



Designation: D 6099 – 9703

Standard Test Method for Polyurethane Raw Materials: Determination of Acidity in Moderate to High Acidity Aromatic Isocyanates¹

This standard is issued under the fixed designation D 6099; 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 determines the acidity, expressed as parts per million (ppm) of HCl, in aromatic isocyanate samples of greater than 100-ppm acidity. The test method is applicable to products derived from toluene diisocyanate and methylene-*bis*-(4-phenylisocyanate) (see Note 1).

NOTE 1—~~This test method is no similar or equivalent to ISO standard: 14898, Test Method A.~~

2. Referenced Documents

2.1 ASTM Standards:

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.

Current edition approved ~~April~~ March 10, 1997, 2003. Published ~~M~~ April 2003. Originally approved in 1997. Last previous edition approved in 1997 as D 6099 - 97.

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

D 883 Terminology Relating to Plastics²

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

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

2.2 ISO Standards:

ISO 14898 Plastics—Aromatic isocyanates for use in the production of polyurethane—Determination of acidity⁵

3. Terminology

3.1 *Definitions*— Terms used in this test method are in accordance with 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 hydrochloric acid.

4. Summary of Test Method

4.1 The isocyanate is mixed with an excess of methanol and a cosolvent. Additional acid is released into the solvent system during urethane formation. The acid then is titrated potentiometrically with methanolic KOH, and the acidity present in the isocyanate sample is calculated from the titer.

5. Significance and Use

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

6. Apparatus

6.1 *250-mL Beakers.*

6.2 *50-mL Pipet or Repipet, Class A volumetric.*

6.3 *100-mL Pipet or Repipet, Class A volumetric.*

6.4 *Automatic Titration Equipment*, such as:

6.4.1 *Titroprocessor*,⁵⁷ and

6.4.2 *Dosimat*,⁵⁶ with magnetic stirrer.

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

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

⁴ *Annual Book of ASTM Standards*, Vol. 14.02.

⁵ Instruments similar to and including the Metrohm 686 Titroprocessor with a Metrohm 665 Dosimat/magnetic stirrer as supplied by Brinkman Instruments Co., Cantiague Road, Westbury.

⁵ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 11590-9974, or an equivalent instrument, have been found to be satisfactory for this analysis: 10036.

6.4.3 *Reference Electrode*,⁶⁷ with saturated LiCl/ethanol solution in both chambers.

6.4.4 *pH Glass Electrode*,⁷⁹ (see Note 2).

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

6.5 *Magnetic Stirrer*.

6.6 *Stir Bars*.

6.7 *Watch Glasses*.

6.8 *Analytical Balance*, capable of weighing to the nearest 1 mg.

7. Reagents and Materials

7.1 *0.02 N KOH in Methanol*—1.32 g KOH pellets (85 % KOH)/1000 mL methanol, standardized with potassium hydrogen phthalate (KHP).

7.2 *Toluene or 1,2,4-Trichlorobenzene (TCB)*, dried for 24 h over molecular sieves.

7.3 *Anhydrous Methanol*.

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling (see Note 3: sampling. (Warning —Organic isocyanates are toxic when they are absorbed through the skin or when the vapors are breathed.) (Warning—Provide adequate ventilation and Note 4: **Precaution**); wear protective gloves and eyeglasses.) Usual sampling methods, for example, sampling with an open drum thief, even when carried out rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample, therefore, sample with dry air or nitrogen at all times. NOTE 3—**Warning**: Organic isocyanates are toxic when they are absorbed through the skin or when the vapors are breathed.

NOTE 4—**Precaution**: Provide adequate ventilation and wear protective gloves and eyeglasses.

9. Calibration

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

10. Test Conditions

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

11. Procedure

11.1 All samples should be done in duplicate.

11.2 Accurately weigh to the nearest 1 mg, 10 g of sample into a 250-mL beaker.

11.3 Add 50 mL of dried toluene or TCB dried over molecular sieves.

NOTE 53—If this test method is used for prepolymers, substitute THF as the solvent.

11.4 Add 100 mL of methanol into the solution.

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

NOTE 64—Samples must be at room temperature before titration. Warm samples cause more frequent electrode clogging.

11.6 Titrate the mixture with 0.02 N methanolic KOH through the titration end point between apparent pH 4 and 9 as determined potentiometrically.

NOTE 75—If 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 end point. If more than one potentiometric end point is found, record the one at highest apparent pH less than 7.

NOTE 86—The inflection point typically is at apparent pH between 4 and 5.

11.7.1 If no clear end point can be identified, calculate results using the end point at apparent pH 7.0, and report the result as acidity at apparent pH 7.0.

12. Calculation

12.1 Calculate the acidity as ppm HCl as follows:

⁶ Instruments similar to and including the Metrohm 686 Titroprocessor with a Metrohm 665 Dosimat/magnetic stirrer as supplied by Brinkman-CAT. #020-94-400-5; Instruments Co., Cantiague Road, Westbury, NY 11590-9974, or its equivalent: bridge electrolyte (double junction), sleeve-type diaphragm, has an equivalent instrument, have been found to be satisfactory for this analysis. See Footnote 5 for the address to Brinkman Instruments Co.

⁷ The Brinkman CAT. #020-91-012-7, #020-94-400-5, or its equivalent: bridge electrolyte (double junction), sleeve-type diaphragm, has been found satisfactory for this analysis. See Footnote 5 for the address to Brinkman Instruments Co.

$$\text{Acidity (ppm HCl)} = \frac{(V_{sam}) \times N \times F}{[\text{sample weight (g)}]} \quad (1)$$

where:

V_{sam} = volume of titrant needed for the sample, mL,

N = normality of the titrant solution, and

$F = 36$ = 36.465 (mol weight of HCl) \times 1000 (factor to change mg/g to $\mu\text{g/g}$, that is, ppm).

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13. Report

13.1 The result is reported as the average of duplicates, expressed as ppm HCl, to the nearest 1 ppm. Any unusual conditions during the operation also should be reported, such as any heating required to effect solution before titration, or end point identified different from that described in 11.7.

14. Precision and Bias

14.1 Table 1 is based on a round robin conducted in 1995 in accordance with Practice ~~E 691~~, E 180, involving twelve laboratories. For each material, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Some laboratories generated a set of results for each of two solvents (toluene and TCB), and some laboratories generated a set of results for each of two different electrode types. Neither change in experimental conditions was found to be a significant source of increased variability. Each of these combinations of conditions was treated as a different laboratory for purposes of calculating the precision data. Each test result was the average of two individual determinations. Each laboratory obtained two test results for each material for each combination of electrode and solvent ~~used~~.

~~NOTE 9—Caution: The used.~~ (Warning—The following explanations of r and R (14.1.1 and 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 the test method should apply the principles outlined in Practice ~~E 691~~ or E 180 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 14.1.1 through 14.1.3 then would 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 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, 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 should be judged not equivalent if they differ by more than the R value for that material.

14.1.3 Any judgment made in accordance with 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; MDI; methylene diphenyldiisocyanate; polyurethane; raw materials; TDI; titration; toluene diisocyanate

⁹ The Brinkman CAT. #020-91-012-7, or its equivalent, has been found satisfactory for this analysis. See Footnote 5 for the address to Brinkman Instruments Co.

SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods. For the convenience of the user,

TABLE 1 Round-Robin Acidity Data in Accordance With Practice E 180

	Values, ppm HCl						
	Average	S_r^A	S_R^B	r^C	R^D	n^E	df^F
Rubinate M	189	5.8	13.5	16.2	37.9	11	23
Mondur MR	414	3.4	27.5	9.5	76.9	11	20

^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.

^F df = degrees of freedom in the data after incorporating multiple data sets from most laboratories due to different combinations of solvent and electrode.

Committee D20 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

D 6099 – 03:

- (1) Updated Note 1 to reflect recent ISO publication.
- (2) Corrected misspelled term in Footnote 5.
- (3) Corrected standard citation in paragraph 14.1. Changed reference from Practice E 691 to Practice E 180.
- (4) Added Practice E 180 to the Warning statement at the end of paragraph 14.1.
- (5) Editorially changed the placement of Warning, Caution, and Precaution statements to conform with ASTM's Form and Style.

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