



Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods¹

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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 to 9
<i>Method B</i> —High Temperature Combustion Method with Iodimetric Titration Detection Procedures	10 to 13
<i>Method C</i> —High Temperature Combustion Method with Infrared Absorption Detection Procedures	14 to 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 Analysis²
- D 1193 Specification for Reagent Water³
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2361 Test Method for Chlorine in Coal²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3176 Practice for Ultimate Analysis of Coal and Coke²
- D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
- D 4208 Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method²
- D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory²

¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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² Annual Book of ASTM Standards, Vol 05.05.

³ Annual Book of ASTM Standards, Vol 11.01.

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures²

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, SO₂, and sulfur trioxide, SO₃) and the chlorine in the sample is released as Cl₂. These products are then absorbed into a solution of hydrogen peroxide (H₂O₂), where they dissolve forming dilute solutions of sulfuric (H₂SO₄) 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 standard reference materials (SRM's), in order 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 Iodimetric 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 standard reference material (SRM).

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 standard reference materials (SRM).

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 standard reference material (coal) 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- μ m) sieve and mixed thoroughly in accordance with Method D 2013 or Method D 346.

NOTE 3—It may be difficult to meet the precision statements of Section 19 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- μ 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 Method D 3176 and Method D 3180.

5.4 Standard Reference Material (SRM) such as SRM Nos. 2682 through 2685—*Sulfur in Coal*⁴ which consist of four different coals that have been individually crushed and ground to pass a 60-mesh sieve, and bottled in 50-g units, or other commercially available reference coals with a certified sulfur content.

METHOD A—HIGH-TEMPERATURE COMBUSTION METHOD WITH ACID-BASE TITRATION DETECTION PROCEDURES⁵

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 4—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 19.

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 gas-tight 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 gas-tight 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) 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 disc 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

⁴ Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg, National Bureau of Standards, Washington, DC 20234.

⁵ 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.

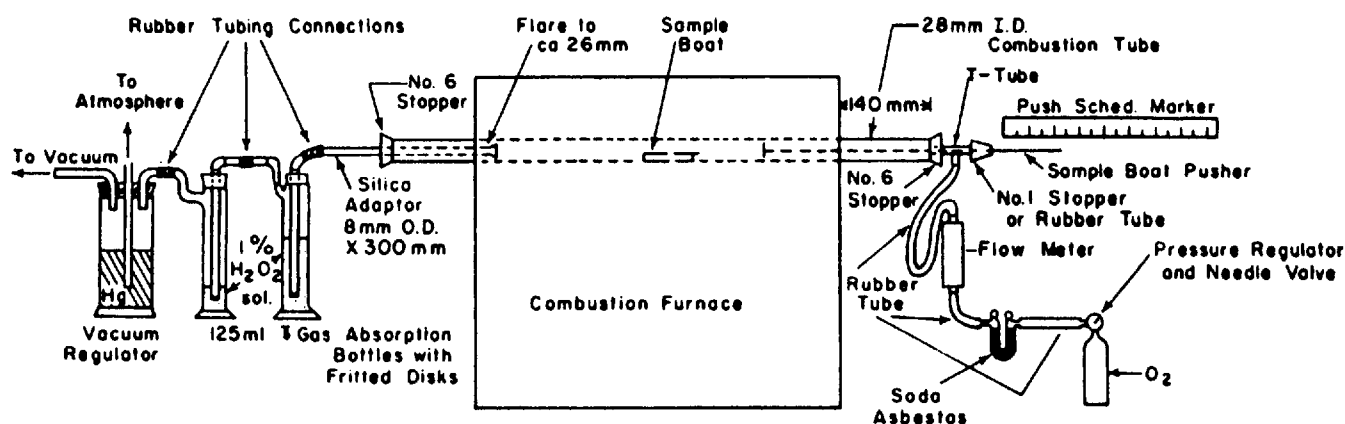


FIG. 1 Apparatus for the Determination of Sulfur Using Acid-Base Titration

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 μm . 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 19 are obtained.

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 Chem-

ical Society, where such specifications are available.⁶ 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 (Al_2O_3), finely divided and dried at 1350°C.

7.4 Hydrogen Peroxide (H_2O_2) Solution—One volume percent (50 mL of 30 % H_2O_2 with 1450 mL of water). The pH is adjusted (using NaOH or H_2SO_4 as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after 2 or 3 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 5) Directions for preparing two acceptable mixed indicators are as follows:

7.5.1 Mix 1 part methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) with 3 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 1 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 1 week.

NOTE 5—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, 0.05 N—

⁶ 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.