Designation: D 6979 – 03

# Standard Test Method for Polyurethane Raw Materials: Determination of Basicity in Polyols, Expressed as Percent Nitrogen[1]

This standard is issued under the fixed designation D 6979; 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 This test method measures the basic constituents in polyols that are soluble in glacial acetic acid and reactive with perchloric acid. Samples containing 0.3 – 10 % nitrogen have been evaluated by this method. This test method is applicable to polyether polyols and polyether polyol blends that are used in urethane reactions. (See Note 1.)

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:* [2]

D 883 Terminology Relating to Plastics

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

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method see Terminology D 883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *percent nitrogen*—the quantity of perchloric acid-titratable base, expressed as a weight percentage of nitrogen in a sample.

## 4. Summary of Test Method

4.1 The sample is dissolved in glacial acetic acid. The resulting single-phase solution is titrated at room temperature to a potentiometric end point with a standardized solution of perchloric acid in acetic acid. Results are reported as percent nitrogen.

## 5. Significance and Use

5.1 This test method is suitable for quality control, as a specification test, and for research. The results are measures of batch-to-batch uniformity and may be useful in estimating reactivity.

5.1.1 The percent nitrogen can be used to characterize a polyol or indicate amounts of certain components in a polyol blend.

5.1.2 It is permissible to also express the results in equivalents of base per gram of sample, if desired.

## 6. Apparatus

6.1 *Potentiometric Automatic Titrator*

6.2 *Autotitrator Buret with Dosing Device, 20-mL*

6.3 *pH Glass Electrode and Reference Electrode or a Combination Glass Electrode*

6.4 *Analytical Balances, capable of weighing to the nearest 0.01g and 0.0001 g*

6.5 *Magnetic Stirrer/Hotplate*

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] It is permissible to use other grades provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Acetic Acid, Glacial*

7.3 *Acetic Anhydride*

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is 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] *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.

7.4 *Perchloric Acid, (70 % nominal)*

7.5 *Perchloric acid in Acetic Acid (0.10 N)*—Prepare 0.10 N perchloric acid in acetic acid. For example, in a 1000-mL volumetric flask dissolve 8.7 g of perchloric acid in 500 mL of glacial acetic acid; add 25 mL of acetic anhydride and dilute to volume with glacial acetic acid.

NOTE 2—Perchloric Acid—is extremely irritating to the skin, eyes and mucous membrane; highly toxic via oral and inhalation routes; and can form explosive mixtures when mixed with carbonaceous material or allowed to dry. Concentrated material shall only be used in a hood approved for perchloric acid use. Skin contact—wash with soap and water. Eye contact—flush with copious amounts of water for 15 minutes. Inhalation - move victim to an uncontaminated area. Ingestion—do not induce vomiting. For all exposures seek professional medical advice.

## 8. Procedure

8.1 Weigh the appropriate amount of sample, W' into a suitable container. Calculate the target weight of sample to be analyzed as follows:

$$W' = 2/P \quad (1)$$

where:

$W'$ = the target weight of the sample to be analyzed in grams, and

$P$ = the expected percent nitrogen content of the sample.

NOTE 3—For sample weights below 10.0 g, record the weight to the nearest 0.1 mg; for sample weights greater than 10.0 grams, record the weight to the nearest 0.01g.

8.2 Add 100 mL of glacial acetic acid and gently stir until the sample dissolves completely.

NOTE 4—If necessary, the mixture can be heated gently until the sample is completely dissolved.

8.3 Titrate the sample solution potentiometrically with 0.10 N perchloric acid through the end point which occurs at ca. 600 mV.

## 9. Calculation

9.1 Calculate the basicity in the sample, as percent nitrogen as follows:

$$\%\,N = \frac{S \times N \times 14.00}{W \times 1000} \times 100\,\% \quad (2)$$

where:

$S$ = the volume of titrant used to reach the end point of the sample solution titration in millilitres,

$N$ = the normality of the 0.10 N perchloric acid solution in milliequivalents per millilitre,

$W$ = the weight of the sample in grams,

*14.00* = the equivalent weight of nitrogen in milligrams per milliequivalent, and

*1000* = the factor for converting milligrams to grams

NOTE 5—It is permissible to also report the results as alkalinity in milligrams of potassium hydroxide per gram of sample as follows:

$$Alkalinity,\ (mg\ KOH/g) = \frac{S \times N \times 56.10}{W}$$

where:

the variables have the same meaning as in 9.1 above and 56.10 is the equivalent weight of KOH in milliequivalents per gram.

## 10. Report

10.1 For samples containing 1 % nitrogen or less, report results no more precisely than the nearest 0.0001 %.

10.2 For samples containing between 1 and 10 %, report results no more precisely than the nearest 0.001 %.

## 11. Precision and Bias [4]

11.1 Table 1 is based on a round robin involving seven laboratories and conducted in 2002 in accordance with Practice E 180. All labs used potentiometric titration for the generation of the data used in this study. All the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was the average of two individual determinations. Each laboratory made duplicate determinations on each material on each of two days.

11.2 *Precision*

**Warning—**The following explanations of *r* and *R* (11.2.1-11.2.3) are intended only to present a meaningful way of considering the approximate precision of this test method. Do not apply rigorously the data in Table 1 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, or laboratories. Users of this test method should apply the principles outlined in Practice E 180 or E 691 to generate data specific to their laboratory and materials or between specific laboratories. The principles of 11.2.1-11.2.3 then would be valid for such data.

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

11.2.2 *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 test results shall be judged not equivalent if they differ by more than the *R* value for that material.

11.2.3 Any judgment in accordance with 11.2.1 and 11.2.2 would have an approximate 95 % (0.95) probability of being correct.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D20–1239. The precision estimates are based on an interlaboratory study performed in 2002 on four samples of polyol or polyol blend. Seven industrial laboratories participated in the test method evaluation.

**TABLE 1 Round-Robin Percent Nitrogen Data in Accordance with Practice E 180[A]**

| Material | Average | $S_r$[B] | $S_R$[C] | $r$[D] | $R$[E] | df[F] |
|---|---|---|---|---|---|---|
| A | 0.317 | 0.0007 | 0.0018 | 0.0020 | 0.0050 | 5 |
| B | 2.51 | 0.0046 | 0.0053 | 0.0129 | 0.0148 | 5 |
| C | 5.86 | 0.0079 | 0.0139 | 0.0221 | 0.0392 | 5 |
| D | 9.45 | 0.0220 | 0.0217 | 0.0616 | 0.0618 | 5 |

[A] Values in units of percent nitrogen.
[B] $S_r$ = within-laboratory standard deviation of the replicates.
[C] $S_R$ = between-laboratories standard deviation of the average.
[D] $r$ = within-laboratory repeatability limit = $2.8 \cdot S_r$.
[E] $R$ = between-laboratories reproducibility limit = $2.8 \cdot S_R$.
[F] df = degrees of freedom in the data.

11.3 There are no recognized standards by which to estimate the bias of this test method.

## 12. Keywords

12.1 alkalinity; polyols; polyurethane; raw materials; test method; titration