Designation: D1652 – 11ε1

Standard Test Method for Epoxy Content of Epoxy Resins[1]

This standard is issued under the fixed designation D1652; 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.

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

ε[1] NOTE—Editorial corrections were made throughout in May 2012.

1. Scope*

1.1 This test method covers the procedure for manual and automatic titration of epoxy resins for the quantitative determination of the percent epoxide content from 0.1 to 26 % epoxide.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* For specific hazard statements, see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

2.2 *Other Documents:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[3]

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 the Manual Titration Method, 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.

3.1.2 In the Automatic Titration Method, the reaction is measuring the millivolt (MV) potential as perchloric acid is added, which combines with the bromide to form the hydrobromic acid, which reacts with the epoxide group. As the reaction progresses, the potential will gradually increase until the reaction nears completion at which point the potential increases very quickly. The titrator measures the rate of the reaction by calculating the change in potential between perchloric acid addition increments. When the change in potential begins to decrease, the titrator determines that the titration is complete. The epoxide content is calculated using the reagent factor entered by the user during standardization, the weight of the sample, and the volume of perchloric acid added during titration.

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

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

Current edition approved Nov. 1, 2011. Published January 2012. Originally approved in 1969. Last previous edition approved in 2004 as D1652 – 04. DOI: 10.1520/D1652-11E01.

[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] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

[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.

***A Summary of Changes section appears at the end of this standard**

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 D1193.

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.

6.2 Consult current OSHA Regulations, Supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

Manual Titration for Epoxy Content of Epoxy Resins

7. Apparatus

7.1 *Buret,* closed-reservoir type, bottom filling, 25-mL with 1/10-mL division, or potentiometric automatic titrator.

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

7.3 *Magnetic Stirrer,* adjustable speed.

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

7.5 *Pipets:*
7.5.1 *Measuring Pipet,* 25-mL.
7.5.2 *Volumetric Pipet,* 50-mL.

7.6 *Volumetric Flask,* 1 L.

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

8. Reagents

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

8.2 *Tetraethylammonium Bromide,* anhydrous crystals.

8.3 *Perchloric Acid* ($HClO_4$), 0.1 N in Glacial Acetic Acid (**Warning**—See Section 6).

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

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

8.6 *Crystal Violet Indicator,* crystals.

8.7 *Potassium Hydrogen Phthalate*—($KHC_8H_4O_4$) primary standard grade.

9. Reagent Preparation

9.1 *Tetraethylammonium Bromide Solution in Glacial Acetic Acid* (**Warning**—See Section 6):
9.1.1 Dissolve, with agitation at room temperature, 100 g of tetraethylammonium bromide in 400 mL of glacial acetic acid.

9.2 *Crystal Violet Indicator Solution*—Prepare 0.1 % solution of crystal violet indicator in glacial acetic acid (**Warnings**—See Section 6).

10. Standardization of 0.1 *N* Perchloric Acid Reagent

10.1 *Standardization with Potassium Hydrogen Phthalate:*

10.1.1 Dissolve 0.4 g of potassium hydrogen phthalate, weighed accurately to the nearest milligram, in 50 mL of glacial acetic acid, and add 6 to 8 drops of crystal violet indicator solution. Insert a clean stirring bar into the sample, and adjust the magnetic stirrer to effect solution. Continue agitation throughout the titration procedure. Titrate with perchloric acid reagent solution to the end point, which is a sharp change in color from blue to green, stabilize for at least 2 min.

10.1.2 Calculate and record the perchloric acid reagent normality as follows:

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

where:

N = normality of perchloric acid reagent,
W = potassium hydrogen phthalate used, g, and
V = volume of perchloric acid reagent required to titrate the standard, mL.

10.2 *Standardization with Potassium Hydrogen Phthalate:*

10.2.1 Dissolve 0.25 to 0.40 g of the potassium hydrogen phthalate accurately weighed to the nearest milligram into a 2 oz wide-mouth bottle or 100 mL disposable beaker. Add 40 to 50 mL of glacial acetic acid. Insert a clean stirring bar into the sample and adjust the magnetic stirrer to effect solution. Continue agitation throughout the titration procedure.

10.2.2 Add 10 mL of tetraethylammonium bromide reagent and 6 to 8 drops of crystal violet indicator solution and titrate to a sharp blue-to-green end point with the perchloric acid reagent solution. The end point should be stable for at least 30 s.

10.2.3 Calculate and record the perchloric acid reagent factor, F, as follows:

$$F = (W_d \times E)/V \quad (2)$$

where:

W_d = potassium hydrogen phthalate standard used, g and
E = epoxide of the potassium hydrogen phthalate standard used (normally 21.05), weight %.

11. Procedure

11.1 Weigh the required amount of specimen into a 2-oz disposable glass bottle or plastic beaker. The amount of specimen weight used is dependent on the expected epoxide equivalent weight (EEW) as follows:

EEW	Approximate Specimen Size, g
170–375	0.4
375–600	0.6
600–1000	0.8
1000–1500	1.3
1500–2000	1.8
2000–2500	2.3
2500–5000	2.8

11.2 Add 10 to 15 mL of methylene chloride to the specimen. Insert a clean stirring bar and adjust the magnetic stirrer to effect solution. Continue agitation through the titration procedure.

11.3 Add 10 mL of tetraethylammonium bromide reagent and 6 to 8 drops of crystal violet indicator solution. Titrate with 0.1 *N* perchloric acid reagent to a sharp blue to green end point which is stable for at least 30 s. Record the volume of perchloric acid reagent used to titrate the specimen.

12. Calculation

12.1 If 10.1 (Standardization of Potassium Hydrogen Phthalate) is used for standardization, calculate weight percent epoxide, *E*, as follows:

$$E = 4.3 \times V \times N/W \quad (3)$$

12.2 If 10.2 (Standardization of Potassium Hydrogen Phthalate) is used for standardization, calculate the weight percent epoxide, *E*, as follows:

$$E = F \times V/W_e \quad (4)$$

where:

W_e = weight of epoxy resin specimen used, g.

12.3 Calculate the epoxy equivalent weight, W_{EEW}, as follows:

$$W_{EEW} = 43 \times 100/E \quad (5)$$

where 43 = mol weight of the epoxy ring.

12.4 Calculate weight percent of oxirane oxygen, *O*, as follows:

$$O = 16/43 \times E = 1.6 \times V \times N/W \quad (6)$$

13. Precision

13.1 A liquid epoxy resin sample with approximately 24.1 % epoxide was tested by seven laboratories where ten analysts obtained the following results:

13.1.1 *Repeatability*—The difference between two results obtained by the same analyst should not vary by more than 1.22 % relative.

13.1.2 *Reproducibility*—The difference between two results, each the mean of two determinations obtained by analysts in different laboratories should not vary by more than 2.97 % relative.

Automatic Titration Method

14. Apparatus

14.1 *Automatic Titrator,* equipped with a 10 mL burette and a pH electrode.

14.2 *A Four Place Analytical Balance.*

15. Reagents and Materials

15.1 *Perchloric Acid,* 0.1N in glacial acetic acid.

15.2 *Tetraethylammonium Bromide (TEAB),* solution in glacial acetic acid.

15.3 *Methylene Chloride (MECL).*

15.4 *Potassium Hydrogen Phthalate (KHP).*

16. Reagent Preparation

16.1 *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.

16.1.1 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.

16.1.2 Allow to stand at least 8 h for completion of reaction between the acetic anhydride and water. A shorter time period may be used if completion of the reaction is analytically verified.

16.2 *Tetraethylammonium Bromide Solution in Glacial Acetic Acid* (**Warning**—See Section 6):

16.2.1 Dissolve, with agitation at room temperature, 100 g of tetraethylammonium bromide in 400 mL of glacial acetic acid.

17. Standardization of 0.1 *N* Perchloric Acid Reagent

17.1 *Standardization with Potassium Hydrogen Phthalate:*

17.1.1 Dissolve 0.25 g of potassium hydrogen phthalate, weighed accurately to the nearest milligram, in 50 mL of glacial acetic acid, and 15 mL 20 % TEAB solution. Titrate with perchloric acid reagent solution.

17.1.2 Calculate and record the perchloric acid reagent normality as follows:

$$N = (W \times 1000)/(204.2 \times V) \quad (7)$$

where:

N = normality of perchloric acid reagent,
W = potassium hydrogen phthalate used, g, and
V = volume of perchloric acid reagent required to titrate the standard, mL.

18. Procedure

18.1 Fill burette with 0.1 N perchloric acid solution in glacial acetic acid.

18.2 Flush all titrator lines to assure no air bubbles are present.

18.3 Add the appropriate amount of sample to a sample cup.

18.4 Add 30 mL of MECL and 15 mL of TEAB to the sample.

18.5 Select the correct method on the titrator and run the sample. The method should prompt when to enter the sample weight.

18.6 The titrator will automatically print out the results using the formula in Section 19.

19. Calculation

19.1 *Calculate:*

$$R2 = R \times C \times 0.1000/M \quad (8)$$

where:

$R2$ = epoxide content,

R = actual mL perchloric acid used to reach equivalence point,
C = constant of 4.3 (see Note 2), and
M = weight of the sample used.

NOTE 1—0.1000 is the normality of the perchloric acid.

NOTE 2—4.3 is the theoretical molecular weight of the epoxide ring, 43, and it is adjusted to 4.3 for the calculation to percent epoxide.

20. Precision

20.1 An epoxy resin sample, with 5.74 % epoxide, was tested by six laboratories in five different countries for % epoxide content and the following results were obtained:

20.1.1 *Repeatability*—The difference between two results obtained by the same analyst should not vary by more than 1.1 % relative.

20.1.2 *Reproducibility*—The difference between laboratories should no vary by more than 0.8 % relative.

21. Keywords

21.1 epoxide equivalent weight (EEW); liquid epoxy resin; oxirane; weight percent epoxide; weight per epoxy equivalent (WPE)

SUMMARY OF CHANGES

Committee D01 has identified the location of selected changes to this standard since the last issue (D1652 - 04) that may impact the use of this standard. (Approved November 1, 2011.)

(1) Updated 8.3.
(2) Deleted 9.1, 9.1.1, and 9.1.2 and renumbered subsequent sections.