



Designation: D 5155 – 01

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

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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 amount of toluene diisocyanate in 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 of crude or modified isocyanates derived from toluene diisocyanate, methylenebis-(4-phenylisocyanate), and polymethylene polyphenylisocyanate.

1.1.3 *Test Method C*—Unheated trichlorobenzene-toluene-dibutylamine determines the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene-bis-(4-phenylisocyanate), and polymethylene polyphenylisocyanate. This test method can also be used to assay isomer mixtures of toluene diisocyanate and methylene-bis-(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.* For specific warning and precautionary statements, see [Note 2](#).

NOTE 1—Method C of this test method is equivalent to Method B of ISO 14896.

2. Referenced Documents

2.1 ASTM Standards:

[D 883](#) Terminology Relating to Plastics²

[D 1193](#) Specification for Reagent Water³

[E 180](#) Practice for Determining the Precision of ASTM

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. These test methods were recommended to ASTM by the Society of the Plastics Industry Polyurethane Raw Materials Analysis Committee.

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

³ *Annual Book of ASTM Standards*, Vol 11.01.

Methods for Analysis and Testing of Industrial Chemicals⁴

2.2 ISO Standard:

ISO 14896 Polyurethane Raw Materials-Determination of Isocyanate Content

3. Terminology

3.1 Definitions:

3.1.1 *polyurethane, n*—a polymer prepared by the reaction of an organic diisocyanate or polyisocyanate with compounds containing hydroxyl groups.

3.1.1.1 *Discussion*—Polyurethanes or urethanes, as they are sometimes called, may be thermosetting, thermoplastic, rigid or soft and flexible, or cellular or solid (see Terminology [D 883](#)).

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 weight percent of the NCO groups present in the sample.

4. Summary of Test Methods

4.1 All three test methods react the isocyanate sample with an excess of dibutylamine to form the corresponding urea. The NCO content is determined from the amount of dibutylamine consumed in the reaction. Each test method varies solvent or heating times to yield accurate assays of the sample in question.

4.1.1 *Test Method A*—The sample is added to an excess 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 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 *Annual Book of ASTM Standards*, Vol 15.05.

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

4.1.3 *Test Method C*—The sample is added to a solution 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.⁵ 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 **D 1193**.

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture to form ureas, take special precautions in sampling (see **Note 2**). Usual sampling methods (for example, sampling an open drum with a thief), 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 2—Warning: Organic isocyanates are toxic when absorbed through the skin, or when the vapors are breathed. **Precaution:** Provide adequate ventilation and wear protective gloves and eyeglasses.

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.

⁵ *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.

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.

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.⁶

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.⁶

12. Procedure

12.1 Run sample and blank determinations side by side. Run the blank determination exactly as described as follows, 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,⁷ 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 3**). 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 3—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 bromcresol green indicator solution. Titrate with 1 *N* HCl solution in a 50 or 100-mL buret⁸ 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 4**).

NOTE 4—Alternatively, the end point may be determined using a potentiometer and electrodes. When using this apparatus, it may be

⁶ The Linde 4A Molecular Sieve, or its equivalent, has been found suitable. The Linde 4A Molecular Sieve is available from Dow Chemical Corp., Specialty Gas-Linde Division, 2 Greenway Plaza, Suite 901, Houston, TX 77046, or from other Dow Chemical locations nationwide.

⁷ 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 C 434*, 1941, available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20025.

⁸ If an isocyanate other than TDI is used, substitute the equivalent weight of the material being analyzed.

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 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:

$$\text{Assay} = (B - S)(N)(87.08)(100)/1000 W \quad (1)$$

When constants are combined, this equation reduces to

$$\text{Assay} = 8.708 N(B - S)/W \quad (2)$$

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,¹⁰
- 1000 = conversion from g to mg, and
- 100 = conversion to percent.

14. Precision and Bias ⁹

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 should 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 should be considered suspect if they differ by 0.4 % TDI.

14.2.2 It has been estimated that results reported by different laboratories should 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 capable of reproducibly delivering $25 \pm .025$ 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.⁶

17. Procedure

17.1 Add 50 mL of dry toluene to a dry 600-mL beaker. Pipet 25⁷ 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:

$$\text{weight of sample (g)} = 105/\text{expected \% NCO} \quad (3)$$

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.

17.4 Cool the beaker and contents to room temperature and add 225 mL of isopropyl alcohol.

17.5 Titrate potentiometrically with 1.0 N HCl to the break that occurs at apparent pH approximately 4.2 to 4.5 (for manual titration see **Note 5**, below).

17.6 Prepare and titrate a blank exactly as described in 17.1-17.5, but without adding the sample.

18. Calculation

18.1 Calculate the amine equivalent as follows:

$$\text{amine equivalent} = \frac{1000(W)}{N(B - S)} \quad (4)$$

18.2 Calculate the percent NCO as follows:

$$\% \text{ NCO} = 42.02 (B - S) (N) / 1000 (W) \quad (5)$$

When constants are combined, this equation reduces to:

$$\% \text{ NCO} = 4.202 (B - S) N / W \quad (6)$$

- B = HCl required for titration of blank, mL,
- S = HCl required for titration of sample, mL,
- N = normality of HCl, meq/mL,
- W = sample used, g, and

⁹ Supporting data are available from ASTM Headquarters. Request RR:D20-1089.