Designation: D 6437 – 99

Standard Test Method for Polyurethane Raw Materials: Alkalinity in Low-Alkalinity Polyols (Determination of CPR Values of Polyols)[1]

This standard is issued under the fixed designation D 6437; 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 covers measuring alkalinity in low-alkalinity (<0.002 meq/g basicity) polyols. This alkalinity is often expressed as CPR (controlled polymerization rate) of polyether polyols. This test method is not applicable to amine-based polyols.

1.2 The values stated in SI units are to be regarded as the standard.

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.*

NOTE 1—There is no similar or 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]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

3. Terminology

3.1 *Definitions:*

3.1.1 The terminology in this test method is in accordance with the standard terminology defined in Terminology D 883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *CPR*—controlled polymerization rate is expressed as basicity in milliequivalents per 30 kg of sample (meq/30 kg).

4. Summary of Test Method

4.1 This test method is a potentiometric titration for sample basicity in methanol solvent. This test method uses a relatively large sample and titration with dilute acid solution to determine trace quantities of basicity.

5. Significance and Use

5.1 This test method is suitable for quality control, as a specification test and for research. The urethane reaction between polyols and isocyanates to form polyurethane polymers is known to be sensitive to the presence of basic substances. This is particularly important in the preparation of polyurethane prepolymers which contain isocyanate groups that are known to react in the presence of trace amounts of basic substances. Since many polyether polyols are often made with strongly basic catalysts, it is important to have an analytical method capable of detecting small quantities of residual basic substances. This test method is capable of detecting ppm levels of base (as KOH).[5]

6. Apparatus

6.1 *Potentiometric Automatic Titrator*, capable of detecting multiple titration end points.

6.2 *Autotitrator Buret, 5 mL (See Note 2)* .

6.3 *Buret or Dosing Device*, capable of dosing 50 mL.

6.4 *pH Glass Electrode and Reference Electrode or a Combination Glass Electrode*.

6.5 *Analytical Balance*, capable of weighing to the nearest 0.01 g.

NOTE 2—A 1–mL titrator buret may be used if available. Due to the low volumes of titrant typically required (0 to 0.5 mL), larger burets will give less precise results.

7. Reagents and Materials

7.1 *HCl Aqueous, 0.01 N*—Standardize to detect changes of 0.0001 *N*.

7.2 *Methanol*, reagent grade

8. Procedure

8.1 Set up the autotitrator to find multiple end points with a maximum volume of 5 mL.

8.2 Place 50 ± 0.1 mL of methanol solvent in a 100–mL titration cup and titrate a blank using 0.01 *N* aqueous HCl.

8.3 Weigh 30 ± 1.00 g of sample into a titration cup. Add 50 ± 0.1 mL of reagent grade methanol, stir to mix well, and

[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Materials—Plastics and Elastomers.

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

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

[4] *Annual Book of ASTM Standards*, Vols 06.03, 08.03, and 14.02.

[5] H.G. Scholten, J.G. Schuhman, R.E. TenHoor, *Journal of Chemical Engineering Data*, 5, 1960, p. 396.

titrate with 0.01 *N* aqueous HCl. There may be as many as three end points (breaks) in these titrations. Use the volume to the last end point for calculation.

NOTE 3—If the viscosity of the sample appears too high, use 100 mL of methanol to dissolve the sample.

9. Calculation

9.1 Calculate the CPR as meq/30 kg of the polyol as follows:

$$\text{CPR} = (V_{\text{sam}} - V_{\text{blk}}) \cdot N \cdot 30\,000/W \quad (1)$$

where:

V_{sam} = volume of titrant to the last break in sample titration,
V_{blk} = volume of titrant to the last break in blank titration,
N = normality of HCl,
30 000 = conversion factor for 30–kg sample, and
W = weight of sample.

9.2 Calculate alkalinity as micromoles per gram of sample as follows:

$$\mu\text{mol/g} = (V_{\text{sam}} - V_{\text{blk}}) \cdot N \cdot 1000/W \quad (2)$$

where:

1000 = conversion from millimole to µmole.

9.3 Calculate alkalinity as micrograms KOH per gram of sample (ppm KOH) as follows:

$$\text{ppm KOH} = (V_{\text{sam}} - V_{\text{blk}}) \cdot N \cdot 56.1/W \quad (3)$$

where:

56.1 = equivalent weight of KOH in mg/meq.

10. Precision and Bias

NOTE 4—**Caution:** The following explanations of *r* and *R* (10.1.1-10.1.3) are only intended 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 691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 10.1.1-10.1.3 would then be valid for such data.

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

Values in CPR Units						
	Average	S_r[A]	S_R[B]	r[C]	R[D]	n[E]
Terathane 1000	0.34	0.07	0.20	0.20	0.56	7
Voranol 4702	0.45	0.06	0.11	0.18	0.32	6
Voranol 2120	0.63	0.04	0.12	0.12	0.33	5
ARCOL E-656	0.60	0.06	0.16	0.16	0.46	7
Multranol 7057	1.24	0.11	0.36	0.30	1.0	6
Pooled data	. . .	0.07	0.21	0.20	0.59	. . .

[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.

10.1 *Precision*—Table 1 is based on a round robin conducted in 1997 in accordance with Practice E 691, involving five samples tested by seven laboratories. Each test result was the average of two individual determinations. Each laboratory made duplicate determinations on each material on each of two days.

10.1.1 *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.

10.1.2 *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.

10.1.3 Any judgment in accordance with 10.1.1 and 10.1.2 would have an approximate 95 % (0.95) probability of being correct.

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

11. Keywords

11.1 alkalinity; basicity; CPR; polyether polyol; polyol; polyurethane; prepolymer; raw materials; test method; titration; urethane