



Designation: D 3177 – 89 (Reapproved 1997)

Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke¹

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1. Scope

1.1 These test methods cover two alternative procedures for the determination of total sulfur in samples of coal and coke. Sulfur is included in the ultimate analysis of coal and coke.

1.2 The procedures appear in the following order:

Method A—Eschka Method	Sections 6-9
Method B—Bomb Washing Method	10 and 11

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.* Specific precautionary statements are given in Sections 11.1.1-11.1.1.7.

1.4 The values stated in SI units are to be regarded as the standard.

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 2015 Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter²
- 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 3286 Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter²
- E 144 Practice for Safe Use of Oxygen Combustion Bombs⁴

3. Summary of Test Methods

3.1 *Eschka Method*—A weighed sample and Eschka mixture are intimately mixed and ignited together. The sulfur is

¹ These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are 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.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

dissolved in hot water and then precipitated from the resulting solution as barium sulfate (BaSO_4). The precipitate is filtered, ashed, and weighed.

3.2 *Bomb Washing Method*—Sulfur is precipitated as BaSO_4 from oxygen-bomb calorimeter washings, and the precipitate is filtered, ashed, and weighed.

4. Significance and Use

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

4.2 Sulfur analysis results obtained by these methods are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, evaluation of the coal quality in relation to contract specification, and other purposes of commercial or scientific interest.

5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250- μm) sieve in accordance with Method D 2013 or Method D 346.

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 Practice D 3176 and Method D 3180.

5.4 Standard Reference Material (SRM), such as SRM Nos. 2682 through 2685—Sulfur in Coal⁵ which consist of four different coals that have been individually crushed and ground to pass a No. 60 (250- μm) sieve, and bottled in 50-g units, or other commercially available reference material coals with a certified sulfur content of $\pm 0.0xx$ precision can be used. Sulfur values obtained by analyzing these coals, using any of the methods described in this test method, may be used for checking the accuracy of analytical results.

ALTERNATIVE PROCEDURES TEST METHOD A—ESCHKA METHOD

6. Apparatus

6.1 *Gas (Note 1) or Electric Muffle Furnace, or Burners,*

⁵ Available from National Institute of Standards and Technology, Gaithersburg, MD 20899.

for igniting the sample with the Eschka mixture and for igniting the barium sulfate (BaSO_4).

NOTE 1—Gas can contain sulfur compounds.

6.2 Crucibles or Capsules—Porcelain capsules, 22 mm ($\frac{7}{8}$ in.) in depth and 44 mm ($1\frac{3}{4}$ in.) in diameter, or porcelain crucibles of 30-mL capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture. Porcelain, platinum, alundum, or silica crucibles of 10 to 15-mL capacity, shall be used for igniting the BaSO_4 .

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.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 Barium, Chloride Solution (100 g/L)—Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and dilute to 1 L with water.

7.4 Eschka Mixture—Thoroughly mix 2 parts by weight of light calcined magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be as free as possible from sulfur. Eschka mixture is also available commercially.

7.5 Hydrochloric Acid (1 + 1)—Mix equal volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) and water.

7.6 Hydrochloric Acid (1 + 9)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 9 volumes of water.

7.7 Methyl Orange Indicator Solution (0.2 g/L)—Dissolve 0.02 g of methyl orange in 100 mL of hot water and filter.

7.8 Sodium Carbonate, Saturated Solution—Dissolve approximately 60 g of crystallized sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) or 22 g of anhydrous sodium carbonate (Na_2CO_3) in 100 mL of water, using a sufficient excess of Na_2CO_3 to ensure a saturated solution.

7.9 Sodium Hydroxide Solution (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in 1 L of water. This solution may be used in place of the Na_2CO_3 solution.

8. Procedure

8.1 Preparation of Sample and Mixture—Thoroughly mix on glazed paper approximately 1 g of the sample, weighed to nearest 0.1 mg and 3 g of Eschka mixture. The amount of sample to be taken will depend on the amount of BaCl_2

solution required in accordance with 8.3. Transfer to a porcelain capsule, or porcelain crucible, or a platinum crucible and cover with about 1 g of Eschka mixture.

8.2 Ignition—Heat the crucible over an alcohol, gasoline, or gas flame as described in 8.2.1, or in a gas or electrically heated muffle as described in 8.2.2 for coal and in 8.2.3 for coke. The use of artificial gas for heating the sample and the Eschka mixture is permissible only when the crucibles are heated in a muffle.

8.2.1 Open Flame—Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter that tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 min, gradually increase the temperature, and occasionally stir until all black particles have disappeared, which is an indication of the completeness of the procedure.

8.2.2 Muffle (Coal)—Place the crucible in a cold-vented muffle and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 1 h. Maintain this maximum temperature until, on stirring, all black particles have disappeared (about $1\frac{1}{2}$ h).

8.2.3 Muffle (Coke)—Place the crucible in a warm-vented muffle (about 200°C) and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 30 min. Maintain this maximum temperature until, on stirring, all black particles have disappeared.

8.3 Subsequent Treatment—Remove the crucible and empty the contents into a 200-mL beaker and digest with 100 mL of hot water for $\frac{1}{2}$ to $\frac{3}{4}$ h, while stirring occasionally. Decant the solution through filter paper, retaining as much insoluble material in beaker as possible. Thoroughly wash the insoluble matter in the beaker with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Make the filtrate, amounting to about 250 mL, just neutral to methyl orange with NaOH or Na_2CO_3 solution; then add 1 mL of HCl (1 + 9). Boil and add slowly from a pipet, while stirring constantly, 10 mL or more of BaCl_2 solution. The BaCl_2 solution must be in excess. If more than 10 mL of BaCl_2 solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion. Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling. Filter through a fine ashless paper, such as Whatman No. 42 or similar, and wash with hot water until 1 drop of silver nitrate (AgNO_3) solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate.

8.3.1 Place the wet filter containing the precipitate of barium sulfate (BaSO_4) in a weighed platinum, porcelain, silica, or alundum crucible, fold the paper loosely over the precipitate to allow a free access of air but prevent spattering. Smoke the paper off gradually in a muffle furnace and at no time allow to burn with flame. After the paper is practically consumed, raise the temperature to approximately $800 \pm 50^\circ\text{C}$ and heat to constant weight. Weigh the barium sulfate to the nearest 0.1 mg.

8.4 Blanks and Corrections—In all cases, a correction must be applied. The preferred method of correction is by the analysis of a weighed portion of a standard sulfate using the

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.