Designation: D6099 – 13

Standard Test Method for
Polyurethane Raw Materials: Determination of Acidity in Moderate to High Acidity Aromatic Isocyanates[1]

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 equivalent to ISO 14898, Test Method A.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

ISO 14898 Plastics—Aromatic isocyanates for use in the production of polyurethane—Determination of acidity[4]

3. Terminology

3.1 *Definitions*—Terms used in this test method are in accordance with 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 methanol and a cosolvent. Additional acid is released into the solvent system during urethane formation. The acid 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,* capable of inflection detection and stirring the sample while, titrating, such as:

6.4.1 *Commerically-available Automatic Titration Apparatus,*

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

6.4.3 *pH Glass Electrode,* (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. Usual sampling

---

[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 Sept. 1, 2013. Published September 2013. Originally approved in 1997. Last previous edition approved in 2008 as D6099 - 08. DOI: 10.1520/D6099-13.

[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**

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.

NOTE 3—Many diisocyanates are known or suspected sensitizers. Over-exposure to diisocyanates can lead to adverse health effects which may include the development of occupational asthma and other respiratory, skin and eye effects. Engineering controls and/or personal protective equipment, including respiratory, skin and eye protection, are to be used when there is a potential for over-exposure to diisocyanates. The product suppliers' Material Data Safety Sheet (MSDS) provides more detailed information about potential adverse health effects and other important safety and handling information. Always follow the specific instructions provided on the MSDS.

9. Calibration

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

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 shall 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.

NOTE 4—THF has been used as a solvent for prepolymers.

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

11.6 With uniform stitrring of the sample, automatically titrate the mixture with 0.02 *N* methanolic KOH through the potentiometrically-determined inflection end point between apparent pH 4 and 9. Follow manufacturer's instructions for instrument-specific parameters for set-up, calibration and analysis of samples.

NOTE 6—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 7—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:

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

where:

Vsam = volume of titrant needed for the sample, mL,

N = normality of the titrant solution, and

F = 36 465 (mol weight of HCl) × 1000 (factor to change mg/g to µg/g, that is, ppm).

TABLE 1 Round–Robin Acidity Data in Accordance With Practice E180

	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 × S_r.
[D] R = between-laboratory reproducibility limit = 2.8 × 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.

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 shall also 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[5]

14.1 Table 1 is based on a round robin conducted in 1995 in accordance with Practice E180, involving two materials tested by 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. (**Warning—**The following explanations of *r* and *R* (14.1.1 and 14.1.2) 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 these data apply on to the materials tested in 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 E691 or E180 to generate data specific to their laboratory and materials (or between specific laboratories). The principles of 14.1.1 through 14.1.2 would then be valid for such data.)

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1195.

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

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D6099 – 08) that may impact the use of this standard. (September 1, 2013)

(1) Revised 3.2.1, 4.1, Note 3, Note 4, and the legend for Eq 1.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).