Designation: D4671 − 16

Standard Test Method for
Polyurethane Raw Materials: Determination of Unsaturation of Polyols[1]

1. Scope*

1.1 This test method measures unsaturation in polyether polyols. (See Note 1.) It uses 2 mL of ca. 0.05 *M* mercuric acetate reagent in methanol and about 1 g of sample or less. This test method uses a potentiometric determination of an end point.

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

1.3 *Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.*

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.*

NOTE 1—This standard is equivalent to ISO 17710.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

2.2 *ISO Standards:*

ISO 17710 Plastics—Polyols for Use in the Production of Polyurethane—Determination of Degree of Unsaturation by Microtitration[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, see Terminology D883.

4. Summary of Test Method

4.1 Carbon-to-carbon unsaturated compounds in the sample are reacted with mercuric acetate and methanol in a methanolic solution to produce acetoxymercuricmethoxy compounds and acetic acid.[5] The amount of acetic acid released in this equimolar reaction, which is determined by titration with standard alcoholic potassium hydroxide, is a measure of the unsaturation originally present. Because the acid cannot be titrated in the presence of excess mercuric acetate, due to the formation of insoluble mercuric oxide, sodium bromide is added to convert the mercuric acetate to the bromide, which does not interfere. Inasmuch as these test methods are based on an acidimetric titration, a suitable correction must be applied if the sample is not neutral to phenolphthalein indicator. Take care to exclude carbon dioxide, which titrates as an acid and gives erroneous results.

5. Significance and Use

5.1 This test method is suitable for quality control, as specification tests, and for research.

5.2 Side reactions that form unsaturated compounds in polypropylene oxides produce small amounts of polymers with only one hydroxyl group per chain. These unsaturated polymers lower functionality and molecular weight, while broadening the overall molecular-weight distribution.

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[1] These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] Sigia, S. and Hanna, J.G., "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, New York, 1979.

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

6. Interferences

6.1 This test method does not apply to compounds in which the unsaturation is conjugated with carbonyl, carboxyl, or nitrile groups. Because water presumably hydrolyzes the reaction products to form basic mercuric salts, quantitative results are obtained only when the system is essentially anhydrous. Acetone in low concentrations does not interfere significantly, although its presence can be detrimental to the end point. Inorganic salts, especially halides, must be absent from the sample because even small amounts of salts can nullify the reaction of the mercuric acetate with the unsaturated compound.

7. Apparatus

7.1 *Pipet,* 2-mL capacity.

7.2 *Autotitrator,* capable of determining acidimetric end points using a 5-mL buret.

7.3 *Combination, Glass, pH Electrode,* for use with the autotitrator.

7.4 *Balance,* capable of weighing samples to 0.0001 g.

7.5 *Titration Vessels,* 50- to 100-mL capacity.

8. Reagents

8.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades are acceptable, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Mercuric Acetate, Methanol Solution (ca. 0.05 M)*—Dissolve 16 g of mercuric acetate ($Hg(C_2H_3O_2)_2$) into 1 L of reagent-grade methanol and add sufficient glacial acetic acid to require a blank titration of 0.5 to 1 mL of 0.05 *N* methanolic KOH for a 2-mL aliquot. Usually several drops of acid are required. Prepare the reagent fresh weekly and filter before using.

8.3 *Methanolic Potassium Hydroxide Solution (0.05 N)*—Prepare a 0.05-N solution using reagent-grade KOH dissolved in methanol. Standardize using standard procedures with potassium hydrogen phthalate.

8.4 *Methanolic Hydrochloric Acid Solution (0.05 N)*—Prepare a 0.05-N solution by successively diluting concentrated acid into methanol. This will introduce less than 0.5 % water in the titration reagent. Standardize by titrating against the 0.05 N methanolic KOH.

8.5 *Sodium Bromide (NaBr).*

9. Procedure

9.1 Use no more than 0.033 millequivalents (meq) of unsaturated species for this test. For samples having 0.033 meq/g or less, add approximately 1 g of sample weighed to 0.1 mg to a 100-mL titration flask. If the unsaturation value is not known for a sample, determine an approximate value by using a 1-g sample. Use this approximate value to calculate a correct sample size that will contribute no more than 0.033 meq of test sample (See Note 2).

NOTE 2—This test method requires at least a 2-fold molar excess of mercury reagent for quantitative reaction of unsaturated species. If too large a sample size is selected, this test method will give inaccurate, low results as well as reduced precision. Calculate sample size, g, using the following equation:

$$\text{Sample size} = 0.033/\text{test sample unsaturation} \tag{1}$$

9.2 Add 2 mL of mercuric acetate reagent solution and swirl to dissolve the sample completely. Cover with a watch glass and allow to stand for a minimum of 30 min. Add 50 mL of methanol followed by approximately 0.25 g of sodium bromide crystals.

9.3 Titrate using 0.05 *N* methanolic KOH to the end point using an automatic titrator.

9.4 Titrate a blank using the same procedure but without adding sample.

9.5 To determine the acidity or basicity of the polyol for correcting the results, prepare a sample exactly as above, but omit the mercuric acetate reagent. Titrate, as above, with 0.05 *N* methanolic KOH to the potentiometric end point. If the solution is determined to be already past the acid end point, repeat this procedure, but titrate with 0.05 *N* methanolic HCl.

10. Calculation

10.1 Calculate the acidity, meq/g, of the sample as follows:

$$V_A \times N\,(\text{KOH})/W_A = A \tag{2}$$

where:

V_A = 0.05 *N* KOH required to neutralize the sample, mL,
N (KOH) = normality of the methanolic KOH solution, meq/mL, and
W_A = weight of sample used, g.

10.2 Calculate the basicity, meq/g, of the sample as follows:

$$V_B \times N\,(\text{HCl})/W_B = B \tag{3}$$

where:

V_B = 0.05 *N* HCl required to neutralize the sample, mL,
N (HCl) = normality of the methanolic HCl, meq/mL, and
W_B = weight of sample used, g.

10.3 Calculate the unsaturation of the sample, meq/g, as follows:

$$\text{Unsaturation} = \left[(Vs - Vb) \times N\,(\text{KOH})/W\right] - A + B \tag{4}$$

where:

Vs = 0.05 N KOH required for the unsaturation sample, mL,
Vb = 0.05 N KOH required for the unsaturation blank, mL,
W = weight of sample, g,
B = sample basicity, meq/g, and
A = sample acidity, meq/g.

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11. Report

11.1 Report the results as the average of duplicates, meq/g, to the nearest 0.001 meq/g.

12. Precision and Bias[7]

12.1 *Precision*—Table 1 is based on a round robin conducted in 1997 in accordance with Practice E180, involving six samples (see Table 2 for sample descriptions) tested by seven laboratories. Each test result was the average of two individual determinations obtained on the same day. In each laboratory, test results were obtained for each material and the two test results for a given material were obtained on two separate days.

NOTE 3—The explanations of *r* and *R* in 12.1.1 – 12.1.3 are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 must not be rigorously applied to the acceptance or rejection of material, as those data are specific to the round robin and are not representative of other lots, conditions, materials and laboratories. Users of this test method must apply the principles outlined in Practice E180 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 12.1.1 – 12.1.3 would then be valid for such data.

12.1.1 *Repeatability, r*—Comparing two replicates for the same material obtained by the same operator using the same equipment on the same day, the two replicate results will be judged not equivalent if they differ by more than the *r* value for that material.

12.1.2 *Reproducibility, R*—Comparing two results, each the mean of replicates, for the same material obtained by different operators using different equipment in different laboratories on different days, the two results will be judged not equivalent if they differ by more than the *R* value for that material.

12.1.3 Any judgment in accordance with 12.1.1 and 12.1.2 would have an approximate 95 % (0.95) probability of being correct.

12.2 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

13. Keywords

13.1 polyether polyol; polyols; polyurethane raw materials; raw material; titration; unsaturation

TABLE 1 Round-Robin Unsaturation Data in Accordance with Practice E180

Sample	Average, meq/g	S_r^A	S_R^B	r^C	R^D	n^E
A	0.0007	0.0011	0.0006	0.0031	0.0017	6
B	0.0728	0.0011	0.0033	0.0031	0.0092	6
C	0.0362	0.0004	0.0015	0.0011	0.0042	5
D	0.0231	0.0008	0.0007	0.0022	0.0020	6
E	0.0231	0.0014	0.0126	0.0039	0.0354	6
F	0.0350	0.0004	0.0010	0.0011	0.0028	6
G	0.1240	0.0018	0.0037	0.0050	0.0104	5

$^{A}S_r$ = within-laboratory standard deviation of the replicates.
$^{B}S_R$ = between-laboratory standard deviation of the averages.
^{C}r = within-laboratory repeatability limit = 2.8 × S_r.
^{D}R = between-laboratory reproducibility limit = 2.8 × S_R.
^{E}n = number of laboratories contributing valid data for this material.

TABLE 2 Description of Round Robin Samples

Sample	Description	Ethylene Oxide, %	Concentration, g/mole
A	Polytetramethylene oxide diol	. . .	1000
B	Polypropylene oxide triol	14	5100
C	Polypropylene oxide diol	. . .	2000
D	Polypropylene oxide triol	10	2850
E	Amine initiated, 4-functional polypropylene oxide	40	570
F	Polypropylene oxide triol	19	4700
G	Polypropylene oxide diol	. . .	4000

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1208.

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D4671 - 05(Reapproved 2010)$^{\varepsilon 1}$) that may impact the use of this standard. (April 1, 2016)

(1) Various changes throughout as a result of removal of Test Method A, a high-volume mercury use method.
(2) Added the ASTM mercury caveat (1.3) and added ISO 17710 as an equivalent.
(3) Added ISO 17710 to the Referenced Documents section.

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