method.

7.4.1 To minimize problems with instrument calibration or calibration verification mix all reference material before removing the test portion from the container. Do not use the reference material for calibration or calibration verification when less than 2 g remain in the container. The remaining material can be used for instrument conditioning.

7.5 *BBOT (2,5-di(5-tert-butylbenzoxazol-2-yl)thiophene, C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S)*—A pure substance and certified reference material for sulfur (7.47 % sulfur).

<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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

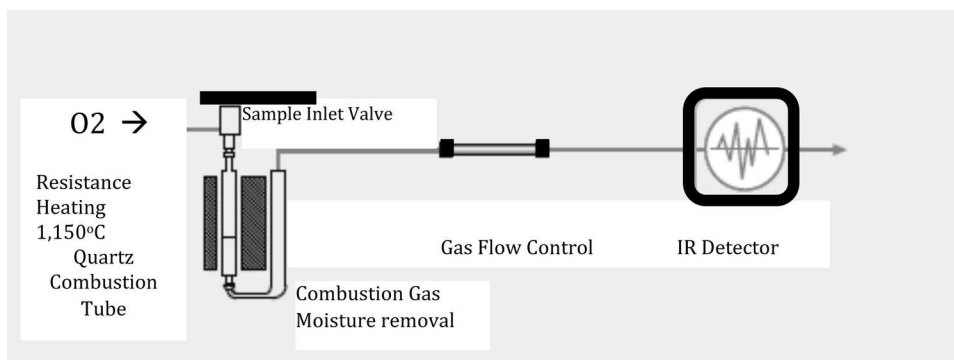


FIG. 2 Apparatus for the Determination of Sulfur by the Infrared Detection, Method B

7.6 *Tungsten Oxide (WO<sub>3</sub>)*—A combustion promoter and a fluxing agent. (**Warning**—Tungsten Oxide is a strong oxidizing agent.)

**8. Procedure**

8.1 *Instrument Preparation*—Perform apparatus set up system checks in accordance with manufacturer’s instructions.

8.1.1 *Balance Calibration*—Calibrate the instrument balance in accordance with manufacturer’s instructions.

8.2 *Calibration of the Infrared Detection System*—If the instrument has been previously calibrated in accordance with the section on instrument calibration, proceed to the Analysis Procedure, otherwise carry out a calibration as specified in the section on instrument calibration following section.

8.2.1 *Calibration with Coal and Coke Certified Reference Materials*—Select reference materials (7.4), in the range of the samples to be analyzed. Use at least three such reference materials, for each range of sulfur values to be tested. Select one reference material containing at least as much sulfur as the highest level of sulfur expected. Select two additional reference materials, one approximately at the mid-point of the range and one below the lowest level of sulfur expected.

8.2.1.1 Use a mass of material recommended by the apparatus manufacturer to carry out a minimum of three determinations to condition the equipment before calibration. Use a material with a sulfur value near the mid point of the expected calibration range.

8.2.1.2 For each reference material—coal or coke employed for calibration, use the as-determined sulfur value previously calculated from the certified dry-basis sulfur value and residual moisture determined using either Test Methods D3173 or D7582 or ISO 11722. Use a mass of material and the calibration procedure recommended by the apparatus manufacturer. Weigh to at least the nearest 1 mg and evenly spread the test portion of the reference material into the sample combustion boat (6.4). Position the sample in the hot zone of the furnace until the instrument returns to baseline as indicated according to settings recommended by the manufacturer. If the analysis time exceeds the maximum analysis time recommended by the manufacturer take corrective action as recommended by the manufacturer.

8.2.2 *Calibration with BBOT*—To meet the precision requirements of this method, six calibration points are required for a linear fit and eight calibration points are required for a nonlinear fit. A calibration point consists of a determination on a single test portion of calibration material. Select test portions of the calibrant that have at least as much sulfur as the highest level of sulfur expected, test portions of the calibrant that have as much sulfur as the lowest level of sulfur expected and test portions spread evenly in between the highest and lowest levels of sulfur.

8.2.2.1 The mass of the calibrant needed can be calculated using the following equation: (Note 1).

$$M_C = \frac{(M_T \times S_{AD})}{S_C} \tag{1}$$

Where

- $M_C$  = Mass of calibrant
- $M_T$  = Mass normally used for test samples
- $S_{AD}$  = Percent sulfur (as-determined) in the test sample
- $S_C$  = Percent sulfur in the pure substance calibrant

NOTE 1—In the interlaboratory study that yielded the data for the precision statement for this method, the mass of BBOT used for calibration ranged from about 15 mg to over 80 mg. Some analyzers may use larger amounts. Amounts less than 15 mg BBOT should only be measured on a five-place analytical balance.

8.2.3 *Calibration Verification*—Carry out a minimum of three determinations to condition the equipment before calibration verification (see 8.2.1.1). Verify the instrument calibration prior to analyzing test samples, upon completion of all test samples and as needed to meet quality control requirements. Analyze a test portion of reference material(s) (7.4) using the apparatus conditions employed for instrument calibration (8.2.1). Use a mass that does not exceed the maximum mass used for instrument calibration and with a sulfur value within the range of the instrument calibration. If the value determined for each reference material employed for verification is not within the specified uncertainty for the assigned sulfur value repeat the instrument calibration in accordance with 8.2.1. Repeat all samples analyzed since the last successful calibration verification.

**TABLE 1 Method A—Repeatability A (Calibration with Coal Reference Materials)—Repeatability and Reproducibility for Sulfur in 250 μm (No.60) Coal and Coke**

	Range, %	Repeatability Limit (r)	Reproducibility Limit (R)
Coal	0.28–5.61	$0.02 + 0.03\bar{X}^A$	$0.02 + 0.09\bar{X}^A$
Coal	0.28–5.61	$0.02 + 0.03\bar{X}^A$	$0.02 + 0.09\bar{X}^A$
Coke	0.52–0.84	0.02	$0.08\bar{X}^A$

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