



Standard Test Method for Polyurethane Raw Materials: Determination of Acidity in Low-Acidity Aromatic Isocyanates and Polyurethane Prepolymers¹

This standard is issued under the fixed designation D 5629; 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 the acidity, expressed as ppm of hydrochloric acid, in aromatic isocyanate or polyurethane prepolymer samples of below 100 ppm acidity. The test method is applicable to products derived from toluene diisocyanate and methylene-bis-(4-phenylisocyanate) (see Note 1).

NOTE 1—There are no equivalent ISO standards.

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.*

2. Referenced Documents

2.1 ASTM Standards:

D 883 Terminology Relating to Plastics²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

3. Terminology

3.1 *Definitions*—The terminology in this test method follows the standard terminology defined in Terminology D 883.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *acidity, n*—the acid strength of a sample expressed in ppm HCl.

4. Summary of Test Method

4.1 The isocyanate is mixed with an excess of n-propanol, a cosolvent, and a known amount of HCl. Additional acid is released into the solvent system during urethane formation. The acid is then titrated potentiometrically with methanolic KOH. The same procedure is performed with a blank solution,

and the difference in titer is used to calculate the acidity present in the isocyanate sample.

5. Significance and Use

5.1 This test method can be used for research or for quality control to characterize aromatic isocyanates and low-acidity prepolymers. Acidity correlates with performance in some polyurethane systems.

6. Apparatus

6.1 *Disposable Beakers*, 250 mL.

6.2 *Repipet*, 50 mL.

6.3 *Pipet*, 100 mL, class A volumetric; or a 50-mL buret dosimat unit, and a dosimat; or a 100-mL repipet, class A volumetric.

6.4 *Automatic Titration Equipment*, such as the following:

6.4.1 *Titroprocessor*.⁴

6.4.2 *Dosimat*, with magnetic stirrer.⁴

6.4.3 *Reference Electrode* (Brinkman Catalogue No. 020-94-400-5 or equivalent: bridge electrolyte (double junction), sleeve-type diaphragm), having saturated LiCl/ethanol solution in both chambers.

6.4.4 *pH Glass Electrode* (Brinkman Catalogue No. 020-91-012-7 or equivalent) (see Note 2).

NOTE 2—A combination pH electrode with internal reference may also be used.

6.5 *Magnetic Stirrer*.

6.6 *Polytetrafluoroethylene-Coated Stir Bars*.

6.7 *Watch Glasses*.

6.8 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

7. Reagents and Materials

7.1 *KOH in Methanol*, 0.01 N: 0.66 g 87.7 % KOH/1000 mL methanol, standardized with potassium hydrogen phthalate (KHP).

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 Plastics.

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

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

⁴ Instruments similar to and including the Metrohn 686 Titroprocessor with a Metrohn 665 Dosimat/magnetic stirrer as supplied by Brinkman Instruments Company, Division of Sybron Corporation, Cantiague Road, Westbury, NY 11590-9974, have been found to be satisfactory for this analysis.

7.2 Toluene or THF (dried for 24 h over 5 A sieves).

7.3 *n*-Propanol, acidified with 120 μ L concentrated hydrochloric acid per 4-L bottle. This solution should be allowed to stand for at least 24 h before use to allow equilibration. The solution should be mixed well before dispensing.

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling (**Warning**—Organic isocyanates are toxic when they are absorbed through the skin or when the vapors are breathed. Provide adequate ventilation, and wear protective gloves and eye glasses.). Usual sampling methods (for example, sampling an open drum thief), even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times.

9. Calibration

9.1 Calibrate the electrodes using pH 4 and 7 aqueous buffers.

10. Test Conditions

10.1 Since isocyanates react with moisture, keep the laboratory humidity low, preferably at approximately 50 % relative humidity.

11. Procedure

11.1 Make a blank determination in conjunction with each series of samples. Prepare the blank in the same manner as a sample, only omitting the sample. All samples and blanks should be made in duplicate.

11.2 Accurately weigh, to the nearest 0.1 mg, 20 g of sample into a 250-mL beaker.

11.3 Add 50 mL of dried toluene (dried over 5-A molecular sieves).

NOTE 3—Substitute THF for toluene for prepolymers.

NOTE 4—If a sample is difficult to get into solution, it may be gently heated and stirred for a longer period of time to affect homogeneity.

11.4 Pipet 100 mL of acidified *n*-propanol into the solution so that the volume can be reproduced to 0.05 mL.

11.5 Add a stir bar, cover with a watch glass, and stir and cool for 20 min.

NOTE 5—Samples must be at room temperature before titration.

11.6 Titrate the mixture with 0.01 N methanolic KOH through the titration endpoint as determined potentiometrically. Continue the titration through an apparent pH of 8.

NOTE 6—If the results indicate a drift in the data or a slow electrode response, the pH electrode should be cleaned by soaking in 2:1 sulfuric:nitric acids for 10 min, followed by soaking in water for 20 min and then rinsing with acetone.

11.7 Record the titrant volume for the potentiometric endpoint. If more than one potentiometric endpoint is found, record the one at the highest apparent pH below 7.

NOTE 7—The inflection point is typically at an apparent pH between 4 and 5.

12. Calculation

12.1 Calculate the acidity, as ppm HCl, as follows:

$$\text{acidity} = \frac{(V_{\text{sam}} - V_{\text{blank}}) \times (\text{KOH}_{\text{normality}}) \times F}{\text{sample weight (g)}} \quad (1)$$

where:

V_{sam} = volume of titrant needed for the sample, mL,
 V_{blank} = volume of titrant needed for the blank, mL,
 $\text{KOH}_{\text{normality}}$ = normality of the titrant solution, and
 F = 36465 = 36.456 (mol weight of HCl) $\times$ 1000 (factor to change mg/g to μ g/g, that is, ppm).

NOTE 8—Acidity is typically calculated as meq/Kg for prepolymers. For this calculation, F = 1000.

13. Report

13.1 Report the result as the average of duplicates, expressed as ppm HCl, to the nearest 1 ppm. See also Note 8.

14. Precision and Bias ⁵

14.1 *Precision*—Table 1 is based on a round robin conducted in 1993 per Practice E 180, involving six materials tested by nine laboratories. All of the samples for each material 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 obtained two test results for each material on each of two days. (**Warning**—The following explanations of r and R (14.1-14.1.3) 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 applied rigorously 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 to generate data specific to their laboratory and materials or between specific laboratories. The principles of 14.1.1-14.1.3 would then be valid for such data.)

⁵ Supporting data are available from ASTM Headquarters. Request RR: D20-1186.

TABLE 1 Round Robin Acidity Data According to Practice E 180

	Values in ppm HCl					
	Average	S_r^A	S_R^B	r^C	R^D	n^E
TD-80 Grade B	73.81	3.14	7.80	8.79	21.84	8
TD-80 Grade A	39.47	1.44	4.28	4.03	11.98	8
Adiprene L-100	23.56	0.99	4.00	2.77	11.20	8
Vibrathane B836	3.37	0.82	2.27	2.30	6.36	7
Isonate 143L	1.12	1.53	2.41	4.28	6.75	7
Mondur M	1.07	0.74	2.53	2.07	7.08	7

^A S_r = within-laboratory standard deviation of the replicates.

^B S_R = between-laboratory standard deviation of the average.

^C r = within-laboratory repeatability limit = $2.8 \times S_r$.

^D R = between-laboratory reproducibility limit = $2.8 \times S_R$.

^E n = number of laboratories contributing valid data for this material.

14.1.1 *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.

14.1.2 *Reproducibility, (R)*—(Comparing two results for the same material, obtained by different operators using different equipment on different days.) The two test results should be judged not equivalent if they differ by more than the *R* value for that material.

14.1.3 Any judgement per 14.1.1 and 14.1.2 would have an approximate 95 % (0.95) probability of being correct.

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

15. Keywords

15.1 acidity; aromatic isocyanates; isocyanates; methylene diphenyldiisocyanate; MDI; prepolymer; polyurethane; raw materials; test method; TDI; titration; toluene diisocyanate

SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D-20 has highlighted those changes that may impact the use of this test method. This section may include descriptions of the changes or the reasons for the changes, or both.

D 5629 – 99:

- (1) In 6.6, added “-Coated.”
- (2) In 7.1, added “87.7 %” for clarification of KOH.
- (3) In 11.5, added “and cool” to ensure sample is at room temperature before testing.
- (4) In 14.1, replaced Practice E 691 with Practice E 180. Upon

review of the protocol used to generate the round-robin data, it is believed that Practice E 180 best describes the methodology. PURMAC uses an E 180-based program to calculate the precision and bias.

(5) In 14.1, corrected reference to 14.1.1.

(6) In 15.1, added TDI as a keyword.

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