Designation: D 4671 – 99

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

This standard is issued under the fixed designation D 4671; 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 measure unsaturation in polyether polyols. (See Note 1.)

1.1.1 *Test Method A, High-Volume Reagent Method*—Uses about 50 mL of 0.1 *M* mercuric acetate reagent in methanol and 15 g or more of sample. This test method uses an indicator for colorimetric determination of an end point. It is recommended for polyols with low values (below 0.01 millequivalents per gram (meq/g)) of unsaturation where large sample sizes are required.

1.1.2 *Test Method B, Low-Volume Reagent Method*—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 *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—There is no equivalent ISO standard.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, see Terminology D 883.

## 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.[4] 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 this test method is 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 These test methods are 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.

## 6. Interferences

6.1 These test methods do 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 may be detrimental to the end point. Inorganic salts, especially halides, must be absent from the

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[1] These test methods are under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Plastics. Test Method A was recommended to ASTM by the Society of the Plastics Industry Polyurethane Raw Materials Analysis Committee.

Current edition approved Nov. 10, 1999. Published February 2000. Originally published as D 4671 – 87. Last previous edition D 4671 – 93.

[2] *Annual Book of ASTM Standards*, Vol 08.01.

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

[4] 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.**

sample because even small amounts of salts may nullify the reaction of the mercuric acetate with the unsaturated compound.

## TEST METHOD A—HIGH-VOLUME REAGENT METHOD

### 7. Apparatus

7.1 *Pipet*, 50-mL capacity.

7.2 *Erlenmeyer Flask*, 250-mL glass-stoppered.

7.3 *Balance*, 1000-g capacity, 0.1-g sensitivity.

7.4 *Buret*, 50-mL capacity.

### 8. Reagents

8.1 *Purity of Reagents*—Use reagent-grade chemicals 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.[5] 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.

8.2 *Mercuric Acetate, Methanol Solution* (40 g/L)—Dissolve 40 g of mercuric acetate ($Hg(C_2H_3O_2)_2$ in sufficient methanol to make 1 L of solution and add sufficient glacial acetic acid to require a blank titration of 1 to 10 mL of 0.1 *N* alcoholic KOH solution/50 mL of reagent. Usually 3 or 4 drops of acid are sufficient. Prepare the reagent fresh weekly and filter before using.

8.3 *Sodium Bromide (NaBr).*

### 9. Procedure

9.1 Add 50 mL of methanol to a sufficient number of 250-mL Erlenmeyer flasks to determine the acidity of each sample in duplicate. Neutralize to a faint pink end point, using a few drops of phenolphthalein indicator solution and 0.1 *N* alcoholic KOH solution. Add 30 g of the sample weighed to the nearest 0.1 g to each flask and swirl to effect complete solution. Titrate with 0.1 *N* alcoholic KOH solution to a pink end point that persists for at least 15 s and record the volume of titrant as *A*.

9.2 Pipet 50 mL of the $Hg(C_2H_3O_2)_2$ solution into each of a sufficient number of 250-mL Erlenmeyer flasks to make all blank and sample determinations in duplicate. Reserve two of the flasks for the blank determination. Into each of the other flasks, introduce 30 g of the sample weighed to the nearest 0.1 g and swirl to effect complete solution. Allow the samples to stand together with the blanks at room temperature for 30 min. Swirl the flasks occasionally. Add 8 to 10 g of NaBr crystals to each flask and swirl to mix thoroughly. Add approximately 1 mL of phenolphthalein indicator solution and titrate immediately with 0.1 *N* alcoholic KOH solution to a pink end point that persists for at least 15 s. Record the volume of titrant used for the samples as *D* and that used for the blank as *E*. The sample titration should not exceed 50 mL of 0.1 *N* alcoholic KOH solution.

### 10. Calculation

10.1 Calculate the concentration of unsaturated compounds, meq/g, as follows:

$$C = (A \times N)/W \qquad (1)$$

where:

$A$ = 0.1 N alcoholic KOH solution required to neutralize the sample, mL,

$N$ = normality of the alcoholic KOH solution, and

$W$ = sample used, g.

therefore:

$$\text{Total unsaturation} = [(D - E)N/W] - C \qquad (2)$$

where:

$D$ = alcoholic KOH solution required for titration of the sample, mL

$E$ = alcoholic KOH solution required for titration of the blank, average mL, and

$C$ = average of results from Eq 1, meq of acidity/g of sample.

### 11. Precision and Bias

11.1 *Precision*—Attempts to develop a precision and bias statement for this test method have not been successful. For this reason, data on precision and bias cannot be given. Because this test method does not contain a numerical precision and bias statement, it shall not be used as a referee test method in case of dispute. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428.

11.1.1 It is estimated that duplicate results by the same analyst should be considered suspect if they differ by more than 0.002.

11.2 *Bias*—The bias for this test method has not yet been determined.

## TEST METHOD B—LOW-VOLUME REAGENT METHOD

### 12. Apparatus

12.1 *Pipet*, 2-mL capacity.

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

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

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

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

### 13. Reagents

13.1 *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

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[5] *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.

of the American Chemical Society, where such specifications are available.[5] 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.

13.2 *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.

13.3 *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.

13.4 *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.

13.5 *Sodium Bromide (NaBr)*.

## 14. Procedure

14.1 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:

$$\text{Sample size} = 0.033/\text{test sample unsaturation} \tag{3}$$

14.2 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.

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

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

14.5 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.

## 15. Calculation

15.1 Calculate the acidity of the sample as follows:

$$V_A \times N\,(\text{KOH})\ /\ W_A = A \tag{4}$$

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.

15.2 Calculate the basicity of the sample as follows:

$$V_B \times N\,(\text{HCl})\ /W_B = B \tag{5}$$

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.

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

$$\text{Unsaturation} = [(Vs - Vb) \times N\,(\text{KOH})\ /W] - A + B \tag{6}$$

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.

## 16. Report

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

## 17. Precision and Bias

17.1 *Precision*—Table 1 is based on a round robin conducted in 1997 per Practice E 180, involving 6 samples (see Table 2 for sample descriptions) tested by 7 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 17.1.1-17.1.3 are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be rigorously applied to the acceptance or rejection of material, as those data are specific to the round robin and may not be representative of other lots, conditions, materials and laboratories. Users of this test method should apply the principles outlined in Practice E 180 to generate data specific to their

**TABLE 1 Round-Robin Unsaturation Data in Accordance with Practice E 180**

| 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 |

laboratory and materials, or between specific laboratories. The principles of 17.1.1-17.1.3 would then be valid for such data.

17.1.1 *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 should be judged not equivalent if they differ by more than the *r* value for that material.

17.1.2 *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 should be judged not equivalent if they differ by more than the *R* value for that material.

17.1.3 Any judgment according to 17.1.1 and 17.1.2 would have an approximate 95 % (0.95) probability of being correct.

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

## 18. Keywords

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

## SUMMARY OF CHANGES

Committee D-20 has identified the location of selected changes to this edition of these test methods since the last issue that may impact the use of these test methods.

*D 4671 – 99:*
(*1*) Added 1.1.1 and 1.1.2 to include descriptions of Test Method A (original version) and Test Method B (added to reduce mercury waste).
(*2*) Added title of Test Method A following Section 6.
(*3*) Deleted 8.2 on Reagent Water, and consequently deleted reference to Specification D 1193 from 2.1.
(*4*) Made editorial changes in 8.2.
(*5*) Added Test Method B.