Designation: D5629 − 16

Standard Test Method for
Polyurethane Raw Materials: Determination of Acidity in Low-Acidity Aromatic Isocyanates and Polyurethane Prepolymers[1]

This standard is issued under the fixed designation D5629; 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 acidity, expressed as ppm of hydrochloric acid (HCl), 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 di(phenylisocyanate) (see Note 1). Refer to Test Method D6099 for determination of acidity in moderate- to high-acidity aromatic isocyanates.

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—This standard is equivalent to ISO 14898, Method B.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D6099 Test Method for Polyurethane Raw Materials: Determination of Acidity in Moderate to High Acidity Aromatic Isocyanates

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *ISO Standards:*[4]

ISO 14898 Plastics—Aromatic Isocyanates for Use in the Production of Polyurethane—Determination of Acidity

3. Terminology

3.1 *Definitions*—The terminology in this test method follows the standard terminology defined in Terminology D883.

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 is suitable 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,* pipet or buret, 50 mL.

6.3 *Pipet,* 100 mL, class A volumetric; or a 100-mL buret with a dosing unit; or a 100-mL repipet, class A volumetric.

6.4 *Potentiometric Titrator:*

6.4.1 *Reference Electrode,* bridge-type electrolyte (double junction), sleeve-type diaphragm, having saturated LiCl/ethanol solution in both chambers, or equivalent.

6.4.2 *pH Glass Electrode* (see Note 2).

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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.

Current edition approved April 1, 2016. Published April 2016. Originally approved in 1994. Last previous edition approved in 2011 as D5629 - 11. DOI: 10.1520/D5629-16.

[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.

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

NOTE 2—A combination pH electrode with internal reference is acceptable.

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

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

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

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods, 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. **Warning—**Diisocyanates are eye, skin and respiratory irritants at concentrations above the occupational exposure limit (TLV or PEL). Diisocyanates can cause skin and respiratory sensitization (asthma) in some people. Once sensitized, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent overexposure to diisocyanates. Consult the product suppliers' Safety Data Sheet (SDS) for more detailed information about potential health effects and other specific safety and handling instructions for the product.

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 laboratory humidity low, preferably around 50 % relative humidity. For further information, see 8.1.

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 are to 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—For prepolymers, THF is an acceptable substitute for toluene.

NOTE 4—If a sample is difficult to get into solution, it is acceptable to gently heat and stir to ensure homogeneity.

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

11.5 Add a stir bar, cover with a watch glass and stir for 20 min. Allow the sample to cool to room temperature after stirring.

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 is to 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:

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

where:

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

NOTE 9—The estimate of precision below was determined using reference and pH glass electrode systems.

14.1 *Precision*—Table 1 is based on a round robin conducted in 1993 per Practice E180, 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 are not to be applied rigorously to the acceptance or rejection of material, as those data are specific to

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

TABLE 1 Round Robin Acidity Data According to Practice E180

	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 × S_r.
[D] R = between-laboratory reproducibility limit = 2.8 × S_R.
[E] n = number of laboratories contributing valid data for this material.

the round robin and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method are to apply the principles outlined in Practice E691 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.)

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 are to 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 are to 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-bis-(4-phenylisocyanate); methylene di(phenylisocyanate); methylene diphenyldiisocyanate; MDI; prepolymer; polyurethane; raw materials; test method; TDI; titration; toluene diisocyanate

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D5629 - 11) that may impact the use of this standard. (April 1, 2016)

(1) Various edits throughout to remove non-mandatory language.
(2) Revised 9.1 to remove non-mandatory language and updated with input from the Center for the Polyurethanes Industry's (CPI) Product Stewardship Committee.
(3) Removed redundant information from Section 10.