



Designation: D 1652 – 97

Standard Test Methods for Epoxy Content of Epoxy Resins¹

This standard is issued under the fixed designation D 1652; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the quantitative determination of the epoxy content of epoxy resins.

1.2 *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 hazard statements, see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis³

3. Summary of Test Method

3.1 The resin is dissolved in a suitable solvent and the resulting solution is titrated with hydrogen bromide either directly or in situ. The hydrogen bromide reacts stoichiometrically with epoxy groups to form bromohydrins; therefore, the quantity of acid consumed is a measure of the epoxy content.

3.1.1 In Test Method A, the titration is direct with a standard solution of hydrogen bromide in glacial acetic acid.

3.1.2 In Test Method B, the titration is with standard perchloric acid in the presence of an excess of tetraethylammonium bromide. Hydrogen bromide generated in situ by the addition of perchloric acid to the quaternary ammonium halide rapidly opens the oxirane ring.

4. Significance and Use

4.1 The epoxy content of epoxy resins is an important variable in determining their reactivity and the properties of coatings made from them. These test methods may be used to determine the epoxy content of manufactured epoxy resins and confirm the stated epoxy content of purchased epoxy resins.

5. Reagents

5.1 *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.⁴ 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6. Hazards

6.1 Hydrogen bromide and glacial acetic acid are corrosive. Chlorobenzene and chloroform are considered hazardous. In addition to other precautions, take care to avoid inhalation and skin or eye contact with these chemicals. Use goggles or a face shield, or both. Protect skin by use of suitable protective clothing. All specimen preparations shall be done in a well ventilated area, such as a fume hood.

TEST METHOD A

7. Apparatus

7.1 *Buret*, closed-reservoir type. The buret tip should be fitted with a rubber stopper of proper size to fit the neck of the Erlenmeyer flask and the stopper should have an additional small hole to permit escape of replaced air during titration.

7.2 *Magnetic Stirrer*, adjustable speed.

7.3 *Magnetic Stirring Bars*, polytetrafluoroethylene (PTFE) coated.

8. Reagents and Materials

8.1 *Chlorobenzene* (**Warning**—See Section 6).

8.2 *Chloroform-Chlorobenzene Mixture* (1+1) (**Warning**—See Section 6).

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 D01.33 on Polymers and Resins.

Current edition approved June 10, 1997. Published October 1997. Originally published as D 1652 – 59 T. Last previous edition D 1652 – 90 (1996).

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

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ *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.

8.3 *Crystal Violet Indicator Solution*—Prepare a 0.1 % solution of crystal violet in glacial acetic acid.

8.4 *Glacial Acetic Acid* (**Warning**—See Section 6).

8.5 *Hydrogen Bromide* (HBr), anhydrous (**Warning**—See Section 6).

8.6 *Potassium Acid Phthalate* ($\text{KHC}_8\text{H}_4\text{O}_4$)—Primary Standard grade.

8.7 *Hydrogen Bromide in Acetic Acid, Standard Solution* (0.1 N) (**Warning**—See Section 6)—Prepare by bubbling anhydrous HBr at a slow rate through glacial acetic acid until the desired normality is attained (approximately 8 g of HBr/L). Standardize each day used against 0.4 g of potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) accurately weighed and dissolved by gently heating in 10 mL of glacial acetic acid.

NOTE 1—Reagent of 0.1 N concentration has been specified. As solutions exceed this concentration they became progressively less stable (for further information see Practice E 200).

9. Procedure

9.1 Use a quantity of specimen that contains 0.001 to 0.002-g equivalents of epoxy groups. Weigh the appropriate amount, to within 1 mg, into an Erlenmeyer flask. Use a 50-mL flask for low-molecular-weight resins (liquid grades) and a 125-mL flask for high-molecular-weight resins (solid grades).

9.2 Dissolve the specimen in a solvent at room temperature. Use 10 mL of chlorobenzene for liquid grade resins or 25 mL of a 1+1 mixture of chloroform and chlorobenzene for solid grade resins. Place a magnetic stirring bar into the flask and mix on the magnetic stirrer to dissolve.

9.3 Add 4 to 6 drops of crystal violet indicator solution and attach the flask to the rubber stopper on the buret tip. Lower the buret tip to a point just above the solution and titrate with the hydrogen bromide in acetic acid solution to a blue-green end point with the magnetic stirrer rotating at a moderate speed to avoid splashing. Slow down the titration near the end point to allow ample time for the reaction to take place. Titrate, as nearly as possible, to the same color at the end point as that obtained during standardization of the reagent.

9.4 Make a blank determination on the reagents in an identical manner.

10. Calculation

10.1 Calculate the normality, N , of the HBr acetic acid as follows:

$$N = (W \times 1000)/(204.2 \times V) \quad (1)$$

where:

W = $\text{KHC}_8\text{H}_4\text{O}_4$ used, g, and

V = HBr solution used, mL.

10.2 Calculate the epoxy content, E , in gram equivalents of epoxy groups per 100 g of resin as follows:

$$E = N(V - B)/10 \times W \quad (2)$$

where:

N = normality of the HBr in acetic acid,

V = HBr solution used for titration of the specimen, mL,

B = HBr solution used for titration of the blank, mL, and

W = specimen used, g.

10.3 Calculate the percent of oxirane oxygen, O , as follows:

$$O = 1.6N(V - B)/W \quad (3)$$

10.4 Calculate the weight per epoxy equivalent, WPE , that is, grams of resin containing 1 g equivalent of epoxy groups, as follows:

$$WPE = 1000W/N(V - B) \quad (4)$$

11. Precision

11.1 *Repeatability*—The difference between two results obtained by the same analyst will approximate 0.7 % of the epoxy content of the resin tested. Two such values should be considered suspect if they differ by more than 2 % absolute.

11.2 *Reproducibility*—The difference between two results, each the mean of two determinations, obtained by analysts in different laboratories, will approximate 2 % of the epoxy content of the resin tested. Two such values should be considered suspect if they differ by more than 6 % absolute.

TEST METHOD B

12. Apparatus

12.1 *Buret*, closed-reservoir type, bottom filling, 25 mL with $\frac{1}{10}$ -mL division, or potentiometric automatic titrator.

12.2 *Erlenmeyer Flasks*, 100-mL, 250-mL, and 500-mL.

12.3 *Magnetic Stirrer*, adjustable speed.

12.4 *Magnetic Stirring Bars*, polytetrafluoroethylene (PTFE) coated.

12.5 *Pipets*:

12.5.1 *Measuring Pipet*, 25-mL.

12.5.2 *Volumetric Pipet*, 50-mL.

12.6 *Volumetric Flask*, 1 L.

12.7 *Bottle*, 2 oz wide-mouth, or 100-mL disposable beaker, or equivalent.

13. Reagents

13.1 *Glacial Acetic Acid* (**Warning**—See Section 6).

13.2 *Tetraethylammonium Bromide*, anhydrous crystals.

13.3 *Perchloric Acid* (HClO_4), 60 % (**Warning**—See Section 6).

13.4 *Acetic Anhydride* (**Warning**—See Section 6).

13.5 *Methylene Chloride* (**Warning**—See Section 6).

13.6 *Crystal Violet Indicator*, crystals.

13.7 *Potassium Acid Phthalate*—($\text{KHC}_8\text{H}_4\text{O}_4$) primary standard grade.

13.8 *Diglycidyl Ether of Bisphenol-A*.

14. Reagent Preparation

14.1 *Perchloric Acid (0.1 N Solution in Glacial Acetic Acid)* (**Warning**—See Section 6)—Prepare in the following manner and sequence in order to avoid an excessive rise in temperature.

14.1.1 Place approximately 250 mL of glacial acetic acid into a 1 L volumetric flask. Add 13 mL of 60 % perchloric acid and mix. Add 50 mL of acetic anhydride, dilute to the mark with glacial acetic acid, and mix thoroughly.