Designation: D5155 – 14ε1

Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates[1]

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 (ε) indicates an editorial change since the last revision or reapproval.

ε[1] 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.

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

[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] 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 engineering 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.

[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.

[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.

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 buret[7] 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:

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

13.2 Calculate the amine equivalent as follows:

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

13.3 Calculate the percent NCO as follows:

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

When constants are combined, this equation reduces to:

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

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 Bias[8]

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 ± .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 25[6] 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:

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

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

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 4, 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:

$$\text{Amine Equivalent} = \frac{1000(W)}{N(B-S)} \quad (7)$$

18.2 Calculate the percent NCO as follows:

$$\%\,NCO = \frac{42.02\,(B-S)\,(N)\,(100)}{1000(W)} \quad (8)$$

When constants are combined, this equation reduces to:

$$\%\,NCO = \frac{4.202\,(B-S)\,N}{(W)} \quad (9)$$

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
4.202 = constant combining the equivalent weight of NCO (42.02) mg/meq, conversion of g to 1000 mg, and conversion to 100 %

19. Precision and Bias[9]

19.1 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 International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

19.2 A limited round robin was conducted.

19.2.1 It has been estimated that duplicate results by the same analyst are to be considered suspect if they differ by 0.80 amine equivalents (0.2 % at 30.0 % NCO).

19.2.2 It has been estimated that results reported by different laboratories are to be considered suspect if they differ by 2.0 amine equivalents (0.4 % at 30 % NCO).

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

TEST METHOD C—UNHEATED TRICHLOROBENZENE-TOLUENE-DIBUTYLAMINE

20. Apparatus

20.1 *Potentiometric Titrator,* or pH meter (Note 4).

20.2 *Calomel Electrode or a combination electrode.*

20.3 *Glass Electrode.*

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

20.5 *Magnetic Stirrer.*

20.6 Pipet or buret capable of reproducibly delivering 20 ± .02 mL.

NOTE 4—If a potentiometric titrator is not available, the titration is performed using a conventional 50-mL buret and bromophenol blue indicator (0.04 % aqueous bromophenol blue, sodium salt, reagent grade). Titrate the blank and the sample solutions to the first appearance of a stable yellow color. (The solution will change from a blue color at the start of the titration, to a bluish-green intermediate color, to a yellow color at the end point. Recognition of the end point is a matter of experience, but better defined color changes are obtained when the acid is titrated rapidly into the solution until the first flash of yellow color is observed. This flash of color normally appears within a few tenths of a millilitre of the end point.)

21. Reagents

21.1 *Dibutylamine.*

21.2 *Methanol.*

21.3 *Toluene,* dry, dried with a drying agent.[5]

21.4 *Trichlorobenzene-1,2,4* (TCB) —Dry over Type 4A molecular sieves.

21.5 *Dibutylamine Solution* (2 *N*)—Dilute 260 g of dibutylamine to 1 L with dry toluene and dry over Type 4A molecular sieves.

21.6 *Methanolic Hydrochloric Acid* (1 *N*)—Prepare 1 *N* hydrochloric acid from methanol and concentrated HCl. Standardize frequently enough to detect changes of 0.001 *N* (Note 5).

NOTE 5—In order to have homogenous titrations, it is recommended that methanolic HCl be used in this procedure. If desired, aqueous HCl is used. However, turbidity will be encountered in some titrations. It is recommended that 200 to 250 mL of methanol be added to the reacted product to minimize the formation of two layers. Experience has shown that if the mixtures are agitated vigorously, inhomogeneity is tolerated without adversely affecting the results.

22. Procedure

22.1 Add 25 mL of TCB to a dry 250-mL wide-mouth Erlenmeyer flask. Pipet 20 mL of the dibutylamine solution into the flask. Swirl to mix the contents.

[9] Supporting data are available from ASTM Headquarters. Request RR:D20-1040. The precision estimates are based on an interlaboratory study performed in 1989 on one sample each of Lupranate M20S (BASF), PAPI 20 and Isonate 143L (Dow), Mondur PF (Bayer), and Rubinate HF185 (Rubicon). Eleven industrial laboratories participated in the test method evaluation.

22.2 Transfer the approximate amount of sample required weighed to the nearest 0.001 g to the flask. The approximate amount of sample required is calculated from the following equation:

$$\text{weight of sample, g} = \frac{84}{\text{expected \% NCO}} \quad (10)$$

22.3 Cover the flask and swirl the contents until the solution is homogeneous. The reaction mixture will warm to approximately 40°C.

22.4 Let the sample stand until the reaction mixture reaches room temperature (20 to 25 min) and add 100 mL of methanol to the flask (see Note 4).

22.5 Titrate potentiometrically with 1.0 *N* HCl to the break that occurs at apparent pH approximately 4.2 to 4.0.

22.6 Prepare and titrate a blank exactly as described in 22.1 – 22.5, but without adding the sample.

23. Calculation

23.1 Calculate the amine equivalent as follows:

$$\textit{Amine Equivalent} = \frac{1000(W)}{N(B-S)} \quad (11)$$

23.2 Calculate the percent NCO as follows:

$$\%\ NCO = \frac{42.02\,(B-S)\,(N)\,(100)}{1000\,(W)} \quad (12)$$

When constants are combined, this equation reduces to:

$$\%\ NCO = \frac{4.202\,(B-S)\,N}{(W)} \quad (13)$$

where:

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
4.202 = constant combining the equivalent weight of NCO (42.02) mg/meq, conversion of g to 1000 mg, and conversion to 100 %.

24. Report

24.1 The result is reported as the average of duplicates, expressed as percent NCO, to the nearest 0.01 %. Any unusual conditions during operation also are to be reported, such as any heating required to effect solution before titration, or end point identified different from that described in 22.5.

25. Precision and Bias[9]

25.1 Table 1 is based on a round robin involving nine laboratories and conducted in 1991 in accordance with Practice E180. All labs used potentiometric titration for the generation of the data used in this study. Except for MDI and TDI, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. The MDI and TDI samples were freshly produced material at the laboratory site. Each test result was the average of two individual determinations. (**Warning—**The following explanations of *r* and *R* (25.2.1 – 25.2.4) are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 are not to be rigorously applied to the acceptance or rejection of material, as those data are specific to the round robin and not necessarily representative of other lots, conditions, materials, or laboratories. Users of this test method are to apply the principles outlined in Practice E180 or E691 to generate data specific to their laboratory and materials or between specific laboratories. The principles of 25.2.1 – 25.2.4 then would be valid for such data.)

TABLE 1 Round-Robin Percent NCO Data In Accordance with PracticeE180[A]

	Average	S_r[B]	S_R[C]	r[D]	R[E]	df[F]
Lupranate M20S	31.30	0.082	0.206	0.230	0.577	9
Rubinate 1850	30.78	0.082	0.194	0.230	0.543	9
PAPI 20	29.57	0.080	0.172	0.224	0.482	8
Isonate 143L	28.83	0.126	0.230	0.353	0.644	9
Mondur PF	22.63	0.048	0.120	0.134	0.336	9
MDI	33.53	0.011	0.080	0.031	0.224	6
TDI (see 25.2.4)	48.18	0.078	0.126	0.218	0.353	2

[A] Values in units of percent NCO.
[B] S_r = within-laboratory standard deviation of the replicates.
[C] S_R = between-laboratories standard deviation of the average.
[D] r = within-laboratory repeatability limit = $2.8 \cdot S_r$.
[E] R = between-laboratories reproducibility limit = $2.8 \cdot S_R$.
[F] df = degrees of freedom in the data.

25.2 *Precision*

25.2.1 *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 are to be judged not equivalent if they differ by more than the *r* value for that material.

25.2.2 *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 are to be judged not equivalent if they differ by more than the *R* value for that material.

25.2.3 Any judgment in accordance with 25.2.2 and 25.2.3 would have an approximate 95 % (0.95) probability of being correct.

25.2.4 There are insufficient degrees of freedom to make a statistically acceptable determination for TDI. The data in Table 1 are provided for information only. The precision for TDI isomers is expected to be similar to results obtained for MDI.

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

26. Keywords

26.1 isocyanates; isocyanates aromatic; methylene-*bis*-(4-phenylisocyanate); polymethylene polyphenylisocyanate; polyurethane; raw materials; test method; titration; toluene diisocyanate

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D5155 – 10) that may impact the use of this standard. (November 1, 2014)

(1) Removed non-mandatory language throughout.
(2) Added 1.2 to comply with ASTM D4968 Standard Guide for Annual Review of Test Methods and Specifications for Plastics.
(3) Modified 8.1 to revised warning from Center for the Polyurethanes Industry Product Stewardship Committee.
(4) Corrected misspellings throughtout.
(5) Removed footnote number in 13.3.