



Designation: ~~D6099-03~~ Designation: D 6099 – 08

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

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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

D 883 Terminology Relating to Plastics

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

E 691 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 acidity³

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 as³, capable of inflection detection and stirring the sample while, titrating, such as:

6.4.1 *Fitroprocessor*, and Commerically-available Automatic Titration Apparatus,

6.4.2 *Dosimat*⁶, with magnetic stirrer.

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

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.

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² Annual Book of ASTM Standards, Vol. 08.01.

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 Annual Book of ASTM Standards, Vol. 15.05.

³ 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.

6.4.4

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. (Warning—Organic isocyanates are toxic when they are absorbed through the skin or when the vapors are breathed.) (Warning—Provide adequate ventilation and 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 with dry air or nitrogen at all times.~~

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.

NOTE 3—**Warning:** 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, should 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 should be done in duplicate.~~

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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.~~

11.3 Add 50 mL of dried toluene or TCB.

NOTE 3—~~If 4—~~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 4—~~Samples must be at room temperature before titration. Warm samples cause more frequent electrode clogging.~~

~~11.6 Titrate the mixture with 0.02 N 5—~~Samples must be at room temperature before titration. Warm samples cause more frequent electrode clogging.

11.6 With uniform stirring of the sample, automatically titrate the mixture with 0.02 N methanolic KOH through the titration end point between apparent pH 4 and 9 as determined potentiometrically. 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 5—~~If 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 6—~~The 7—~~The inflection point typically is at apparent pH between 4 and 5.