Designation: D 3177 – 02

Standard Test Methods for
Total Sulfur in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3177; 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 (ε) indicates an editorial change since the last revision or reapproval.

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:

	Sections
Method A—Eschka Method	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 Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Practice for Preparing Coal Samples for Analysis[2]

D 2015 Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 3286 Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter[2]

E 144 Practice for Safe Use of Oxygen Combustion Bombs[4]

3. Summary of Test Methods

3.1 *Eschka Method*—A weighed sample and Eschka mixture are intimately mixed and ignited together. The sulfur is 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 Coal[5] 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 ± 0.0xx precision can be used. Sulfur values obtained by analyzing these coals, using any of

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[1] These test methods are under the jurisdiction of ASTM Committee D05 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 05.06.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 14.04.

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

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,* 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 (7⁄8 in.) in depth and 44 mm (1¾ 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 ($BaCl_2 \cdot 2H_2O$) 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 ($Na_2CO_3 \cdot 10H_2O$) 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 ± 25°C in about 1 h. Maintain this maximum temperature until, on stirring, all black particles have disappeared (about 1½ h).

8.2.3 *Muffle (Coke)*—Place the crucible in a warm-vented muffle (about 200°C) and gradually raise the temperature to 800 ± 25°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 ½ to ¾ 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.

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[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.

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 ± 50°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 prescribed reagents and operations in full compliance with the standard. It is acceptable but less accurate to make corrections by running a reagent blank in duplicate using procedures exactly as described in Section 9 of the standard, using the same amount of all reagents that were employed in the routine determination. If the standard sulfate analysis procedure is carried out once a week, or if a new supply of a reagent is used, for a series of solutions covering the approximate range of sulfur concentrations in the samples, add to or subtract from the weight of $BaSO_4$ determined for the sample, the deficiency or excess found by the appropriate check determination. This is more accurate than the simple reagent blank because, for the amounts of sulfur in question and the conditions of precipitation prescribed, the solubility error for $BaSO_4$, is probably the largest one to be considered. Barium sulfate is soluble[7] in acids and pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, if very high-purity reagents are used or extra precaution is exercised, there may be no sulfate apparent in the blank. In other words, the solubility limit for $BaSO_4$ has not been reached or, at any rate, not exceeded; consequently, some sulfate in the sample can remain in solution or redissolve.

9. Calculation

9.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \%, in the analysis sample} = \frac{(A - B) \times 13.738}{C} \qquad (1)$$

where:

A = grams of $BaSO_4$ precipitated,

B = grams of $BaSO_4$ correction, and

C = grams of sample used.

TEST METHOD B—BOMB WASHING METHOD[8]

10. Reagents

10.1 *Purity of Reagents*—(See 7.1.)

10.2 *Purity of Water*—(See 7.2.)

10.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

10.4 *Hydrochloric Acid* (1 + 1)—(See 7.5.)

10.5 *Sodium Carbonate Solution*—Dissolve 20.90 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°C.

10.6 *Wash Solution*—Dilute 1 mL of a saturated solution of methyl orange to 1 L with water.

11. Procedure

11.1 *Ignition*—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination (Test Method D 2015 or D 3286). The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified in the calorimetric determination (Test Method D 2015 or D 3286). The bomb shall stand in the calorimeter water for not less than 5 min after firing.

11.1.1 **Warning**—The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Practice E 144.

11.1.1.1 The weight of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

11.1.1.2 Carefully inspect bomb parts after each use. Frequently check the threads on the main closure for wear. Replace cracked or significantly worn parts. Return the bomb to the manufacturer occasionally for inspection and possibly proof firing.

11.1.1.3 Equip the oxygen supply cylinder with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 300 to 500-psi (2070 to 3440 KPa) discharge pressure are obtainable from commercial sources of compressed gas equipment. Check the pressure gage periodically for accuracy.

11.1.1.4 During ignition of a sample, the operator must not permit any portion of his body to extend over the calorimeter.

11.1.1.5 Exercise extreme caution when combustion aids are employed so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material, such as unpelleted benzoic acid, unless thoroughly mixed with the sample.

11.1.1.6 Admit oxygen slowly into the bomb so as not to blow powdered material from the crucible.

11.1.1.7 Do not fire the bomb if it has been filled to greater than 30 atm (3 MPa) pressure with oxygen, the bomb has been dropped or turned over after loading, or there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

11.2 *Subsequent Treatment*—Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 min. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, discard the determination. Wash carefully all parts of the interior of the bomb, including the capsule, with a fine jet of water containing methyl orange (10.6) until no acid reaction is observed. It is essential to wash through the valve opening in the case of

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[7] *Journal of the American Chemical Society*, JACSA, Vol 32, 1910, p. 588; Vol 33, 1911, p. 829.

[8] Selvig, W. A., and Fieldner, A. C. "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-Washing and Sodium Peroxide Fusion Methods," *Industrial and Engineering Chemistry*, JECHA, Vol 29, 1927, pp. 729–733.

bombs equipped with compression valves, or other types of valves with large openings, as considerable spray can collect in such valve openings.

11.3 Collect the washings in a 250-mL beaker and titrate with standard sodium carbonate solution (10.5) to obtain the acid correction for the heating value, as specified under the calorimetric determination Test Method D 2015 or D 3286. Adjust the pH from 5.5 to 7.0 with dilute NH_4OH, heat the solution to boiling, and filter through a qualitative paper. Wash the residue and paper thoroughly five or six times with hot water. Adjust the acidity of the filtrate and washings, amounting to about 250 mL, precipitate, and determine the sulfur as specified under the Eschka method, Sections 6-9, inclusive.

NOTE 2—If the use of 1-g sample weight in the calorimetric determination produces an excess amount of sulfate that cannot be precipitated by the addition of 10 mL of barium chloride solution, either of the following alternatives may be used: (*1*) increase the amount of the baruim chloride solution from 10 mL in increments of 5 mL up to a maximum of 20 mL of solution, or (*2*) reduce the amount of sample from 1 to 0.5 g and add 0.5 g of benzoic acid in order to maintain appropriate temperature rise so the precision of the gross calorific value determination is not adversely affected.

12. Report

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

12.2 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.

12.3 Use the percentage of moisture as determined by Test Method D 3173 to calculate the as-determined results from the analysis basis to a dry basis.

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

13. Precision and Bias

13.1 The precision of this test method for the determination of Total Sulfur in Coal are shown in Table 1.

13.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations carried out on the same sample, in the same laboratory, by the same operator, using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

13.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results carried out in different laboratories, using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

13.2 *Bias*—These are stoichiometric methods that agree with each other very well when known amounts of solutions or compounds containing predetermined quantities of sulfur (preferably as sulfate) are added to blanks determined as described in 8.4.

TABLE 1 Concentrations Range and Limits for Repeatability and Reproducibility of Total Sulfur in Coal

Range, %	Repeatability Limit, *r*	Reproducibility Limit, *R*
Under 2	0.05	0.10
Over 2	0.10	0.20
Coke	0.03	0.05