



Designation: E 775 – 87 (Reapproved 1996)

## Standard Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel<sup>1</sup>

This standard is issued under the fixed designation E 775; 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 approval. A superscript epsilon ( $\epsilon$ ) 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 prepared analysis samples of solid forms of refuse-derived fuel (RDF). Sulfur is included in the ultimate analysis of RDF.

1.2 The test methods appear in the following order:

Test	Sections
Eschka Method	8-11
Bomb Washing Method	12 and 13

1.3 These test methods may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.4 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are for information only.

1.5 *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.* For specific precautionary statements see Section 6.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

E 711 Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter<sup>4</sup>

E 829 Practice for Preparing Refuse-Derived Fuels (RDF) Laboratory Samples for Analysis<sup>4</sup>

### 3. Terminology

#### 3.1 Definitions of Term Specific to This Standard:

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.06 on Recovery and Reuse.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.05.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.04.

3.1.1 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:<sup>5</sup>

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

### 4. Summary of Test Methods

4.1 *Eschka Method*—A weighed sample and Eschka mixture are ignited together and the sulfur is precipitated from the resulting solution as barium sulfate ( $\text{BaSO}_4$ ). The precipitate is filtered, ashed, and weighed.

4.2 *Bomb Washing Method*—Sulfur is precipitated as  $\text{BaSO}_4$  from the oxygen-bomb calorimeter washings and the precipitate is filtered, ashed, and weighed.

### 5. Significance and Use

5.1 The standards are available to producers and users of RDF for determining the total sulfur content of the fuel.

### 6. Precautions

6.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under negative pressure hood when possible; and washing hands before eating or smoking.

<sup>5</sup> *Thesaurus on Resource Recovery Terminology*, ASTM STP 832, ASTM, 1983, p.72.

## 7. Sampling

7.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

7.2 The sampling method for this procedure should be based on agreement between the involved parties.

7.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Practice E 829. This procedure must be performed carefully to preserve the sample's representative characteristics (other than particle size) while preparing the analysis sample to be used in the procedures.

### TEST METHOD A—ESCHKA METHOD

## 8. Apparatus

8.1 *Gas* (Note 1) or *Electric Muffle Furnace or Burners*, for igniting the sample with Eschka mixture and for igniting the barium sulfate ( $\text{BaSO}_4$ ).

NOTE 1—Gas may contain sulfur compounds in sufficient quantities to affect the results.

8.2 *Crucibles or Capsules*—Porcelain capsules,  $\frac{7}{8}$  in. (22 mm) in depth and  $1\frac{3}{4}$  in. (44 mm) 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 the final ignition step (see 10.3.8).

## 9. Reagents

9.1 *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 American Chemical Society, where such specifications are available. Other grades<sup>6</sup> 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.

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III conforming to Specification D 1193.

9.3 *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.

9.4 *Bromine Water* (saturated)—Add an excess of bromine to 1 L of water.

9.5 *Eschka Mixture*—Thoroughly mix 2 parts by weight of light calcined magnesium oxide ( $\text{MgO}$ ) with 1 part of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Both materials should be as free as possible from sulfur.

9.6 *Hydrochloric Acid* (1 + 1)—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

9.7 *Hydrochloric Acid* (1 + 9)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 9 volumes of water.

9.8 *Methyl Orange Indicator Solution* (0.2 g/L)—Dissolve 0.2 g of methyl orange in 1000 mL of hot water and filter.

9.9 *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 20 g of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in 100 mL of water, using a sufficient excess of  $\text{Na}_2\text{CO}_3$  to ensure a saturated solution.

9.10 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide ( $\text{NaOH}$ ) in 1 L of water. This solution may be used in place of  $\text{Na}_2\text{CO}_3$  solution.

## 10. Procedure

10.1 *Preparation of Sample and Eschka Mixture*—Weigh to the nearest 0.1 mg about 1 g of mixed air-dried analysis sample and 3 g of Eschka mixture on glazed paper. Mix thoroughly. The amount of sample to be taken will depend on the amount of  $\text{BaCl}_2$  solution required (see 10.3.5 and Note 2).

10.1.1 Quantitatively transfer the mixture to a porcelain capsule or porcelain crucible or platinum crucible, and cover with about 1 g of Eschka mixture.

10.2 *Ignition*—Heat the crucible over a gas flame as described in 10.2.1, or in a gas- or electrically heated muffle furnace as described in 10.2.2. The use of artificial gas for heating the sample and Eschka mixture is permissible only when the crucibles are heated in a muffle (see Note 2).

10.2.1 Heat the crucible, placed in a slanting position partially covered on a triangle, over a very low flame. This prevents rapid expulsion of the volatile matter and affords more complete oxidation of the sulfur. After 30 min of low flame heating, gradually increase the temperature and occasionally stir the mixture until all black particles have disappeared, which is an indication of complete combustion.

10.2.2 Place the crucible in a cold muffle furnace and gradually raise the temperature to  $800 \pm 25^\circ\text{C}$  in about 1 h. Maintain this maximum temperature until upon stirring all black particles have disappeared (about  $1\frac{1}{2}$  h).

### 10.3 Subsequent Treatment:

10.3.1 Remove the crucible, cool, and empty the contents quantitatively into a 200-mL beaker. Digest with 100 mL of hot water for  $\frac{1}{2}$  to  $\frac{3}{4}$  h with occasional stirring.

10.3.2 Decant the supernatant liquid through a filter into a 600-mL beaker. Wash the insoluble matter with hot water several times using 25 mL of water at each washing and filter the washings through the filter paper into the 600-mL beaker. After washing, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated, collecting the wash waters in the 600-mL beaker.

10.3.3 Treat the filtrate with 10 to 20 mL of saturated bromine water. Make slightly acid with HCl and boil to expel the liberated bromine.

10.3.4 Neutralize using methyl orange indicator with NaOH or  $\text{Na}_2\text{CO}_3$  solution; then add 1 mL of HCl solution (1 + 9).

10.3.5 Boil again and then, while stirring constantly, add slowly from a pipet 10 mL or more of  $\text{BaCl}_2$  solution.

NOTE 2—Barium chloride solution must be added in excess. If more than 10 mL of  $\text{BaCl}_2$  solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion.

<sup>6</sup> "Reagent Chemicals, American Chemical Society Specification," *American Chemical Society*, Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U. K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."



10.3.6 Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling.

NOTE 3—When standing overnight at a temperature slightly less than boiling, cover the flask with a watchglass to prevent the solution from evaporating to dryness and to protect it from external contamination.

10.3.7 Filter the solution and the precipitate of barium sulfate ( $\text{BaSO}_4$ ) through an ashless paper and wash the  $\text{BaSO}_4$  residue with hot water until 1 drop of silver nitrate ( $\text{AgNO}_3$ ) solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate.

10.3.8 Place the wet filter containing the precipitate of barium sulfate ( $\text{BaSO}_4$ ) in a preweighed platinum, porcelain, silica, or Alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering.

10.3.9 Smoke the paper off gradually over a gas burner or in a gas or electrically heated muffle furnace. At no time allow it to burn with a flame (see Note 4). After charring of the paper, raise the temperature to approximately  $925^\circ\text{C}$  and heat to constant weight.

NOTE 4—Partially covering the crucible while smoking and smoldering will aid in the prevention of the flaming of the paper.

10.3.10 Transfer the crucibles to a desiccator and weigh when cooled to room temperature.

10.4 *Blanks and Corrections*—In all cases a correction must be applied. Either a reagent blank may be run exactly as described above, using the same amount of all reagents that were employed in the routine determination, or a more accurate correction may be made by analyzing a weighed portion of a standard sulfate using the prescribed reagents and operations.

NOTE 5—If the latter procedure is carried out once a week, or whenever a new supply of a reagent is used for a series of solutions covering the approximate range of sulfur concentrations in the samples, it is only necessary to add or subtract from the weight of  $\text{BaSO}_4$  determined for the sample the deficiency or excess found by the appropriate “check” determination. This procedure is more accurate than the simple reagent blank because, for the amounts of sulfur in question and condition of precipitation prescribed, the solubility error for  $\text{BaSO}_4$  is probably the largest one considered. Barium sulfate is soluble in acids<sup>7</sup> and in 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  $\text{BaSO}_4$  has not been reached or at any rate not exceeded; consequently, some sulfate in the sample may remain in solution or has redissolved.

## 11. Calculation

11.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \%} = (A - B) \times 13.738/W \quad (1)$$

where:

- A = grams of  $\text{BaSO}_4$  precipitated,  
B = grams of  $\text{BaSO}_4$  correction,  
W = grams of sample used, and  
13.738 = percentage of sulfur in  $\text{BaSO}_4$ .

## TEST METHOD B—BOMB WASHING METHOD<sup>8</sup>

### 12. Reagents

12.1 *Purity of Reagents*—see 9.1.

12.2 *Purity of Water*—see 9.2.

12.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

12.4 *Bromine Water* (saturated)—see 9.4.

12.5 *Hydrochloric Acid* (1 + 1)—see 9.6.

12.6 *Sodium Carbonate Solution*—Dissolve 18.02 g of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in water and dilute to 1 L. The  $\text{Na}_2\text{CO}_3$  should be previously dried for 24 h at  $105^\circ\text{C}$ .

NOTE 6—Other concentrations of sodium carbonate solution may be used.

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

### 13. Procedure

13.1 *Ignition*—Sulfur is determined in the washings from the oxygen-bomb calorimeter following calorimetric determination in accordance with Test Method E 711. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination. The bomb shall stand in the calorimeter water for not less than 5 min after firing.

13.2 *Subsequent Treatment*:

13.2.1 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.

13.2.2 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 (12.7) until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

13.2.3 Collect the washings in a 250-mL beaker and titrate with standard sodium carbonate solution (12.6) to obtain the acid correction for the heating value, as specified in the calorimetric determination of Test Method E 711.

13.2.4 Adjust the pH to between 5.5 and 7.0 with dilute  $\text{NH}_4\text{OH}$  and heat the solution to boiling.

<sup>7</sup> Allen, E. T., and Johnston, John, “The Exact Determination of Sulfur in Soluble Sulfates,” *Journal of the American Chemical Society*, Vol 32, No. 5, 1910, pp. 588-617; and Johnston, John, and Adams, L. H., “The Phenomenon of Acclusion in Precipitates of Barium Sulfate, and its Relation to the Exact Determination of Sulfate,” *Journal of the American Chemical Society*, Vol 33, No. 6, 1911, pp. 829-845.

<sup>8</sup> Selvie, 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*, Vol 29, 1927, pp. 729-733.



13.2.5 Filter through a qualitative filter paper and wash the residue and paper thoroughly five or six times with hot water collecting the filtrate and washings.

13.2.6 To the filtrate and washings add 1 mL of saturated bromine water (12.4) and sufficient HCl (12.5) to make it slightly acid. Boil the solution to expel the excess bromine.

13.2.7 Adjust the acidity, precipitate and determine the sulfur as described in 10.3.4-11.1 inclusive.

#### **14. Precision and Bias <sup>9</sup>**

##### 14.1 *Precision:*

<sup>9</sup> Data from preliminary testing and round-robin tests are on file in ASTM Research Report RR-E38-1000. A copy of the report is available on loan from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103.

14.1.1 The standard deviation of individual determinations in percent absolute, are as follows:

Typical average value	0.35 %
Within-laboratory	0.03 %
Between-laboratory	0.06 %

14.1.2 The above precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.<sup>9</sup>

14.2 *Bias*—The bias of this test method has not been determined because of the lack of a recognized standard reference material.

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