Designation: D 1757 – 96 (Reapproved 2002)

Standard Test Method for Sulfate Sulfur in Ash from Coal and Coke[1]

This standard is issued under the fixed designation D 1757; 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 This test method pertains to the determination of sulfate sulfur in coal or coke ash.

1.2 The values stated in SI units (Practice E 380) shall be regarded as the standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 2795 Test Methods for Analysis of Coal and Coke Ash[3]

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[3]

D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[3]

D 3682 Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes[3]

D 4326 Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence[3]

E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)[4]

2.2 *British Standard:*

BS 1016, Part 14 Analysis of Coal Ash and Coke Ash[5]

3. Summary of Test Methods

3.1 *Test Method A—Modified British Method*—A specified quantity of ash is digested in boiling dilute hydrochloric acid solution to which bromine water is added to convert sulfite that may be present to the sulfate form. After neutralization and precipitation of iron with ammonium hydroxide, the mixture is filtered and sulfate in the filtrate is determined gravimetrically as barium sulfate ($BaSO_4$).

3.2 *Test Method B—Eschka Mixture*—A specified quantity of ash and Eschka mixture are ignited together in air. The sulfates are dissolved in hot water and separated from undissolved ash residue and magnesium oxide by filtration. Sulfate in the filtrate is determined gravimetrically as barium sulfate ($BaSO_4$).

4. Significance and Use

4.1 Laboratory furnace temperature and furnace ventilation have an influence on SO_3 retention in laboratory ash. Consequently, sulfur in ash as determined in the laboratory cannot be assumed to be equivalent to sulfur present in the mineral matter in coal or to the retention of sulfur in ash produced under the conditions of commercial utilization.

4.2 The sulfate sulfur determined by these test methods can be used to calculate the sulfur trioxide portion of ash so that the ash content or ash composition can be reported on a sulfur trioxide free basis.

5. Interferences

5.1 Barium in coal ashes can result in incomplete recovery of sulfate sulfur.

5.2 High iron content can be encountered in coal and coke ash and can introduce error if, during the sulfate precipitation, the iron is either partially adsorbed by the $BaSO_4$ precipitate or coprecipitated as iron sulfate.

6. Apparatus

6.1 *Muffle Furnace*, electric, capable of maintaining a temperature of 800 ± 25°C for igniting barium sulfate.

6.2 *Crucibles or Capsules*, porcelain, platinum, alundum, or silica of 10 to 15-mL capacity, for igniting $BaSO_4$.

7. Purity of 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 Analytical Reagents of the American Chemical Society,

---

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

Current edition approved April 10, 1996. Published June 1996. Originally published as D 1757 – 60 T. Last previous edition D 1757 – 96.

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

[3] *Annual Book of ASTM Standards*, Vol 05.06.

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

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036..

where such specifications are available.[6]

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

8. Analysis Sample

8.1 The analysis sample shall be prepared in accordance with the section on Preparation of Coal Ash and Coke Ash in one of the following Test Methods: D 2795, D 3174, D 3682, or D 4326.

8.2 Prior to analysis re-ignite at the original conditions a sufficient quantity of thoroughly mixed analysis sample for a period of not less than 1 h.

8.3 For purposes of comparison of results between laboratories the analysis sample shall be taken from a common analysis sample prepared according to the conditions specified in 8.1 and 8.2.

ALTERNATIVE PROCEDURES
TEST METHOD A—MODIFIED BRITISH STANDARD

9. Reagents

9.1 *Ammonium Chloride-Ammonium Hydroxide Solution*—Dissolve 20.1 g of ammonium chloride (NH_4Cl) in approximately 500 mL of water, add 10 mL of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90), dilute to 1 L with water, and mix thoroughly.

9.2 *Ammonium Hydroxide*, Concentrated (NH_4OH, sp gr 0.90).

9.3 *Barium Chloride Dihydrate Solution (100 g/L)*—Dissolve 100 g of barium chloride ($BaCl_2$ $2H_2O$) and dilute to 1 L with water.

9.4 *Bromine Water*, Saturated—Add an excess of bromine to 1 L of water.

9.5 *Hydrochloric Acid, Concentrated*—(HCl, sp gr 1.19).

9.6 *Hydrochloric Acid, Dilute—(1 + 9)*—Mix 1 volume of concentrated hydrochloric acid (HCl) with 9 volumes of water.

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

9.8 *Potassium Sulfate Solution*—Dissolve 2 g of potassium sulfate (K_2SO_4) and dilute to 1 L with water.

9.9 *Silver Nitrate Solution—(0.02 N)*—Dissolve 3.4 g of silver nitrate ($AgNO_3$) in 1 L of water.

10. Procedure

10.1 *Extraction of Sulfate Sulfur*—Weigh 0.5 g ± 0.0001 g of prepared ash sample and transfer to a 250-mL beaker. Add 100 mL of dilute HCl and 5 mL of bromine water. Cover the beaker, boil 15 min, and digest an additional 30 to 45 min at a temperature just below boiling.

10.2 *Precipitation of Iron*—While the solution is hot, add a few drops of methyl orange indicator. Precipitate iron by slowly adding concentrated NH_4OH (sp gr 0.90) until a slight excess is present as noted by the change in the methyl orange indicator, then add 5 mL excess (Note 1) constantly stirring to coagulate the yellowish-brown ferric hydroxide precipitate. Heat to just below boiling, hold for 15 min, and allow to settle and stand for an additional 15 min. Filter the solution through an ashless, close textured, double-acid-washed paper into a 400-mL beaker, washing the paper with four 20-mL portions of NH_4Cl—NH_4OH solution. Discard the filter.

NOTE 1—The excess of strong ammonium hydroxide minimizes the possibility of sulfate being carried down with the iron hydroxide precipitate.

10.3 *Precipitation of Sulfate Sulfur*:

10.3.1 Add a few drops of methyl orange to the filtrate from 10.2. Make it just neutral with dilute HCl (1 + 9), then add 10 mL in excess. Boil the solution and slowly add 9 mL of $BaCl_2$ solution from a pipet, while stirring constantly. Continue boiling for 15 min and allow to stand 2 h, or preferably overnight, at a temperature just below boiling. Add 1 mL $BaCl_2$. If additional precipitate forms repeat the digestion and precipitation steps using half the weight of sample.

10.3.2 Filter through an ashless, close-textured, acid-washed paper and wash with hot water until 1 drop of $AgNO_3$ solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate. Three to five washings are usually adequate.

10.3.3 For samples calculating to less than 2 % SO_3(see Section 13) the test should be repeated with the addition of 25.0 mL of potassium sulfate solution (2 g/L) to the filtrate from 10.2. This "standard addition" method minimizes solubility losses of $BaSO_4$ for tests on samples containing low quantities of SO_3.

10.4 *Ignition of Barium Sulfate*—Place the wet filter containing the precipitate of $BaSO_4$ in a weighed crucible. Fold the paper over the precipitate loosely to allow free access of air. To prevent spattering, smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to 800 ± 25°C and ignite to constant weight.

10.5 *Blank*—Complete a blank without any sample using the same amount of reagents employed in the 10.2 through 10.3.

TEST METHOD B—ESCHKA METHOD

11. Reagents

11.1 See the section on Reagents in Test Methods D 3177.

12. Procedure

12.1 *Ignition of Sample*:

12.1.1 Weigh out 4 ± 0.2 g of Eschka mixture (Note 2) on glazed paper. Thoroughly mix 0.5 g ± 0.0005 g of ash sample and about 3 g of Eschka mixture (Note 3) on a separate piece of glazed paper. Transfer to a crucible and cover with the remaining Eschka mixture.

NOTE 2—Eschka mixture is the major source of contamination (2 to 4 mg of $BaSO_4$) and quantities therefore must be controlled.

NOTE 3—Incomplete mixing of ash and Eschka mixture can result in incomplete recovery of sulfate sulfur.

---

[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.

12.1.2 Place the crucible in a muffle furnace (less than 200°C) and gradually raise the temperature to 800 ± 25°C in 30 min. Maintain this temperature 1 h.

12.2 *Precipitation of Sulfate Sulfur*—Remove the crucible from the muffle furnace and allow it to cool. Transfer the contents into a 400-mL beaker and digest with 100 mL of hot water for ½ to ¾ h, while stirring occasionally. Decant the solution through qualitative filter paper, retaining as much insoluble material in the 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, acid to methyl orange with approximately 10 mL of HCl (1 + 1). Add 4 mL of saturated bromine water and bring the solution to a boil. Continue boiling until the excess bromine is expelled, as indicated by a colorless solution. Make the solution just neutral to methyl orange with sodium carbonate (Na_2CO_3) solution and then add 10 mL of HCl (1 + 9). Finish the determination of $BaSO_4$ as in 10.3 beginning with the addition of barium chloride solution.

12.3 *Blank*—Complete a blank without any sample using the same amount of reagents employed in the 12.1 through 12.2.

13. Calculation

13.1 Calculate the percent of SO_3 in the ash sample as follows:

$$SO_3\text{, wt \%} = [(A - B) \times 34.3]/C \tag{1}$$

where:
A = $BaSO_4$ precipitated (sample), g,
B = $BaSO_4$ precipitated (blank), g, and
C = ash sample used, g.

14. Report

14.1 Report results as weight percent SO_3 in the ash.

14.2 Report the method used to prepare the ash sample.

15. Precision and Bias

15.1 *Precision Statement for the Modified British Method*:

15.1.1 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample of ash, in the same laboratory, by the same operator using the same apparatus should exceed the repeatability limit specified in the Table 1 for not more than 5 % of such paired values. When such a difference is found to exceed the repeatability limit there is reason to question one or both of the test results.

15.1.2 *Reproducibility*—The difference in absolute value between two consecutive test results, carried out on representative portions of the same sample of ash, in the different laboratories, by the different operators using different apparatus should exceed the reproducibility limit specified in the Table 1 for not more than 5 % of such paired values. When such a difference is found to exceed the reproducibility limit there is reason to question one or both of the test results.

15.2 *Precision Statement for the Eschka Method*:

15.2.1 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample of ash, in the same laboratory, by the same operator using the same apparatus should exceed the repeatability limit specified in the Table 2 for not more than 5 % of such paired values. When such a difference is found to exceed the repeatability limit there is reason to question one or both of the test results.

15.2.2 *Reproducibility*—The difference in absolute value between two consecutive test results, carried out on representative portions of the same sample of ash, in the different laboratories, by the different operators using different apparatus should exceed the reproducibility limit specified in the Table 2 for not more than 5 % of such paired values. When such a difference is found to exceed the reproducibility limit there is reason to question one or both of the test results.

15.3 *Bias*—Bias has not been determined.

16. Keywords

16.1 coal ash; coke ash; sulfur

TABLE 1 Precision for the Modified British Method

SO_3 Content	Repeatability	Reproducibility
<1	0.1	0.2
≥1≤ 5	0.2	0.3
>5 ≤10	0.4	0.4
>10 ≤20	0.6	1.0

TABLE 2 Precision for the Eschka Method

SO_3 Content	Repeatability	Reproducibility
<1	0.1	0.2
≥1≤ 5	0.3	0.4
>5 ≤10	0.4	0.8
>10 ≤20	0.5	1.0