Designation: E775 – 15

Standard Test Methods for
Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[1]

This standard is issued under the fixed designation E775; 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 present two alternative procedures for the determination of total sulfur in prepared analysis samples of solid 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 SI units are to be regarded as standard. Inch-pound units are provided for information.

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:*[2]

D1193 Specification for Reagent Water

D5681 Terminology for Waste and Waste Management

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E711 Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter (Withdrawn 2011)[3]

E829 Practice for Preparing Refuse-Derived Fuel (RDF) Laboratory Samples for Analysis (Withdrawn 2002)[3]

3. Terminology

3.1 For definitions of terms used in this standard, refer to Terminology D5681.

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 ($BaSO_4$). The precipitate is filtered, ashed, and weighed.

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

5. Significance and Use

5.1 These procedures are used by 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, precautions should be observed when conducting tests on samples. Recommended safety 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 upon completion of activity and before eating or smoking.

7. Sampling

7.1 RDF products are frequently inhomogeneous. For this reason significant care should be exercised to obtain a representative 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 through a 0.5-mm screen as described in Practice E829. This procedure must be performed carefully to preserve the sample's representativeness beyond just particle size while preparing the analysis sample to be analyzed according to these procedures.

---

[1] These test methods are under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.03 on Treatment, Recovery and Reuse.

Current edition approved Sept. 1, 2015. Published September 2015. Originally approved in 1981. Last previous edition approved in 2008 as E775 – 87(2008)$^{\varepsilon 1}$. DOI: 10.1520/E0775-15.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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 ($BaSO_4$).

NOTE 1—Gas used can contain sulfur compounds in sufficient quantities to positively bias the results. The gas may require sulfur compound removal prior to use.

8.2 *Crucibles or Capsules*—Porcelain capsules, ⅞ in. (22 mm) in depth and 1¾ 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[4] may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without impacting 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 D1193.

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

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 (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_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 ($Na_2CO_3 \cdot 10H_2O$) or 20 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.

9.10 *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 Na_2CO_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 $BaCl_2$ 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 furnace (see Note 3).

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 ± 25°C in about 1 h. Maintain this maximum temperature until upon stirring all black particles have disappeared (about 1½ 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 ½ to ¾ 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 filter paper into a 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 washings 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 Na_2CO_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 $BaCl_2$ solution.

NOTE 2—Barium chloride solution must be added 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.

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 ($BaSO_4$) through ashless paper and wash the $BaSO_4$ residue 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.

---

[4] "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."

10.3.8 Place the wet filter containing the precipitate of barium sulfate ($BaSO_4$) in a preweighed platinum, porcelain, silica, or Alundum crucible, allowing a free access of air by loosely placing and folding filter paper over the precipitate to prevent spattering.

10.3.9 Burn off the filter paper 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°C and heat to constant weight.

NOTE 4—Partially covering the crucible while the filter paper is smoking and smoldering will prevent the paper from burning with a flame.

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

10.4 *Blanks and Corrections*—In all analyses 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 sample sulfur content determination, or a more accurate correction may be made by analyzing a weighed portion of a sulfate standard using the prescribed reagents and operations.

NOTE 5—If the weighed portion of a sulfate standard procedure is performed once a week, or whenever a new supply of a reagent is used, it is only necessary to add or subtract the "check" standard value from the weight of $BaSO_4$ determined for the sample. This procedure is more accurate than the simple reagent blank procedure because the solubility error for $BaSO_4$ is probably the largest factor impacting measurements according to this procedure. Barium sulfate is soluble in acids[5] 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 not be sulfate measurable in the "blank." This is due to the solubility limit for $BaSO_4$ not being reached or 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 $BaSO_4$ precipitated,
B = grams of $BaSO_4$ correction,
W = grams of sample used, and
13.738 = percentage of sulfur in $BaSO_4$.

TEST METHOD B—BOMB WASHING METHOD[5]

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 (NH_4OH).

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 (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°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 collected washings from the oxygen-bomb calorimeter according to calorimetric determination in accordance with Test Method E711. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under Test Method E711. 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 constant rate such that 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 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 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 E711.

13.2.4 Adjust the pH to between 5.5 and 7.0 with dilute NH_4OH and heat the solution to boiling.

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 acidic. Boil the solution to expel 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[6]

14.1 *Precision:*

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 %

---

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

[6] Data from preliminary testing and round-robin tests are on file at ASTM International Headquarters. Request Research Report RR-E38-1000.

14.1.2 The above precision estimates are based on an interlaboratory study conducted in accordance with Practice E180.[6]

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

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/