Designation: D 1847 – 93 (Reapproved 1998)

Standard Test Methods for Total Chlorine Content of Epoxy Resins[1]

This standard is issued under the fixed designation D 1847; 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 cover the determination of the total chlorine content, in concentrations below 1 weight percent, of epoxy resins. Both organic and inorganic chlorine compounds contained in the resin are determined. Epoxy resin is defined as the reaction product of a chlorohydrin and a di- or polyfunctional phenolic compound.

1.2 Two alternative test methods for determining chloride ion concentration resulting from combustion of the sample are included as follows:

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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]

3. Summary of Test Method

3.1 The resin is oxidized by combustion in a bomb containing oxygen under pressure. The chlorine compounds thus liberated are absorbed in a sodium carbonate solution. In Test Method A the amount of chlorine present is determined by potentiometric titration with standard silver nitrate solution. In Test Method B the amount of chlorine present is determined gravimetrically by precipitation as silver chloride.

4. Significance and Use

4.1 The total chlorine content of epoxy resins is an important variable in determining reactivity of epoxy resins and performance of coatings prepared from them. These test methods may be used to determine the total chlorine content of manufactured epoxy resins to confirm specification limits.

5. Purity of Reagents

5.1 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.[3] 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.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

TEST METHOD A—POTENTIOMETRIC TITRATION

6. Apparatus

6.1 *Combustion Apparatus*—An oxygen bomb[4] apparatus for combustion of the sample.

6.2 *Titration Apparatus*—A suitable pH meter equipped with a glass-silver electrode system and titration stand, stirrer, beakers, and 10-mL buret.

7. Reagents

7.1 *Methyl Red Indicator* (0.2 % alcohol solution)—Dissolve 0.2 g of methyl red in 100 mL of methanol, ethanol or *iso*propanol.

7.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

7.3 *Oxygen*, free of combustible materials and halogen compounds, available at a pressure of 40 atm.

7.4 *Silver Nitrate, Standard Solution* (0.01 *N*)—Dissolve in water 1.70 ± 0.01 g of crystalline silver nitrate ($AgNO_3$) which

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D 01.33 on Polymers and Resins.

Current edition approved April 15, 1993. Published June 1993. Originally published as D 1847 – 61 T. Last previous edition D 1847 – 87.

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

[3] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] The sole source of supply of the double-valve, self-sealing oxygen bomb equipped with a safety-relief-type oxygen filling connection, ignition circuit, fuse wire, sample cups, and water bath, known to the committee at this time is Parr Instrument Co., 209 53rd St., Moline, IL 61265. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

previously has been pulverized, dried at 150°C for 1 h, and stored in a glass-stoppered bottle, and dilute to 1 L. Standardize against an accurately weighed amount of sodium chloride (NaCl) dissolved in 75 to 100 mL of water.

7.5 *Sodium Carbonate Solution* (20 g/L)—Dissolve 20 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

8. Procedure

8.1 *Combustion of Specimen*:

8.1.1 Place 25 mL of Na_2CO_3 solution in the bottom of the bomb. Incline the bomb and rotate it in such a manner that the interior surface is moistened by the solution.

8.1.2 Weigh to 1 mg 0.8 to 1.2 g of sample into the metal sample cup. Grind solid resins to pass a No. 60 (250-µm) sieve and moisten with a few drops of acetone before combustion.

8.1.3 Insert the cup containing the sample in the loop electrode and attach the fuse wire so that it hangs slightly above the specimen. Assemble the bomb and tighten the cover securely; however, do not use auxiliary tools to tighten the cover.

8.1.4 Attach the filling connection to the oxygen-filling valve and admit oxygen slowly (to avoid blowing the sample from the cup) until a pressure of 35 atm is indicated on the gage; then close the control valve. Open the relief valve to reduce the pressure in the tube and in the connection to atmospheric pressure. Detach the filling connection from the bomb and replace with the bomb thumb nut. Tighten the thumb nut with finger pressure.

8.1.5 Immerse the bomb in the water bath, then connect the terminals to the electrical circuit. Ignite the charge within the bomb by closing the switch for not more than 5 s, or until the pilot light goes out. Allow the bomb to stand in the water bath for 10 min while cooling.

8.1.6 Remove the bomb from the water bath, and invert and rotate it so that maximum washing of the inside surface is achieved. Release the pressure at a uniform rate over a period of not less than 1 min.

8.2 *Titration*:

8.2.1 Transfer the absorbing solution from the combustion of the sample to a 250-mL tall-form titration beaker. Wash all the inside surfaces of the bomb with a fine stream of water and transfer the washings to the beaker. Adjust the volume of the solution to 150 to 200 mL with water. Add three drops of methyl red indicator solution and neutralize with HNO_3; then add 6 drops in excess.

8.2.2 Place the beaker on the titration stand and adjust its position so that the electrodes are about half immersed. Fill the buret with 0.01 *N* $AgNO_3$ solution, and place the buret in position on the titration assembly so that the tip extends approximately 25 mm below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring without splattering. Record the initial buret and meter (cell potential) readings.

8.2.3 Add small portions of 0.01 *N* $AgNO_3$ solution and, after waiting until a constant potential has been established, record the buret and meter readings. In regions between inflections where the potential change is small for each increment of $AgNO_3$ solution, add volumes as large as 0.5 mL. When the rate of change of cell potential becomes greater than 5 mV per 0.1 mL, use 0.1-mL increments of 0.01 *N* $AgNO_3$ solution.

8.2.4 Continue the titration until the rate of change of cell potential is less than 2 mV per 0.1 mL of $AgNO_3$ solution. Remove the titrated solution, rinse the electrodes well with water, wipe with a dry cloth, and burnish the silver electrode lightly with a fine emery cloth. Between determinations, immerse the electrodes in water.

8.2.5 Plot the cumulative volumes of 0.1 *N* $AgNO_3$ solution added against the corresponding cell potentials. Select as the end point the midway point on the steepest portion of the inflection curve.

8.2.6 Make a blank determination in accordance with 8.2.1-8.2.4, but omit the specimen. This procedure will give a measure of the chlorine in the reagents used.

9. Calculation

9.1 Calculate the chlorine content of the sample as follows:

$$\text{Chlorine, \%} = [(V - B)N \times 0.0355/S] \times 100 \tag{1}$$

where:

V = $AgNO_3$ solution required for titration of the specimen, mL
B = $AgNO_3$ solution required for titration of the blank, mL
N = normality of the $AgNO_3$ solution, and
S = specimen weight used, g.

10. Precision

10.1 The following criteria should be used for judging the acceptability of results at the 95 % confidence level.

10.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.02 weight %.

10.1.2 *Reproducibility*—The results, each the mean of two determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.05 weight %.

TEST METHOD B—GRAVIMETRIC DETERMINATION

11. Apparatus

11.1 *Combustion Apparatus*—See 6.1.

11.2 *Fritted-Glass*, medium porosity.

12. Reagents

12.1 **Warning**—*Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

12.2 **Caution**—*Nitric Acid* (1 + 99)—Mix 1 volume of HNO_3(sp gr 1.42) with 99 volumes of water.

12.3 *Oxygen*—See 7.3.

12.4 *Potassium Iodide Solution* (300 g/litre)—Dissolve 300 g of potassium iodide (KI) in water and dilute to 1 L.

12.5 *Silver Nitrate Solution* (100 g/L)—Dissolve 100 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

12.6 *Silver Nitrate, Standard Solution* (0.01 *N*)—See 7.4.

12.7 *Sodium Carbonate Solution* (20 g/L)—See 7.5.

13. Procedure

13.1 Oxidize the specimen by combustion in accordance with 8.1.1-8.1.6.

13.2 Transfer the absorbing solution from the combustion of the specimen to a 250-mL beaker. Wash all the inside surfaces of the bomb with a fine stream of water and transfer the washings to the beaker. Add 1 mL of HNO_3(sp gr 1.42) to the solution; then, with stirring, add 1 mL of $AgNO_3$ solution (100 g/L). Heat the solution to boiling as rapidly as possible. Allow the mixture to cool in a dark cabinet for at least 1 h.

13.3 Filter the precipitate by suction on a clean, fritted-glass filter funnel. Wash the silver chloride (AgCl) precipitate thoroughly with HNO_3(1 + 99). Dry the filter and precipitate at 110°C for 1 h. Cool in a desiccator and weigh accurately to 0.1 mg.

13.4 Dissolve the AgCl from the filter, using KI solution. Wash the filter thoroughly with HNO_3 (1 + 99). Dry the filter at 110°C for 1 h, cool in a desiccator, and reweigh. The weight of AgCl obtained from the sample is the difference between the weight of the filter funnel containing the precipitate and the weight of the filter funnel obtained at this time.

13.5 Make a blank determination in accordance with 13.2 and 13.4, but omit the specimen. This procedure will give a measure of the chlorine in the reagents used.

14. Calculation

14.1 Calculate the chlorine content of the specimen as follows:

$$\text{Chlorine, \%} = [(P - B) \times 0.2474/S] \times 100 \quad (2)$$

where:

P = AgCl precipitate from the specimen, g,

B = AgCl found in the blank, g, and

S = specimen used, g.

15. Precision and Bias

15.1 The following criteria should be used for judging the acceptability of results at the 95% confidence level.

15.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.05 weight percent.

15.1.2 *Reproducibility*—Two results, each the mean of two determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.05 weight percent.

15.2 *Bias*—No bias can be determined since no standard epoxy resin exists.

16. Keywords

16.1 chlorine; chlorine content; epoxy; oxygen bomb; total chlorine