



Designation: D5155 – 14^{ε1}

Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates¹

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^{ε1} NOTE—Editorially corrected Eq 2 in January 2016.

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 is also applicable 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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—Method C of this test method is equivalent to Method B of ISO 14896.

¹ 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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2. Referenced Documents

2.1 *ASTM Standards*:²

D883 Terminology Relating to Plastics

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³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

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.

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

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.

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 are to 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.⁴ Other grades are allowed, 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**—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, further exposure to diisocyanates should be eliminated. A combination of engi-

neering controls and personal protective equipment, including respiratory, skin and eye protection, may be used to prevent over-exposure 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. 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 weighs 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 ± .05 mL.

10.4 Buret capable of dispensing 0.05 mL at a time.

11. Reagents

11.1 *Bromocresol Green Indicator Solution*—Using 1.5 mL of 0.1 *N* sodium hydroxide, extract the bromocresol green from 0.100 g of bromocresol 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.⁵

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.⁵

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,⁶ 50 mL of dibutylamine solution and mix carefully.

⁵ 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.

⁶ 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.

⁴ *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.

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 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 buret⁷ 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 is determined using a potentiometer and electrodes. When using this apparatus, it occasionally is 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:

$$\% \text{TDI} = \frac{(B - S)(N)(8.708)}{(W)} \quad (2)$$

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,
- 1000 = conversion from g to mg, and
- 100 = conversion to percent.

⁷ 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.

14. Precision and Bias⁸

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 are not 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 ± 0.025 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.⁵

17. Procedure

17.1 Add 50 mL of dry toluene to a dry 600-mL beaker. Pipet 25⁶ 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 is calculated from the following equation:

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

⁸ Supporting data are available from ASTM Headquarters. Request RR:D20-1089.