



Designation: D 4239 – 02

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

This standard is issued under the fixed designation D 4239; 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.

### 1. Scope

1.1 These test methods cover three alternative procedures using high-temperature tube furnace combustion methods for the rapid determination of sulfur in samples of coal and coke.

1.2 These test methods appear in the following order:

	Sections
<i>Method A</i> —High-Temperature Combustion Method with Acid Base Titration Detection Procedures	6-9
<i>Method B</i> —High-Temperature Combustion Method with Iodometric Titration Detection Procedures	10-13
<i>Method C</i> —High-Temperature Combustion Method with Infra-red Absorption Detection Procedures	14-16

1.2.1 When automated equipment is used to perform any of the three methods of this test method, the procedures can be classified as instrumental methods. There are several manufacturers that offer to the coal industry equipment with instrumental analysis capabilities for the determination of the sulfur content of coal and coke samples.

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.* See 7.8 and 15.2.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2013 Method of Preparing Coal Samples for Analysis<sup>2</sup>
- D 2361 Test Method for Chlorine in Coal<sup>2</sup>
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>2</sup>
- D 3176 Practice for Ultimate Analysis of Coal and Coke<sup>2</sup>
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>2</sup>

<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.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.06.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

D 4208 Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method<sup>2</sup>

D 4621 Guide for Quality Management in an Organization that Samples or Tests Coal and Coke<sup>2</sup>

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures<sup>2</sup>

### 3. Summary of Test Methods

3.1 *Method A—High-Temperature Combustion Method with Acid-Base Titration Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen. During combustion, all sulfur contained in the sample is oxidized to gaseous oxides of sulfur (sulfur dioxide, SO<sub>2</sub>, and sulfur trioxide, SO<sub>3</sub>) and the chlorine in the sample is released as Cl<sub>2</sub>. These products are then absorbed into a solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) where they dissolve forming dilute solutions of sulfuric (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric (HCl) acids. The quantities of both acids produced are directly dependent upon the amounts of sulfur and chlorine present in the original coal sample. Once the amounts of each acid present have been determined, the percentage of sulfur contained in the coal may be calculated.

3.1.1 This method is written to include commercially available sulfur analyzers that must be calibrated with appropriate certified reference materials to establish recovery factors or a calibration curve based on the range of sulfur in the coal or coke samples being analyzed.

NOTE 1—Elements ordinarily present in coal do not interfere in Method A (3.1), with the exception of chlorine; results must be corrected for chlorine content of the samples (9.1).

3.2 *Method B—High-Temperature Combustion Method with Iodometric Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to ensure the oxidation of sulfur. The combustion products are absorbed in an aqueous solution that contains iodine. When sulfur dioxide is scrubbed by the diluent, the trace iodine originally present in the solution is reduced to iodide, thus causing an increase in resistance. The detection system of the instrument consists of a polarized dual platinum electrode. Any change in resistance of the solution in

the vessel is detected. Iodine titrant is then added proportionally to the reaction vessel until the trace excess of iodine is replenished and the solution resistance is reduced to its initial level. The volume of titrant expended is used to calculate the sulfur concentration of the sample. The method is empirical; therefore, the apparatus must be calibrated by the use of certified reference materials.

3.2.1 This method is designed to be used with commercially available sulfur analyzers, equipped to perform the preceding operation automatically, and must be calibrated with an appropriate sample (5.4) based on the range of sulfur in each coal or coke sample analyzed.

NOTE 2—Nonautomatic systems may be used with the titration procedures and calculations performed manually by qualified laboratory technicians. The resulting loss in accuracy or speed, or both, would then negate the advantages of using the fully automated instrumental approach.

3.3 *Method C—High-Temperature Combustion Method with Infrared Absorption Detection Procedures*—The sample 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 method is empirical; therefore, the apparatus must be calibrated by the use of certified reference materials.

3.3.1 This method is for use with commercially available sulfur analyzers equipped to carry out the preceding operations automatically and must be calibrated using certified reference materials of known sulfur content based on the range of sulfur in each coal or coke sample analyzed.

#### 4. Significance and Use

4.1 Determination of sulfur is, by definition, part of the ultimate analysis of coal.

4.2 Results of the sulfur analysis are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, and evaluation of the coal quality in relation to contract specifications, as well as other scientific purposes.

4.3 The instrumental analysis provides a reliable, rapid method for determining the concentration of sulfur in a lot of coal or coke and are especially applicable when results must be obtained rapidly for the successful completion of industrial, beneficiation, trade, or other evaluations.

#### 5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250- $\mu$ m) sieve and mixed thoroughly in accordance with

Method D 2013 or Practice D 346.

NOTE 3—It may be difficult to meet the precision statements of Section 18 when high mineral content coals are ground to pass 60 mesh. When the precision of analysis required cannot be obtained, it is recommended that the coals be ground to pass through a No. 100 (150- $\mu$ m) sieve. The reduced particle size should result in a more homogeneous sample.

5.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, so that calculation to other than the as-determined basis can be made.

5.3 Procedures for converting as-determined sulfur values obtained from the analysis sample to other bases are described in Practices D 3176 and D 3180.

5.4 *Certified Reference Materials*, or other commercially available reference coals or calibrating agents with certified dry-basis values must be used. The materials must be supplied by or have traceability to internationally recognized certifying organizations (Note 4).

NOTE 4—Certified Reference Materials such as those available as the Standard Reference Materials (SRMs) Series 2682 through 2685 from the National Institute of Standards and Technology (NIST) or South African Reference Materials (SARMS) from the South African Bureau of Standards have proven to be suitable for calibration. Other Certified Reference Materials can be used provided they are supplied by an internationally recognized certifying agency.

### METHOD A—HIGH-TEMPERATURE COMBUSTION METHOD WITH ACID-BASE TITRATION DETECTION PROCEDURES<sup>4</sup>

#### 6. Apparatus

6.1 *Tube Furnace*—Capable of heating 150- to 175-mm area (hot zone) of the combustion tube (6.2) to at least 1350°C. It is usually heated electrically using resistance rods, a resistance wire, or molybdenum disilicide elements. Specific dimensions may vary with manufacturer's design.

NOTE 5—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 18.

6.2 *Combustion Tube*—Approximately 28-mm internal diameter with a 3-mm wall thickness and 750 mm in length made of porcelain, zircon, or mullite. It must be gastight at working temperature. The combustion may be carried out in a tapered-end tube that is closely connected to the gas absorber by high-temperature tubing with gastight joints. Acceptable configurations include connecting the tapered-end tube directly to the elbow of the fritted gas bubbler or to a 10/30 standard taper-ground joint that is attached to a heat-resistant glass right angle bend. The temperature at the tapered end of the tube should be maintained high enough to prevent condensation in the tube itself.

6.2.1 Alternatively, a high-temperature straight refractory tube may be used, if available. It requires a silica adaptor (6.11)

<sup>4</sup> Based on the method of Mott, R. A., and Wilkinson, H. C., "Determination of Sulfur in Coal and Coke by the Sheffield High Temperature Method," *Fuel*, Fuel B, Vol. 35, 1956, p. 6. This method is designed for the rapid determination of sulfur in coal and coke. It is not applicable to coals or coal density fractions that have been subjected to treatment with chlorinated hydrocarbons because of the potentially high acidity of the combustion gases.

with a flared end that fits inside the combustion tube and serves as an exit for the gases.

6.3 *Flowmeter*, for measuring an oxygen flow rate up to 2.0 L/min.

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

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

6.5.1 If the boat puller is to remain within the combustion tube while the boat is moved into the hot zone, it is necessary to pass the puller through a T-piece that is fitted into a rubber stopper at the inlet of the combustion tube. The open end of the T-piece is sealed with a rubber stopper to permit movement of the pusher and prevent escape of the oxygen that enters at the side limb of the T. The rubber stopper or tube should be checked often to avoid leakage.

6.6 *Gas Absorber or Analyzer Titration Vessel*—A narrow vessel of such diameter that the end of the tube from which the gasses exit is inside the vessel and submerged to a depth of at least 90 mm, when 200 mL of the peroxide solution (7.4) is added to the vessel.

6.6.1 Alternatively, 125-mL capacity bottles with fritted disk can be used for gas absorption. The bottles should be of such a diameter that the fritted end is covered by the peroxide solution to a depth of at least 50 mm. The fritted glass end porosity should be 15 to 40  $\mu\text{m}$ . The bottles are fitted in a series of two to the outlet end of the combustion tube.

6.7 *Gas-Purifying Train*—Designed to be used with specific instruments, or a U-tube packed with soda asbestos may be used. See configuration in Fig. 1.

6.8 *Vacuum Source*—Needed if a negative pressure is used to transport the gasses and combustion products through the system.

6.9 *Vacuum Regulating Bottle*, containing mercury with an open-ended tube dipping into the mercury, used with a vacuum source.

6.10 *Silica Adaptor*, 300 mm long by 8 mm in outside diameter and flared at one end to 26 mm. To be used with a straight refractory combustion tube.

6.11 *Other Configurations of Apparatus*—Complete sulfur analyzer assembly units designed to perform functions similar

to this method with automated features that perform the sulfur analysis in a more rapid manner are commercially available. These instruments may have combustion tube dimensions and oxygen-purifying apparatus that differ slightly from those described in this method, but are acceptable, provided equivalent values within the precision statement of Section 18 are obtained. (See Fig. 2 and Fig. 3.)

## 7. Reagents

7.1 *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 Available Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> 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.

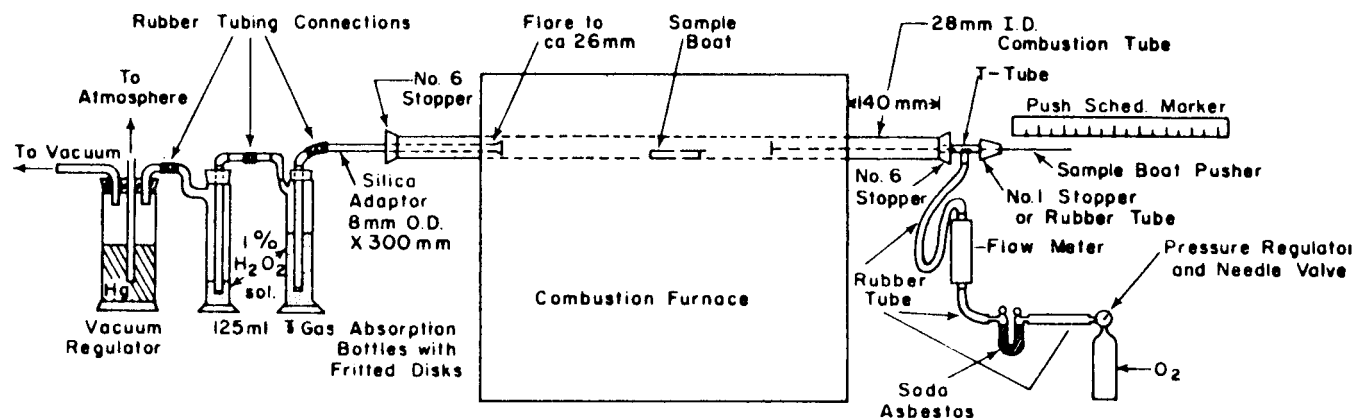
7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

7.3 *Aluminum Oxide ( $\text{Al}_2\text{O}_3$ )*—Finely divided and dried at 1350°C.

7.4 *Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) Solution*—One volume percent (50 mL of 30 %  $\text{H}_2\text{O}_2$  with 1450 mL of water). The pH is adjusted (using NaOH or  $\text{H}_2\text{SO}_4$  as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after two or three days.

7.5 *Indicator*—Indicators that change color (titration end point) between pH 4 and 5 are recommended, but in no case should the pH exceed 7. Adequate lighting and stirring to ensure proper detection of the end point is essential. A choice of indicators or use of a pH meter is permitted (Note 6). Directions for preparing two acceptable mixed indicators are as follows:

7.5.1 Mix one part methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) with three



**FIG. 1 Apparatus for the Determination of Sulfur Using Acid-Base Titration**

<sup>5</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.

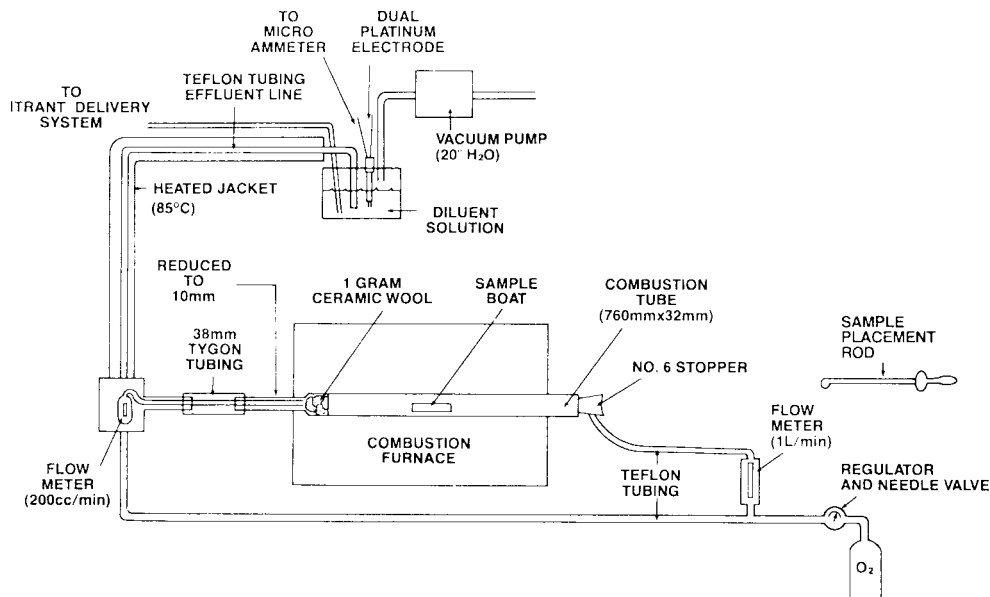


FIG. 2 Apparatus for the Determination of Sulfur by the Iodimetric Detection Method

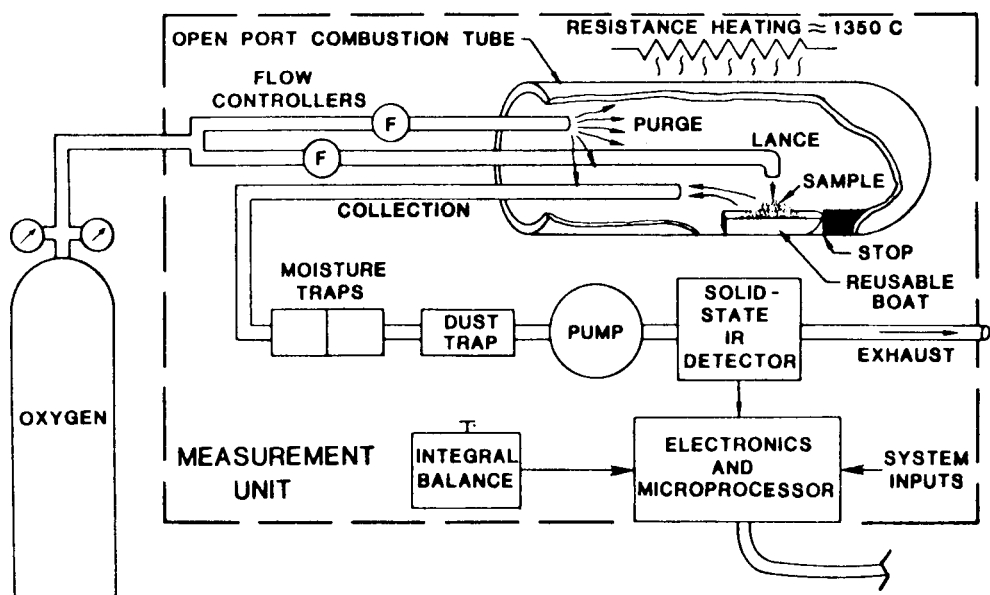


FIG. 3 Apparatus for the Determination of Sulfur by the Infrared Detection Method

parts bromcresol green solution (dissolve 0.083 g in 20 mL of ethanol and dilute to 100 mL with water). Discard the mixed solution after one week.

7.5.2 Mix equal volumes of methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) and methylene blue solution (dissolve 0.083 g in 100 mL of ethanol and store in a dark glass bottle). Discard the mixed solution after one week.

NOTE 6—Although two end-point indicators or a pH meter method are described, the use of the pH meter is accepted as more definitive of the end point of the titration process and considered to give more reproducible results.

7.6 Soda-Asbestos, 8 to 20 mesh, if a U-tube is used.

7.7 Sodium Hydroxide, Standard Solution, 0.05N—Dissolve 2.05 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize against a primary standard.

7.8 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. All regulators, lines, and valves should be free of grease and oil.)

## 8. Procedure

8.1 Assemble the apparatus, as directed, by the instructions of the instrument manufacturer. Alternatively, the apparatus shown in Fig. 1 can be assembled except do not initially connect the rubber tube from the oxygen supply to the soda asbestos U-tube.

8.2 Calibration—Sulfur analyzers must be calibrated at least once on each day they are used, following the analysis procedure outlined in Section 8, using coal or coke standards (5.4) with sulfur values in the range of the samples being

analyzed. A recovery factor ( $F$ ) or calibration curve must be established and appropriately used in each calculation.

$$F = \frac{\text{Actual Sulfur in Standard, Dry Basis}}{\text{Analyzed Sulfur in Standard, Dry Basis}} \quad (1)$$

8.3 *Furnace Adjustment*—Raise the temperature of the furnace to at least 1350°C. Bring the temperature up slowly, allowing approximately 3 to 4 h in advance, to allow sufficient time to come to a stable temperature. Be sure to check the manufacturer's instructions for raising the temperature of the furnace and heed any precautions for protecting heating elements from deterioration or thermal shock.

8.4 *Titration Vessel Preparation*—Fill the titration vessel in accordance with the manufacturer's instructions with approximately 200 mL of the gas absorption fluid (hydrogen peroxide) (7.4). Adjust the pH of the solution to make it definitely acidic by adding dilute sulfuric acid. If chemical indicators (instead of a pH meter) are used, add five or six drops of the indicator and then add a very small quantity (as required) of dilute sodium hydroxide (NaOH) to reach the end point color that will be developed in the sulfur analysis.

8.4.1 If the apparatus with two gas absorption bottles is used, add 100 mL of 1 % H<sub>2</sub>O<sub>2</sub>(7.4) to the bottles so that at least 50 mm of the fritted disk is covered in the first bottle.

8.5 *Oxygen Flow*—Connect the oxygen supply and adjust the oxygen flow to approximately 2 L/min with the oxygen baffle inserted in the entrance end of the combustion tube. Be sure to check manufacturer's instructions. The flow rate at the temperature of 1350°C should be sufficient to prevent the formation of oxides of nitrogen. Allow the oxygen to flow through the combustion tube for at least 1 min before inserting any sample. Check the system for any possible leaks.

8.5.1 If a vacuum source is used, draw air through the apparatus at about 350 mL/min, then connect the oxygen supply to the U-tube and adjust the rate of flow of the oxygen to 300 mL/min. The flow rate is adjusted by changing the depth of the penetration into the mercury of the open-ended glass tube in the vacuum regulating bottle. The preliminary adjustment to 350 mL/min of air ensures that the connections at the outlet end of the combustion tube are under slightly reduced internal pressure and no leak of combustion products should occur.

NOTE 7—A gastight combustion train must be established with an adequate flow of approximately 300 mL/min of pure acid-free oxygen before analyzing samples on the equipment. This is best accomplished during the period the high-temperature tube furnace is brought to its operating temperature of 1350°C. The required gas flow may be established by the use of reduced internal pressure, or should the manufacturer specify or the operator prefer, it can be obtained by the use of a positive pressure train operated at slightly above atmospheric pressure to obtain the required oxygen flow rate. In all cases, the instructions of the manufacturer of the equipment should be followed. This also applies to the addition of sufficient gas absorption fluid as well as to the assembly of the apparatus.

8.6 *Analysis Sample Size*—Weigh out 0.5 g of the analysis sample to the nearest 0.1 mg for coals containing up to 4.0 % sulfur and 0.25 g to the nearest 0.1 mg of analysis sample for coals containing over 4.0 % sulfur. Spread the sample evenly in a combustion boat.

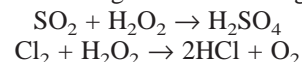
8.6.1 A thin layer of Al<sub>2</sub>O<sub>3</sub> can be used to line the sample

boat and cover the sample to ensure complete combustion and reduce splattering or loss of sample.

8.7 *Sample Combustion*—Remove the oxygen baffle or rubber stopper or both from the combustion tube and put the charged sample boat into the inlet end of the combustion tube approximately 270 mm from the center of the combustion tube hot zone. Close the combustion tube by replacing the oxygen baffle or rubber stopper or both and, if necessary, readjust the rate of flow of the oxygen. Leave the boat in this position for 1 to 3 min until the volatiles have been driven off. This will also eliminate the "popping" and soot accumulation in the right angle bend. Remove the oxygen baffle or rubber stopper and move the sample boat slowly forward until the boat is in the center of the hot zone, approximately 30 mm at the beginning of each minute for 6 min is the suggested schedule to ensure a slow heating rate. Be sure to remove the boat puller from the hot zone and replace the baffle or stopper after each movement. Allow the sample to burn in the hot zone for approximately 3 to 4 min until all sulfur in the sample is oxidized to sulfur dioxide (SO<sub>2</sub>) or sulfur trioxide (SO<sub>3</sub>). The complete sample burning time is not more than 14 to 15 min. This heating program has been established for all types of coal. Where it is shortened for a particular coal or by instruction of the manufacturer of a particular sulfur analyzer, results should be checked against those obtained by using the longer heating schedule.

8.7.1 If the rubber stopper with the T-piece is used (6.5.1), the rubber stopper remains in the end of the combustion tube and the boat puller is permitted movement into the furnace through the T-piece. See Fig. 1.

8.8 *Titration*—The gasses of combustion leave the combustion tube through the exit end and are dissolved in the hydrogen peroxide in the gas absorption bottles or analyzer titration vessel forming a dilute sulfuric acid. Titrate the contents of this vessel with 0.05N sodium hydroxide (7.7), backwashing the titration vessel and inlet tubes according to manufacturer's instructions. The total acidity, because of oxides of sulfur and chlorine, is given according to the following reactions:



8.8.1 If the contents of the gas absorption bottles must be transferred to a suitable titration flask, be sure to wash the bottles and inlet tube or silica adaptor with water (7.2) and add these washings and five or six drops of indicator to the titration flask before titrating with the 0.05N NaOH solution (7.7).

8.8.2 High-temperature combustion acid/base titration sulfur analyzers may be designed to give a buret reading directly in percent sulfur content of the coal sample, but a correction still must be made for acidity caused by chlorine present in the sample using Test Methods D 2361 or D 4208.

NOTE 8—Often *no* correction is made for the presence of chlorine in the sample, or a percentage value (found as a relatively invariant value based upon prior knowledge of the coals being analyzed) is subtracted from the percent sulfur determined. This method can be acceptable for coals of known chlorine content; however, for work of the highest accuracy, the percentage of chlorine present in the sample must be determined analytically, and correction for its presence made by subtracting an equivalent value from a value equivalent to the total acidity determined by the sulfur titration.

## 9. Calculations

9.1 Some sulfur analyzers are designed to give buret readings in percent sulfur if the titrant is adjusted and standardized to exactly 0.05*N* and the sample weight is exactly 0.500 g. After the observed percent sulfur has been adjusted using the recovery factor or calibration curve, then it must be corrected for chlorine using the following calculation:

$$S_c = 1.603 (S_b / 1.603 \times F - \text{Cl, \%} / 3.546) \quad (2)$$

where:

$S_c$  = sulfur corrected for chlorine (as determined), %;

$S_b$  = sulfur from buret reading, %;

$F$  = the recovery factor or factor taken from a calibration curve for the analyzer; and

Cl, % = chlorine in sample (as determined), %.

9.2 On analyzers that are designed to give buret readings in percent sulfur, but where the normality of the titrant or sample weight may vary from that prescribed, the following calculation must be used:

$$S_c = 1.603 [(S_b \times N_1 \times F \times 10) - \text{Cl, \%} / 3.546] / W \quad (3)$$

where:

$S_c$  = sulfur corrected for chlorine (as determined), %;

$S_b$  = sulfur taken from buret reading, %;

$N_1$  = normality of the sodium hydroxide;

$F$  = recovery factor or factor taken from a calibration curve for the analyzer;

Cl, % = chlorine in sample (as determined), %; and

$W$  = weight of sample, g.

9.3 When sulfur analyzers are used that have buret readings in millilitres of titrant, the following calculation will apply:

$$S_c = 1.603 [(V_1 \times N_1 \times F) - \text{Cl, \%} / 3.546] / W \quad (4)$$

where:

$S_c$  = sulfur corrected for chlorine (as determined), %;

$S_b$  = sulfur taken from buret reading, %;

$V_1$  = sodium hydroxide, mL;

$N_1$  = normality of sodium hydroxide;

Cl, % = chlorine in sample (as determined), %;

$F$  = the recovery factor or factor taken from a calibration curve for the analyzer; and

$W$  = weight of sample, g.

## METHOD B—HIGH-TEMPERATURE COMBUSTION METHOD WITH IODIMETRIC TITRATION DETECTION PROCEDURES

### 10. Apparatus

10.1 *Analytical Apparatus*—Designed to perform the analysis procedure described in 3.2 automatically.

NOTE 9—It is recommended that the analytical equipment be an automated sulfur analyzer. Otherwise, the restrictions and limitations given in Note 3 for nonautomated systems apply.

10.2 *Tube Furnace*—See 6.1.

10.3 *Combustion Tube*—Made of mullite, porcelain, or zircon, approximately a 27-mm inner diameter, a 33-mm outer diameter, and 750 mm in length, with the last 23 mm of the exit end reduced to 10-mm outer diameter and 5-mm inner diameter

to facilitate exit and collection of the gases in the titration vessel.

10.4 *Sample Combustion Boats*—See 6.4.

10.5 *Boat Puller*—See 6.5.

### 11. Reagents

11.1 *Purity of Reagents*—See 7.1.

11.2 *Purity of Water*—See 7.2.

11.3 *Iodine Titrant*—Dissolve 2.5 g of iodine in 280 mL of pyridine. Mix well and be certain all iodine is dissolved. Add 700 mL of methanol and 20 mL of water. (See Note 10.)

11.4 *Diluent*—Mix 280 mL of pyridine with 700 mL of methanol and 20 mL of water. Mix well.

NOTE 10—Alternative formulations may be substituted to the extent that they can be demonstrated to yield equivalent results in regard to accuracy and precision.

11.5 *Oxygen*—See 7.8.

### 12. Procedure

12.1 *Instrument Preparation:*

12.1.1 Assemble the analytical apparatus according to the manufacturer's instructions. Check all connections carefully to avoid leaks.

12.1.2 Set furnace temperature to 1350°C.

12.1.3 Set oxygen flow rate according to manufacturer's instructions.

12.1.4 Place approximately 150 mg of a coal sample in a boat and insert into the 1350°C region of the furnace. Sample boat should remain within the hot zone of the furnace for at least 2 min or until sample is completely burned. This action will serve to condition the apparatus in all functions.

12.2 *Calibration:*

12.2.1 Select a coal certified reference material, as described in 5.4, which has a sulfur value in the range of the sample to be analyzed. Weigh out about 150 mg of this previously dried coal standard and record the weight to the nearest 0.1 mg.

12.2.2 Enter the weight and sulfur content of the certified reference material sample into the memory of the analyzer.

12.2.3 Insert the certified reference material sample into the 1350°C region of the furnace.

12.2.4 After endpoint is reached, not less than 2 min, record the titrant factor as milligrams sulfur per millilitre of titrant (mgS/mL). If analyzer does not have an integral computer, record the volume of titrant used and calculate titrant factor as instructed in 13.1.

12.2.5 Remove sample boat and repeat Steps 12.2.1-12.2.4 two more times.

12.2.6 If analyzer does not automatically average the titrant factors obtained in the calibration step and enter the average into the microprocessor, then do so manually. Successive calibrations should yield titrant factors within 0.01 mgS/mL of each other.

12.3 *Analysis Procedure:*

12.3.1 Use an instrument that has been conditioned and calibrated according to 12.1 and 12.2.

12.3.2 Weigh to the nearest 0.1 mg, approximately 150 mg of the coal analysis sample into a boat.

12.3.3 Enter the sample weight into the sulfur analyzer memory.

12.3.4 Insert the coal sample into the 1350°C region of the furnace.

12.3.5 After the endpoint is reached (not less than 2 min), record the sulfur concentration of the sample. If analyzer does not have an integral computer, record the volume of titrant used and calculate the sulfur concentration as instructed in 13.2.

### 13. Calculations

13.1 On analyzers that do not calculate the titrant factor automatically, the following calculation must be used:

$$T = S_s \times W/100 \times V_t \quad (5)$$

where:

$T$  = titrant factor, mg of sulfur/mL;

$S_s$  = sulfur concentration of standard, dry basis;

$W$  = weight of standard, mg; and

$V_t$  = volume of titrant, mL.

13.2 On analyzers that do not calculate the percent sulfur in the analysis sample automatically, the following calculation must be used:

$$S = 100 (T \times V_t)/W \quad (6)$$

where:

$S$  = percent sulfur (as determined),

$T$  = titrant factor (see 13.1),

$V_t$  = volume of titrant, mL, and

$W$  = weight of sample, mg.

## METHOD C—HIGH-TEMPERATURE COMBUSTION METHOD WITH INFRARED ABSORPTION PROCEDURE

### 14. Apparatus

14.1 *Measurement Apparatus*—Equipped to combust the sample as described in 3.3 automatically. (See Note 9.)

14.2 *Tube Furnace*—See 6.1.

14.3 *Combustion Tube*—Made of mullite, porcelain, or zircon with provisions for routing the gasses produced by combustion through the infrared cell.

14.4 *Sample Combustion Boats*—See 6.4.

14.5 *Boat Puller*—See 6.5.

### 15. Reagents

15.1 *Purity of Reagents*—See 7.1.

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

15.3 *Oxygen*—See 7.8.

15.4 *Certified Reference Materials*, such as SRM Nos. 2682 through 2685—*Sulfur in Coal*,<sup>6</sup> reference coals or calibrating agents with certified dry-basis sulfur values must be used. The materials must be supplied by or have traceability to internationally recognized certifying organizations, such as the National Institute of Standards and Technology.

15.4.1 All certified reference materials, reference coals, or calibrating agents must have precision values of less than or equal to method repeatability. Such certified reference materials, reference coals, or calibrating agents must be stable with respect to moisture and be pulverized to pass 100 % through a 0.250-mm (No. 60) USA Standard Sieve. Certified reference materials, reference coals, or calibrating agents must be mixed thoroughly before each use.

### 16. Procedure

16.1 *Instrument Preparation*—Perform system update checks in accordance with manufacturer's instructions.

16.1.1 *Balance Calibration*—Calibrate internal balance in accordance with manufacturer's instructions.

16.2 *Calibration of the Infrared Detection System*—Select certified reference materials, reference coals, or calibrating agents 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 certified reference materials, reference coals, or calibrating agents are recommended for each range of sulfur values to be tested. When performing a single-point calibration (Note 11) the certified reference materials, reference coal, or calibrating agent containing the highest sulfur value for the expected range should be used for calibration. The other two certified reference materials, reference coals, or calibrating agents should represent the low and midpoints of the expected range. When performing a multiple point calibration, two of the certified reference materials, reference coals, or calibrating agents should bracket the range of sulfur values to be tested with the third falling within the range. All results obtained must be within the allowable limits of the certified reference materials, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Guide D 4621.

16.2.1 All certified reference materials, reference coals, or calibrating agents used for calibrating the instrument should comply with the provisions of 15.4. (**Warning**—An indicated problem with linearity of the instrument during calibration could result from contamination of the certified reference material, reference coal, or calibrating agent as the container becomes depleted. It is, therefore, suggested that extreme care be used in mixing the certified reference material, reference coal, or calibrating agent before removing any sample from the container and that it be discarded when less than 5 g remain in the container.)

NOTE 11—When performing a single-point calibration, the technique of calibrating the instrument with the certified reference materials, reference coal, or calibrating agent corresponding to the highest sulfur value expected for the range uses the optimum linear range available for calibration. Single-point calibration is most linear from the point of calibration to zero.

16.2.2 *Calibration Procedure*—Make a minimum of two determinations to condition the equipment before calibrating the system. The as-determined sulfur value of the certified reference material, reference coal, or calibrating agent used for calibration of the instrument must have been previously calculated from the certified dry-basis sulfur value and residual moisture determined using either Test Methods D 3173 or D 5142. Alternately, a quantity of the certified reference

<sup>6</sup> Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Bureau of Standards, Washington, DC 20234.

material, reference coal, or calibrating agent allocated to be used within a normal production period (Note 12) can be dried using either Test Methods D 3173 or D 5142, in which case, the dry basis sulfur value will be used. The dried material must be stored in a desiccator, and any remaining at the end of the normal production period must be discarded. Weigh five samples of the certified reference material, reference coal, or calibrating agent (Note 13) chosen to represent the range of sulfur values being tested. Follow the calibration procedure recommended by the manufacturer. For verification of the calibration curve, use certified reference materials, reference coals, or calibrating agents that bracket the range of values to be tested. All results obtained must be within the allowable limits of the certified reference materials, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Test Method D 4621.

NOTE 12—A normal production period would routinely be considered an 8-h shift. Dried certified reference materials, reference coals, or calibrating agents should not be maintained beyond one day for the purposes of instrument calibration. (**Warning**—Previously dried material should not be redried as oxidation can readily occur.)

NOTE 13—Weigh to the nearest 1.0 mg. Since the sulfur content of the certified reference materials, reference coals, or calibrating agents bracket the range of sulfur values being determined from the samples, the mass of the certified reference materials, reference coals, or calibrating agents used for calibration and the samples to be analyzed should be approximately the same so that both materials produce about the same amount of infrared cell saturation (60 to 70 %).

16.2.3 *Periodic Calibration Verification*—On a periodic basis, verify the stability of the instrument and its calibration by analyzing a portion of the certified reference materials, reference coal, or calibrating agent used to calibrate the instrument. The value determined for this material, when used as an unknown sample, must be within the certified value plus or minus the stated precision limits of the material. If the criteria for a successful verification of calibration in accordance with Test Method D 4621 is not met, the calibration procedure of 16.2.1 must be repeated and samples analyzed since the last successful verification must be repeated.

16.3 *Analysis Procedure*—Stabilize and calibrate the analyzer (see 16.2).

16.3.1 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C. Weigh the sample (Note 13). Spread the sample evenly in a combustion boat and use a boat puller to position the sample in the hot zone of the furnace for at least 2 min (Note 14) or until completely combusted.

NOTE 14—The analytical cycle should begin automatically as soon as sulfur is detected.

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

## 17. Report

17.1 The percent sulfur value obtained using any of the described methods is on an as-determined basis.

17.2 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

17.3 Use the percentage of moisture in the sample passing a

No. 60 (250- $\mu$ m) sieve to calculate the as-determined results of the analysis sample to a dry basis.

17.4 Procedures for converting the value obtained on the analysis sample to other bases are described in Practices D 3176 and D 3180.

## 18. Precision and Bias

18.1 These are empirical methods that are highly dependent upon the calibration of the equipment, the closeness of the standards to the samples in sulfur content, chlorine content, iron content, and so forth.

18.2 *Precision Statement for High-Temperature Combustion Method Using Acid Base Titration Detection Procedures*—The relative precision of this method for the determination of total sulfur covers the concentration range from 0.5 to 6.0 %.

18.2.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, 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 calculated by use of the following equation:

$$I(r) = 0.06 + 0.03 \bar{x} \quad (7)$$

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

NOTE 15—This equation 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 total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 % and the calculated repeatability  $I(r)$  is 0.11. The difference between the two sulfur values is 0.05 and does not exceed the  $I(r)$  of 0.11; therefore, these two values are acceptable at the 95 % confidence level.

18.2.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh 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 calculated by the use of the following equation:

$$I(R) = 0.03 + 0.11 \bar{x} \quad (8)$$

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

NOTE 16—This equation 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 total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated  $I(R)$  interval is 0.46 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the  $I(R)$ , these two values are acceptable at the 95 % confidence level.

18.3 *Precision Statement for High-Temperature Combustion Method Using Iodimetric Detection Procedures*—The relative precision of this method for the determination of total sulfur

covers the concentration range from 0.5 to 6.0 %.

18.3.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, 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:

$$I(r) = 0.08 \bar{x} \quad (9)$$

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

NOTE 17—This equation 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 total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 %, and the calculated repeatability interval  $I(r)$  is 0.12. The difference between the two sulfur values is 0.05 and does not exceed the  $I(r)$  of 0.12; therefore, these two values are acceptable at the 95 % confidence level.

18.3.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh 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:

$$I(R) = 0.08 + 0.09 \bar{x} \quad (10)$$

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

NOTE 18—This equation 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 total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated  $I(R)$  interval is 0.43 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the  $I(R)$ , these two values are acceptable at the 95 % confidence level.

#### 18.4 Precision Statement for High-Temperature Combustion Method Using Infrared Absorption Detection Procedures:

18.4.1 *Precision—250- $\mu$ m (No. 60) Samples*—The relative precision of this test method for the determination of sulfur covers the concentration range from 0.28 to 5.61 %.

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

$$I(r) = 0.02 + 0.03 \bar{x} \quad (11)$$

where  $\bar{x}$  is the average of the two test results (see Note 19).

18.4.1.2 *Reproducibility*—The difference in absolute value 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 (limit)  $I(R)$  more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval (limit), there is reason to question one or both of the test results. The reproducibility interval on a dry basis may be determined by use of the following equation:

$$I(R) = 0.02 + 0.09 \bar{x} \quad (12)$$

where  $\bar{x}$  is the average of the two test results (see Note 19).

NOTE 19—These equations apply to the relative spread of a measurement that is expressed as a percentage as derived from a statistical evaluation of the round-robin results.

18.4.2 *Precision—2.36-mm (No. 8) Samples*—The relative precision of this test method for determination of sulfur covers the concentration range from 0.2 to 3.0 % for bituminous coals and 0.3 to 1.6 % for subbituminous and lignite coals.

18.4.2.1 *Repeatability*—The difference in absolute value between test results obtained in the same laboratory, by the same operator, using the same apparatus, determined on a single test specimen of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250- $\mu$ m (No. 6) and prepared from the same bulk sample, should not exceed the repeatability interval for 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 more of the test results. The repeatability interval for this method is as follows:

Bituminous coals	0.05 %
Subbituminous and lignite coals	0.08 %

18.4.2.2 *Reproducibility*—The difference in absolute value between test results obtained in laboratories calculated as the average of determinations on single test specimens of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250- $\mu$ m (No. 60) and prepared from the same bulk sample, should not exceed the reproducibility interval for 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 more of the test results. The reproducibility interval for this test method is as follows:

Bituminous coals	0.09 %
Subbituminous and lignite coals	0.13 %

NOTE 20—Supporting data for 2.36-mm (No. 8) coal has been filed at ASTM Headquarters and may be obtained by requesting RR: D05-1015.

18.5 *Bias*—Bias is eliminated when the instrument is properly calibrated against certified reference standards. Proper calibration includes comparison of instrumental results to certified sulfur values. Results for certified standards above and below anticipated analysis sample results should be within certified precision levels for all standards over the calibration range for the instrument.

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