



Designation: **E776–87 (Reapproved 2009) E776 – 16**

Standard Test Method for Determination of Forms of Chlorine in Refuse-Derived Fuel¹

This standard is issued under the fixed designation E776; 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 covers the determination of the forms of chlorine in refuse-derived fuel-three (RDF): total chlorine, water-soluble chloride, and water-insoluble chlorine.

1.2 This test method may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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 precaution statements see Section 6 and 11.2.1.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

E144 Practice for Safe Use of Oxygen Combustion Vessels

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³

E287 Specification for Laboratory Glass Graduated Burets

E711 Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter (Withdrawn 2011)³

E829 Practice for Preparing Refuse-Derived Fuel (RDF) Laboratory Samples for Analysis (Withdrawn 2002)³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 *Definitions of Terms Specific to This Standard:*

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*:⁴

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.

3.1.2 *total chlorine*—all chlorine as determined in the refuse-derived fuel.

3.1.3 *water-insoluble chlorine*—water-insoluble chlorides and chlorine in the refuse-derived fuel.

3.1.4 *water-soluble chloride*—those chlorides which are water-solubilized by water extraction as determined in the refuse-derived fuel.

4. Summary of Test Method

4.1 The forms of chloride and chlorine are determined. The various procedures in the method convert the forms of chlorine into a water-soluble chloride form that can be quantitated by titration.

¹ This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.03 on Treatment, Recovery and Reuse.

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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.

⁴ *Thesaurus on Resource Recovery Terminology, ASTM STP 832*, ASTM, 1983, p. 72.

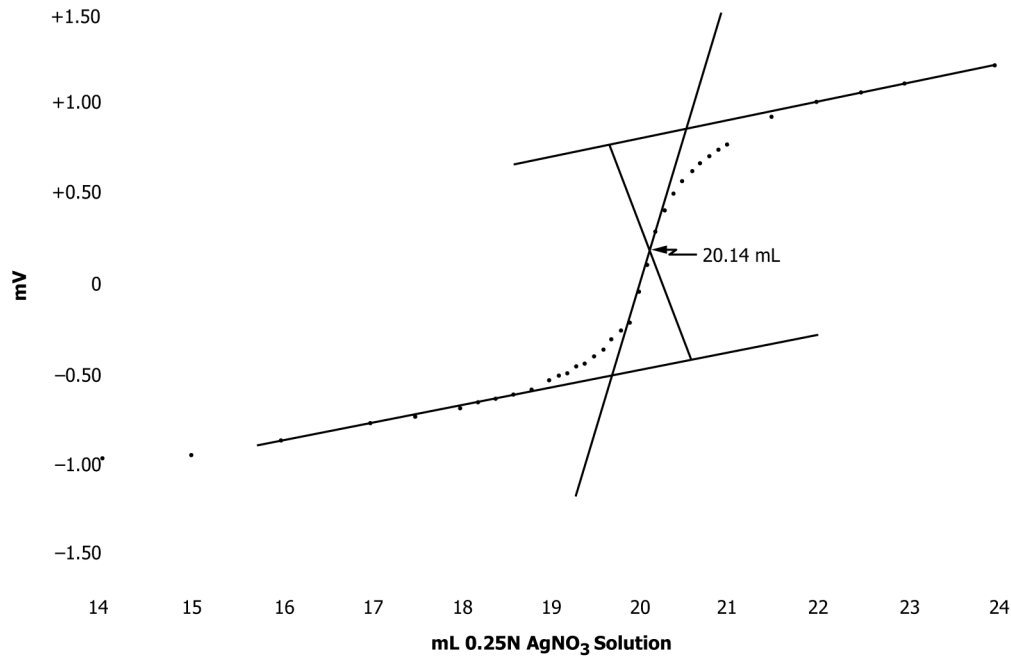


FIG. 1 Graph From a Potentiometric Titration of Chloride

4.1.1 *Total Chlorine*—The sample is combusted in an oxygen atmosphere. The chlorine is converted to chloride and absorbed in an alkaline solution.

4.1.2 *Water-Soluble Chlorides*—A portion of the analysis sample is successively extracted with hot chloride-free water.

4.1.3 *Water-Insoluble Chlorine*—Water-insoluble chlorine is calculated from the results of the total chlorine and the water-soluble chloride determination where:

$$\text{water - insoluble chlorine} = \text{total chlorine} - \text{water - soluble chlorides} \quad (1)$$

4.2 The chlorides contained in the alkaline solution (4.1.1) and the extraction solution (4.1.2) are determined by potentiometric (see Section 13) or modified Volhard titration (see Section 14).

5. Significance and Use

5.1 The standard is available to producers and users of RDF for determining the content and forms of chlorine present in 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 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. Interferences

7.1 Potentiometric Titration Method A:

7.1.1 Iodide and bromide are also titrated—interferences that will titrate as chloride. Ferricyanide causes high biased results and must be removed. Chromate and dichromate interfere and should be reduced to the chromic state or be removed. Ferric iron interferes if present in an amount substantially higher than the amount of chloride. Chromic ions, ferrous ions, and phosphates do not interfere.

7.1.2 Grossly contaminated sample solutions usually require pretreatment. Where contamination is minor, some contaminants can be destroyed simply by the addition of nitric acid.

7.2 Volhard Titration Method B:

7.2.1 Compounds that have a strong oxidizing action interfere by reacting with thiocyanate. These compounds should be reduced beforehand by treatment with ferrous sulfate or a similar reducing agent.

7.2.2 Salts of mercury and palladium interfere by reacting with thiocyanate. They may be removed by precipitation with hydrogen sulfide before the addition of silver nitrate. The excess of sulfide is easily removed by gently boiling the acid solution for a few minutes. Sulfite can be eliminated in the same way.

7.2.3 Cyanide is also precipitated by silver nitrate. It is usually determined separately by the Liebig-Deniges method and a correction is applied to the results of the Volhard titration.⁵

7.2.4 The Volhard method, as with the potentiometric method, directly applied to a mixture of halides can determine only total halide content excluding fluoride. Preliminary treatment is necessary for the determination of chloride alone in a mixture.⁶

8. Apparatus

8.1 *Balance*, having a sensitivity of balance capable of weighing with an accuracy of 0.1 mg.

8.2 *Apparatus for Bomb Combustion of the Sample*.

8.2.1 *Oxygen Bomb*, similar to that used in the determination of the calorific value of refuse-derived fuels as described in Test Method E711.

8.2.2 *Capsule*, for holding the sample, approximately ~~25 mm~~ 25 mm in diameter at the top, approximately 12 mm deep, and conforming to Test Method E711.

8.2.3 *Firing Wire*, as specified in Test Method E711.

8.2.4 *Firing Circuit*, as specified in Test Method E711.

8.2.5 *Metal Vessel*, cylindrical, such that the bomb will be fully immersed when approximately 2 L of water are added.

8.3 *Magnetic Stirrer and Stirring Bars*.

8.4 *Apparatus for Potentiometric Titration*:

8.4.1 *Potentiometric Titration Assembly*, using a silver indicator electrode and a calomel reference electrode containing a saturated sodium nitrate solution as a bridge.

NOTE 1—All glassware and graduated apparatus should be Class A or equivalent as described in Specification E287.

8.5 *Centrifuge*, capable of centrifuging 100-mL centrifuge tubes at approximately 1200 rpm.

8.6 *Centrifuge Tubes*, for chloride solution preparation (alternative method).

8.7 *Filter Paper*, used to filter chloride solution.

NOTE 1—All glassware and graduated apparatus should be Class A or equivalent as described in Specification E287.

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 Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁷ 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.

9.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean at least Type III reagent water conforming to Specification D1193.

9.3 *Potassium Hydroxide Solution (0.2 N)*—Dissolve 13.2 g of potassium hydroxide (KOH) in water and dilute to 1 L with water.

9.4 *Oxygen*—The oxygen used for combustion shall be free of combustible matter. Oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, will meet this requirement.

9.5 *Sodium Chloride (NaCl)*—Primary standard quality (purity of 100 ± 0.02 %).

9.6 *Sodium Chloride, Primary Standard Solution (0.025 N)*—Crush 10 to 20 g of primary standard sodium chloride (NaCl) to 100-mesh fineness and dry in a glass container at 120°C for 2 h. Stopper and keep desiccated. Dissolve 5.844 g \pm 0.1 mg of dried primary standard NaCl in water and dilute to 1 L. Dilute 25.00 mL of this solution to 100.0 mL.

9.7 *Methanol*.

9.8 *Nitric Acid (1 + 1)*—Mix equal volumes of concentrated nitric acid (HNO₃, sp, gr, 1.42) and water.

9.9 *Silver Nitrate, Standard Solution (0.025 N)*—Dissolve 4.247 g of silver nitrate (AgNO₃) in water and dilute to ~~1 L~~ 1 L. Store in an amber glass bottle. Standardize against 0.025 N sodium chloride solution as directed in ~~13.1~~ 13.1 and 14.1.1.

9.10 *Potassium Chromate – Potassium Dichromate Indicator*—(K₂CrO₄ – K₂Cr₂O₇)—Dissolve 4.2 g of K₂CrO₄ and 0.7 g of K₂Cr₂O₇ in 100 mL of water.

9.11 *Nitrobenzene*.

⁵ Scott's *Standard Method of Chemical Analysis*, edited by M. H. Furman, D. Van Nostrand Co., Inc., New York, NY.

⁶ Koltoff, I. M., and Stenger, V. A., *Volumetric Analysis II*, Interscience Publishers, Inc., New York, NY.

⁷ *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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

9.12 *Ferric Ammonium Sulfate Indicator Solution*—Add sufficient concentrated HNO_3 (sp gr 1.42) to a cold saturated solution of ferric ammonium sulfate [$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] to remove the brown color.

9.13 *Potassium Thiocyanate, Standard Solution (0.025 N)*—Dissolve 3 g of potassium thiocyanate (KCNS) in freshly distilled or boiled water, dilute to 1 L, and standardize against 0.025 N AgNO_3 solution as directed in 14.1.2.

10. Sampling

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

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

10.3 The laboratory sample must be air-dried and the 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 ~~representative characteristics (other than particle size)~~representativeness beyond just particle size while preparing the ~~analysis~~ sample to be ~~used in the~~ analyzed in accordance with these procedures.

PREPARATION OF CHLORINE SOLUTIONS FOR ANALYSIS

11. Total Chlorine (Oxygen Bomb Method)

11.1 *Preparation of Sample and Bomb* (see Note 3):

11.1.1 *Sample Weight*—Weigh to the nearest 0.1 mg about 1 g of thoroughly mixed air-dried ~~analysis~~-RDF sample into the bomb capsule. A pellet may be made from the air-dried ~~analysis~~-RDF sample, accurately weighed, and placed into the bomb capsule. Place the capsule containing the sample into the capsule holder.

NOTE 2—There is a tendency for chlorine to adhere to the bomb walls, especially if the bomb is pitted or has been used previously to determine high levels of chlorine. Unless the bomb is thoroughly cleaned before use, the blanks may have ~~values in excess of reality~~high background chlorine values.

11.1.2 *Firing Wire*—Connect a length of firing wire to the ignition terminals in such a manner that the loop of firing wire is in contact with the sample.

11.1.3 *Bomb Preparation*—Add 20 to 25 mL of 0.02 N potassium hydroxide solution to the bomb and wet the entire internal surface of the bomb with this solution (see Note 3). Assemble the bomb.

NOTE 3—Sodium hydroxide solution at appropriate concentration may be used.

11.2 *Addition of Oxygen*—Admit oxygen to the bomb slowly to avoid blowing the sample from the capsule until a pressure of 25 atm is reached.

11.2.1 **Warning**—The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Practice E144.

11.2.1.1 The weight of RDF sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

11.2.1.2 Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. Cracked or significantly worn parts should be replaced. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof firing.

11.2.1.3 The oxygen supply cylinder should be equipped 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 codes. Suitable reducing valves and adaptors for 300 to 500 psi (2070 to 3450 kPa) discharge pressures are obtainable from commercial sources of compressed gas equipment. The pressure ~~gage~~gauge shall be checked periodically for accuracy.

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

11.3 *Preparation of the Chlorine Solution*—Immerse the bomb in a cold-water bath, connect it to the firing circuit, and close the circuit to ignite the sample. Allow the bomb to stand in the water bath for not less than 10 min after firing. Remove the bomb from the water bath, invert the bomb and shake for about 10 min (Note 4). Release the pressure at a slow, uniform rate so that the pressure is reduced to atmospheric in not less than 1 min. Open the bomb and examine the inside for traces of unburned material or sooty deposits. If any are found, discard the determination and thoroughly wash all parts of the bomb interior before using it again. If no unburned material or sooty deposits are present, rinse the interior of the bomb, the sample capsule, and the interior surface of the bomb cover with a fine jet of hot water and collect the contents and washings in a beaker or flask.

NOTE 4—Inverting and shaking a heavy, wet, and possibly slippery bomb may present a hazard. Precautions should be taken when performing this function.

12. Extraction of Water-Soluble Chlorides

12.1 *Preparation of the Chloride Solution*—Weigh to the nearest 0.1 mg about 5 g of thoroughly mixed, air-dried RDF ~~analysis~~ sample. Transfer to a 500-mL beaker and add 100 mL of hot water. Heat to ~~close to~~near boiling for ½ h with occasional stirring