



Designation: **E776—16 E776 – 23**

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

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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, safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific precaution statements, see Section 6 and 11.2.1.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³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

E829 Practice for Preparing Refuse-Derived Fuel (RDF) Laboratory Samples for Analysis

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

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—ASTM International, 1983, p. 72.

- 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.-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.

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:

$$\text{water - insoluble chlorine} = \text{total chlorine} - \text{water - soluble chlorides} \tag{1}$$

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 refuse-derived fuel.

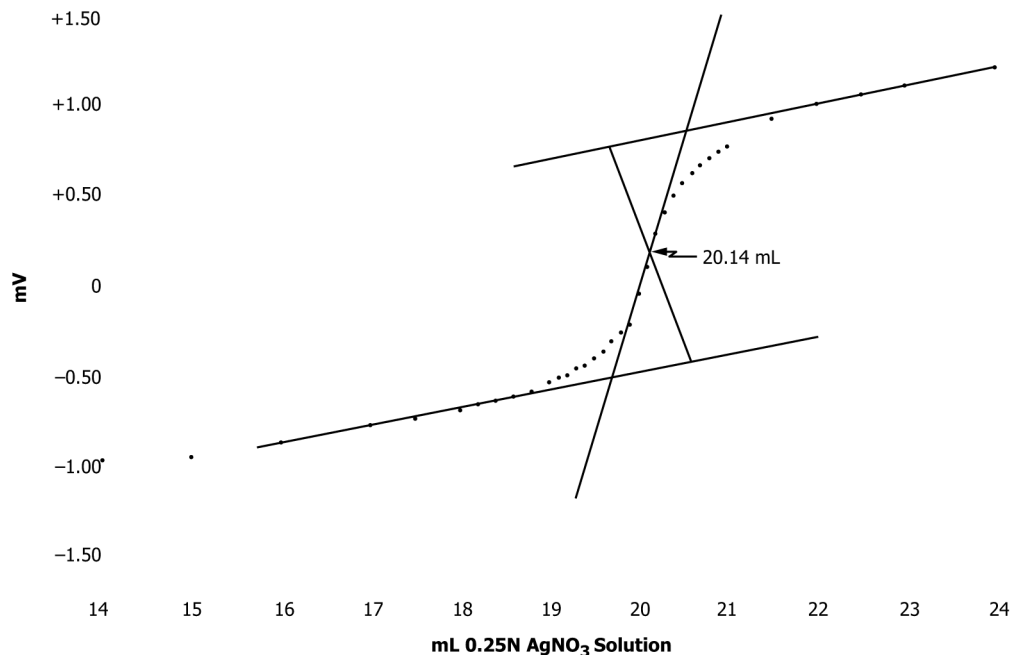


FIG. 1 Graph From a Potentiometric Titration of Chloride

6. Precautions

6.1 Due to the origins of RDF in ~~municipal~~ waste, precautions should be ~~observed~~employed when conducting tests on samples. ~~Recommended safety~~ Safety practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under a 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 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*, 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 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*:

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.

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.

8.5 *Centrifuge*, capable of centrifuging ~~100-mL~~ 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 ~~$\pm 20^\circ\text{C}$~~ 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 (HNO_3 , ~~sp. gr.~~ sp. gr. 1.42) and water.

9.9 *Silver Nitrate, Standard Solution (0.025 N)*—Dissolve 4.247 g of silver nitrate (AgNO_3) in water and dilute to 1 L. Store in an amber glass bottle. Standardize against 0.025 N sodium chloride solution as directed in **13.1** and **14.1.1**.

9.10 *Potassium Chromate – Potassium Dichromate Indicator*—(K_2CrO_4 – $\text{K}_2\text{Cr}_2\text{O}_7$)—Dissolve 4.2 g of K_2CrO_4 and 0.7 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 100 mL of water.

9.11 *Nitrobenzene*.

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**.

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~~ *Analabs 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.

10. Sampling

10.1 RDF products are frequently inhomogeneous. For this reason, significant care ~~should be exercised~~ is needed 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~~ 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 sample to be 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~~ 1 g of thoroughly mixed air-dried RDF sample into a bomb capsule. A pellet may be made from the air-dried 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 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 needed for safe calorimeter operation. Additional precautions are given in Practice E144.~~ 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~~ are checked frequently for wear. Cracked or significantly worn parts ~~should~~ must 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 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~~ their 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~~measurement 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 sample. Transfer to a ~~500-mL~~500 mL beaker and add 100 mL of hot water. Heat to near boiling for ½ h with occasional stirring to ensure thorough wetting of the sample. Decant the supernatant liquid through a ~~fast-qualitative~~fast-qualitative filter paper collecting the filtrate in a beaker. Repeat the extraction two more times, each time using 100 mL of water and pooling the filtrates. After the third extraction, wash the sample thoroughly using 100 mL of hot water, adding the wash water to the pooled filtrates.

12.2 *Preparation of the Chloride Solution (Alternative Method)*—Weigh to the nearest 0.1 mg about 5 g of thoroughly mixed air-dried analysis sample (**Note 5**). Transfer to a ~~500-mL~~500 mL beaker and add 100 mL of hot water. Heat to near boiling for ½ h with occasional stirring to ensure thorough wetting of the sample. Remove the beaker from the hot plate and allow the sample to settle. Decant the supernatant to a ~~100-mL~~100 mL centrifuge tube and centrifuge for ½ h at approximately 1200 rpm. Decant the supernatant through a ~~fast-qualitative~~fast-qualitative filter paper. Repeat the extraction and centrifuging two more times, each time using 60 mL of water and pooling the filtrates. After the third extraction, wash the centrifuge tube and filter paper thoroughly using 60 mL of hot water, adding the wash water to the pooled filtrates (**Notes 6 and 7**).

NOTE 5—The weight of the sample used can be adjusted when higher or lower concentrations of water-soluble chlorides are anticipated.

NOTE 6—When high concentrations of chlorides are anticipated, dilute the cooled extraction solution to volume in a suitably sized volumetric flask and continue the analysis with a suitably sized aliquot.

NOTE 7—If the chloride solution is highly colored or turbid, the potentiometric method (Section 13) should be used. If the Volhard method is to be used (Section 14), the color and turbidity must first be removed by aluminum hydroxide [Al(OH)₃] coagulation or by some other suitable method of turbidity or color removal without interfering with the chloride content of the solution.⁸

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<https://standards.iteh.ai/catalog/standards/astm/e776-23/8c9-a65edc016974/astm-e776-23> **ALTERNATIVE PROCEDURES**

13. Potentiometric Titration (Method A)

13.1 *Standardization of Reagents*—Prepare a standard solution of silver nitrate by adding 10.0 mL of standard 0.025 N NaCl solution to a ~~250-mL~~250 mL beaker. Add 40 to 50 mL of water and 50 mL of methanol (**Note 9**). Add 2 mL of HNO₃ (1 + 1) and titrate potentiometrically with the AgNO₃ solution as directed in 13.3. Calculate the normality of the AgNO₃ solution as follows:

$$\text{Normality of AgNO}_3 = \text{mL of NaCl solution used} \quad (2)$$

$$\times \text{normality of NaCl solution/mL of AgNO}_3 \text{ solution required}$$

NOTE 8—Methanol increases the sensitivity of the inflection point. However, it may be omitted if it is found to interfere with or damage certain electrode systems.

13.2 *Blank Determination*—Prepare a solution for blank determination in the same manner as the preparation of chlorine solutions for the respective type of chlorine desired as described in ~~Sections~~Section 11 or 12 using all the reagents in the same quantities and eliminating the RDF sample. Add to that blank solution 0.025 N NaCl solution as used in the standardization of AgNO₃ solution (13.1). Proceed as directed in 13.3. The difference in the volume of AgNO₃ solution required in this titration and that volume required for the standardization titration (13.1) is the true titer blank.

$$A - B = \text{true titer blank} \quad (3)$$

⁸ APHA, 14th ed., Method 408-A, Section 3a.

where:

A = millilitres of AgNO_3 required for the blank determination and

–

B = millilitres of AgNO_3 required for the standardization determination (13.1).

–

A = milliliters of AgNO_3 required for the blank determination, and

B = milliliters of AgNO_3 required for the standardization determination (13.1).

13.3 Procedure:

13.3.1 Concentrate the chlorides in the prepared solution (11.3, 12.1, or 12.2, respectively) for the type of chlorine desired by evaporation to about 50 mL. Add 50 mL of methanol and neutralize with HNO_3 (1 + 1) using phenolphthalein as an indicator. Add 2 mL of HNO_3 (1 + 1) in excess. Immerse the electrodes into the sample solution. While gently stirring on a magnetic stirrer, titrate by adding ~~0.10 mL~~ 0.10 mL increments of standard AgNO_3 solution and record the millivolt reading after each addition (Notes 9 and 10). Titrate well beyond the end point.

NOTE 9—Larger increments of AgNO_3 solution may be added before and after the end point. However, as the end point is reached, the ~~0.10 mL~~ 0.10 mL increment will give the most accurate end point.

NOTE 10—The end point is reached when the change of voltage is greatest upon the addition of the given increment of standard AgNO_3 .

13.3.2 Plot the millivolt readings versus the ~~millilitres~~ milliliters of standard AgNO_3 solution added. Determine the end point (point of inflection) graphically from the titration curve or mathematically (second derivative) from the tabulated data. (See Table 1 and Fig. 2 for examples.)

13.4 Calculations—Calculate the weight percent of chloride as follows:

TABLE 1 Typical Data Sheet and Calculation of End Point from a Potentiometric Titration of Chloride

Volume of 0.025 N AgNO_3 solution, mL	Millivolt Reading	Volume of 0.025 N AgNO_3 solution, mL	Millivolt Reading	Volume of 0.025 N AgNO_3 solution, mL	Millivolt Reading
0.0	-1.38	18.4	-0.65	20.2	+ 0.26
1.0	-1.29	18.6	-0.63	20.3	+ 0.38
2.0	-1.26	18.8	-0.59	20.4	+ 0.47
4.0	-1.21	19.0	-0.55	20.5	+ 0.55
6.0	-1.18	19.1	-0.53	20.6	+ 0.60
8.0	-1.14	19.2	-0.51	20.7	+ 0.65
10.0	-1.10	19.3	-0.48	20.8	+ 0.69
12.0	-1.04	19.4	-0.46	20.9	+ 0.72
14.0	-0.97	19.5	-0.42	21.0	+ 0.75
15.0	-0.95	19.6	-0.38	21.5	+ 0.90
16.0	-0.86	19.7	-0.33	22.0	+ 0.98
17.0	-0.79	19.8	-0.27	22.5	+ 1.04
17.5	-0.75	19.9	-0.19	23.0	+ 1.09
18.0	-0.70	20.0	-0.06	24.0	+ 1.17
18.2	-0.67	20.1	+ 0.08	25.0	+ 1.24

The greatest change of voltage per unit increment addition of AgNO_3 solution occurs between 19.8 and 20.5 mL. Determine the end point and titer as follows:

mL	mV	1st Derivative	2nd Derivative
19.8	-0.27		
19.9	-0.19		
20.0	-0.06	+ 0.08	+ 0.05
20.1	+ 0.08	+ 0.13	+ 0.01
20.2	+ 0.26	+ 0.14	+ 0.04
20.3	+ 0.38	+ 0.18	-0.06
20.4	+ 0.47	+ 0.12	-0.03
20.5	+ 0.55	+ 0.09	-0.01
		+ 0.08	

Interpolation:

$$20.1 \text{ mL} + \left(\frac{0.04}{0.10} \times 0.1 \right) = 20.14 \text{ mL}$$