



Designation: D5155 – 10

# Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates<sup>1</sup>

This standard is issued under the fixed designation D5155; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods measure the isocyanate content of aromatic isocyanates used as polyurethane raw materials.

1.1.1 *Test Method A*—Unheated toluene-dibutylamine determines the toluene diisocyanate content, the amine equivalent and the isocyanate content of refined toluene-2,4-diisocyanate and toluene-2,6-diisocyanate, or mixtures of the two. Other isomers, if present, will be included in the determination. This test method may also be applied to other isocyanates of suitable reactivity and solubility.

1.1.2 *Test Method B*—Heated toluene-dibutylamine determines the amine equivalent and the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene di-(4-phenylisocyanate) and polymeric (methylene phenylisocyanate).

1.1.3 *Test Method C*—Unheated trichlorobenzene-toluene-dibutylamine determines the amine equivalent and the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene-di-(4-phenylisocyanate) and polymeric (methylene phenylisocyanate).

1.2 *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—Method C of this test method is equivalent to Method B of ISO 14896.

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

D883 Terminology Relating to Plastics

D1193 Specification for Reagent Water

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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<sup>2</sup> 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.

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)<sup>3</sup>

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

2.2 *ISO Standard*:

ISO 14896 Polyurethane Raw Materials-Determination of Isocyanate Content

## 3. Terminology

3.1 *Definitions*—For definitions of terms that appear in this test method, refer to Terminology D883.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *amine equivalent*—the weight of sample that will combine with 1.0-g equivalent weight of dibutylamine.

3.2.2 *assay*—the percent by weight of toluene diisocyanate present in the sample.

3.2.3 *isocyanate (NCO) content*—the percent by weight of NCO groups present in the sample.

## 4. Summary of Test Methods

4.1 All three test methods react the isocyanate sample with an excess amount of dibutylamine to form the corresponding urea. The NCO content is determined from the amount of dibutylamine consumed in the reaction. The test methods differ in the reaction conditions, or solvents used, or both.

4.1.1 *Test Method A*—The sample is added to an excess amount of dibutylamine in toluene and allowed to stand at room temperature for 15 min. The reaction mixture is diluted with isopropyl alcohol, and the excess dibutylamine is back-titrated with hydrochloric acid.

4.1.2 *Test Method B*—The sample is added to an excess amount of dibutylamine in toluene and stirred for 20 min. The resulting solution is then heated rapidly to 100°C, removed from the heat, and allowed to stand for 30 min. The reaction mixture is diluted with isopropyl alcohol, and the excess dibutylamine is back-titrated with hydrochloric acid.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

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

4.1.3 *Test Method C*—The sample is added to an excess amount of dibutylamine in toluene and trichlorobenzene. The resulting solution is allowed to stand until it has cooled to room temperature. The reaction mixture is diluted with methanol and back-titrated with hydrochloric acid.

## 5. Significance and Use

5.1 These test methods can be used for research or for quality control to characterize isocyanates used in polyurethane products.

## 6. Interferences

6.1 Phosgene, the carbamyl chloride of the isocyanate, hydrogen chloride, and any other acidic or basic compounds will interfere. In refined isocyanates, these impurities are usually present in such low amounts that they do not affect the determination. While some crude or modified isocyanates contain acidities of up to approximately 0.05 %, the NCO content is not normally corrected.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types I through IV of Specification **D1193**.

## 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**—Many diisocyanates are known or suspected sensitizers. Over-exposure to diisocyanates can lead to adverse health effects, which 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.)

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 9. Test Conditions

9.1 Since isocyanates react with moisture, keep the laboratory humidity low, preferably below 50 % relative humidity.

### TEST METHOD A—UNHEATED TOLUENE-DIBUTYLAMINE

## 10. Apparatus

10.1 Any weighing device that can weigh a liquid by difference to the nearest 0.001 g.

10.2 *Cooling Bath*—Any container approximately 50 mm deep filled with ice and water.

10.3 Pipet capable of reproducibly delivering  $50 \pm .05$  mL.

10.4 Buret capable of dispensing 0.05 mL at a time.

## 11. Reagents

11.1 *Bromcresol Green Indicator Solution*—Using 1.5 mL of 0.1 *N* sodium hydroxide, extract the bromcresol green from 0.100 g of bromcresol green indicator-grade powder, stirring vigorously until the amount of insoluble residue remains constant. Decant the aqueous portion into a 100-mL volumetric flask and dilute to the mark with water.

11.2 *Dibutylamine Solution (260 g/L)*—Dilute 260 g of dry dibutylamine to 1 L with dry toluene. Dry the solution with a drying agent.<sup>5</sup>

11.3 *Hydrochloric Acid (1 N)*—Prepare 1 *N* HCl (hydrochloric acid) and standardize frequently enough to detect changes of 0.001 *N*.

11.4 *Isopropyl Alcohol*.

11.5 *Toluene*, dry with a drying agent.<sup>5</sup>

## 12. Procedure

12.1 Run sample and blank determinations side by side. Run the blank determination exactly as described in **12.2-12.4**, but without adding the sample.

12.2 Add a magnetic stirring bar and 40 mL of dry toluene to a 500-mL Erlenmeyer flask that has been rinsed successively with water, alcohol, and high-purity acetone, dried at 100°C, and allowed to cool in a desiccator. Accurately add, by pipet or buret,<sup>6</sup> 50 mL of dibutylamine solution and mix carefully.

12.3 While stirring the contents of the flask, slowly add 6.5 to 7.0 g of the sample weighed to the nearest 0.001 g (**Note 2**). Wash down the sides of the flask with 10 mL of dry toluene, then stopper the flask loosely and allow it to stand at room temperature for 15 min.

**NOTE 2**—If spattering is anticipated, cool the flask and contents in the cooling bath before adding the sample and continue to cool until the heat

<sup>5</sup> The 4A Molecular Sieve, or its equivalent, has been found suitable. The 4A Molecular Sieve is available from VWR International, Inc., 1310 Goshen Parkway, West Chester, PA 19380.

<sup>6</sup> Pipets and burets shall conform to National Institute of Standards and Technology tolerances, as given in Peffer, E. L., and Mulligan, G. C., "Testing of Glass Volumetric Apparatus," *NIST Circular C434*, 1941, available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20025.

of reaction is dissipated. Add 10 mL of dry toluene, stopper the flask loosely, and allow the contents to come to room temperature.

12.4 Add 225 mL of isopropyl alcohol and 0.8 mL of bromocresol green indicator solution. Titrate with 1 *N* HCl solution in a 50 or 100-mL buret<sup>7</sup> while stirring the flask contents with the magnetic stirring bar. Near the end point, slowly add the HCl dropwise. The end point is reached when the blue color disappears and a yellow color appears that persists for at least 15 s (Note 3).

NOTE 3—Alternatively, the end point may be determined using a potentiometer and electrodes. When using this apparatus, it may be necessary to transfer the solution to a 600-mL beaker prior to titration. After transfer, rinse the Erlenmeyer flask with 25 mL of isopropyl alcohol and add the rinse to the 600-mL beaker. To titrate, immerse the calomel and glass electrodes or a combination electrode of the pH meter (standardized with pH 4.0 and pH 7.0 standard buffers) and titrate the sample to the break that occurs at approximately pH 4.2 to 4.5 with 1.0 *N* HCl while stirring the solution with a stirring bar.

### 13. Calculation

13.1 Calculate the assay as follows:

$$\% \text{TDI} = \frac{(B - S)(N)(87.08)(100)}{1000(W)} \quad (1)$$

When constants are combined, this equation reduces to:

$$\% \text{TDI} = \frac{(B - S)(N)(87.08)}{(W)} \quad (2)$$

13.2 Calculate the amine equivalent as follows:

$$\text{Amine Equivalent} = \frac{1000(W)}{N(B - S)} \quad (3)$$

13.3 Calculate the percent NCO as follows:

$$\% \text{NCO} = \frac{42.02(B - S)(N)(100)}{1000(W)} \quad (4)$$

When constants are combined, this equation reduces to:

$$\% \text{NCO} = \frac{4.202(B - S)(N)}{(W)} \quad (5)$$

where:

- B* = HCl required for titration of the blank, mL,
- S* = HCl required for titration of the sample, mL,
- N* = normality of the HCl, meq/mL,
- W* = sample used, g,
- 87.08 = equivalent weight of TDI, mg/meq,<sup>6</sup>
- 1000 = conversion from g to mg, and
- 100 = conversion to percent.

### 14. Precision and Bias<sup>8</sup>

14.1 Attempts to develop a precision and bias statement for this test method have not been successful due to the limited number of laboratories participating in round-robin tests. Data on precision and bias cannot be given for this reason. Anyone wishing to participate in the development of precision and bias

data are to contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

14.2 A limited round robin was conducted.

14.2.1 It has been estimated that duplicate results by the same analyst are to be considered suspect if they differ by 0.4 % TDI.

14.2.2 It has been estimated that results reported by different laboratories are to be considered suspect if they differ by 0.8 % TDI.

14.3 There are no recognized standards by which to estimate the bias of this test method.

## TEST METHOD B—HEATED TOLUENE-DIBUTYLAMINE

### 15. Apparatus

15.1 *Potentiometric Titrator*, or pH meter.

15.2 *Calomel Electrode or a combination electrode*.

15.3 *Glass Electrode*.

15.4 Any weighing device suitable for weighing a liquid sample by difference to the nearest 0.001 g.

15.5 *Magnetic Stirrer*.

15.6 *Thermometer*, from – 10 to 100°C range.

15.7 Pipet or buret capable of reproducibly delivering 25 ± .025 mL.

### 16. Reagents

16.1 *Dibutylamine Solution* (260 g/L)—Dilute 260 g dry dibutylamine to 1 L with dry toluene.

16.2 *Hydrochloric Acid* (1 *N*)—Prepare 1 *N* hydrochloric acid (HCl) and standardize frequently enough to detect changes of 0.001 *N*.

16.3 *Isopropyl Alcohol*, 99 % minimum purity.

16.4 *Toluene*, dry, dried with a drying agent.<sup>5</sup>

### 17. Procedure

17.1 Add 50 mL of dry toluene to a dry 600-mL beaker. Pipet 25<sup>6</sup> mL of the dibutylamine solution into the beaker. Swirl the beaker to mix the contents.

17.2 Transfer to the beaker 0.02 to 0.03 equivalents of the sample weighed to the nearest 0.001 g. The amount of sample needed can be calculated from the following equation:

$$\text{weight of sample (g)} = \frac{105}{\text{expected \% NCO}} \quad (6)$$

Start the magnetic stirrer carefully and rinse the sides of the beaker with an additional 10 mL of dry toluene. Cover the beaker and continue mixing for an additional 20 min.

17.3 Place the beaker on a hot plate with the – 10 to 100°C thermometer in the sample. Heat the sample mixture rapidly with stirring, so that the solution reaches a temperature of 95 to 100°C in 3½ to 4½ min. Do not overheat. Quickly remove the beaker from the hot plate, cover it with a watchglass, and allow it to stand for 30 min.

<sup>7</sup> If an isocyanate monomer other than TDI is used, substitute the equivalent weight of the material being analyzed. The calculated assay result will be percent by weight of the monomer used.

<sup>8</sup> Supporting data are available from ASTM Headquarters. Request RR:D20-1089.