

**ASTM-D4239**

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# 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 Iodimetric 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>
- 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 standard reference materials (SRMs) 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

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.06.

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

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 SRMs.

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- $\mu$ 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 Standard Reference Material (SRM) such as SRM Nos. 2682 through 2685—*Sulfur in Coal*<sup>4</sup> 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 PROCEDURES<sup>5</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 4—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) 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.

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

<sup>5</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.

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  $\mu$ 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>6</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 (Al<sub>2</sub>O<sub>3</sub>)*—Finely divided and dried at 1350°C.

7.4 *Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Solution*—One volume percent (50 mL of 30 % H<sub>2</sub>O<sub>2</sub> with 1450 mL of water). The pH is adjusted (using NaOH or H<sub>2</sub>SO<sub>4</sub> 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 5). 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 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.

<sup>6</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.

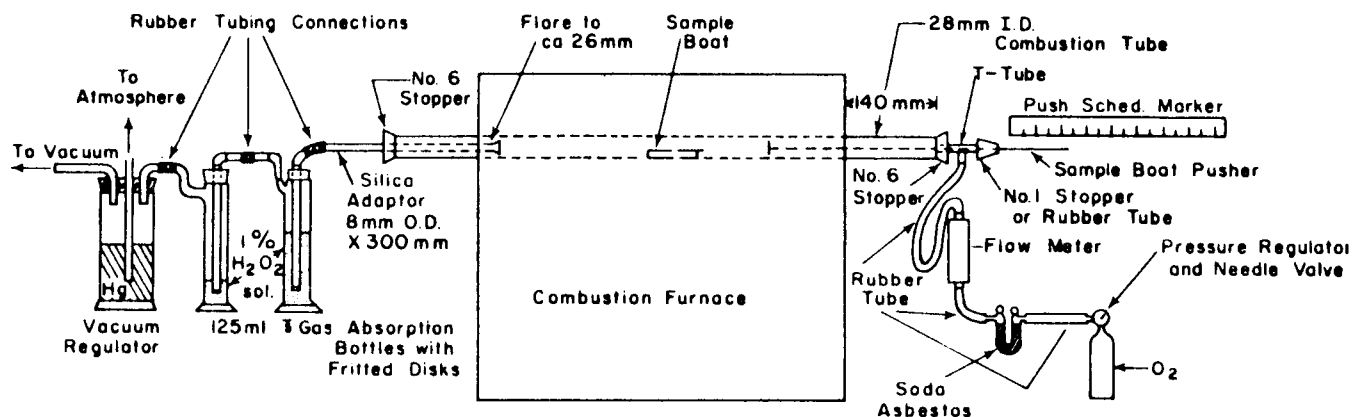


FIG. 1 Apparatus for the Determination of Sulfur Using Acid-Base Titration

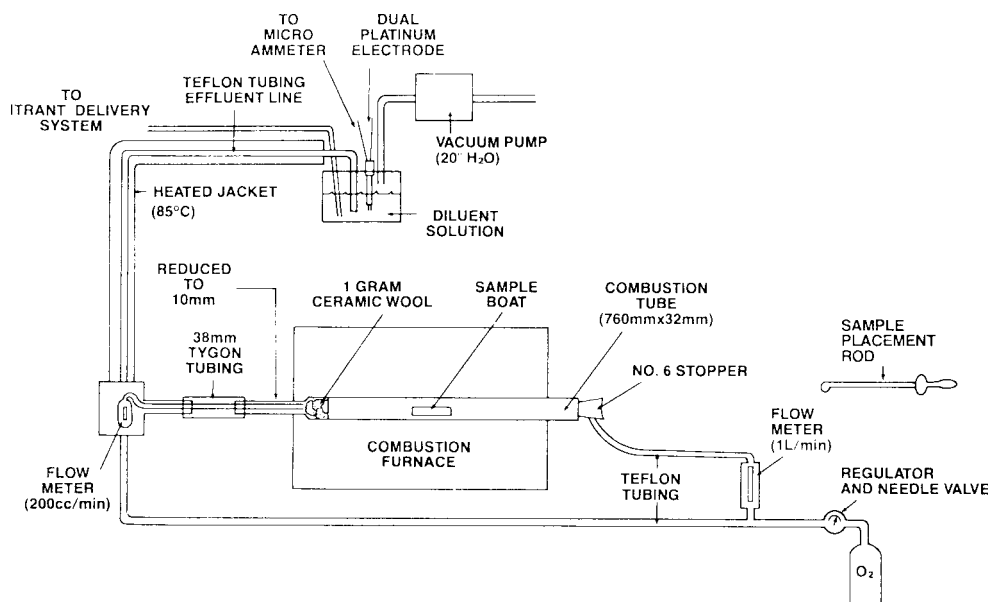


FIG. 2 Apparatus for the Determination of Sulfur by the Iodimetric Detection Method

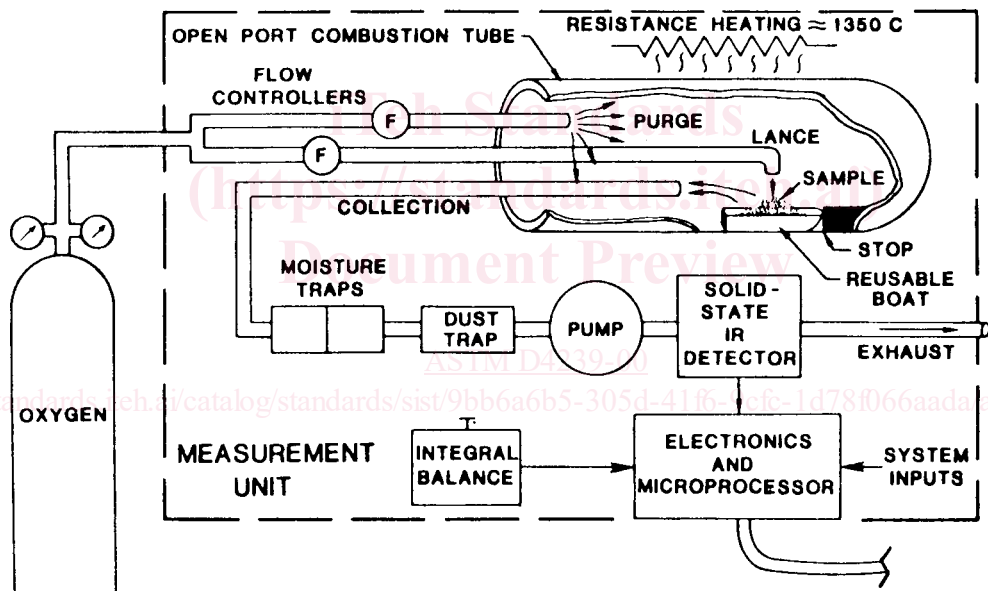


FIG. 3 Apparatus for the Determination of Sulfur by the Infrared Detection Method

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, 0.05N*—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 6**—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.

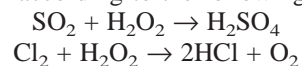
**8.6.1** A thin layer of Al<sub>2</sub>O<sub>3</sub> can be used to line the sample boat and cover the sample to ensure complete combustion and reduce splattering or loss of sample.

**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 0.05*N* 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 0.05*N* 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 7**—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