Designation: D4660 – 12

Standard Test Methods for Polyurethane Raw Materials: Determination of the Isomer Content of Toluenediisocyanate[1]

This standard is issued under the fixed designation D4660; 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.

1. Scope*

1.1 These test methods measure the amount of toluene-2,6-diisocyanate (2,6-TDI) isomer or toluene–2,4–diisocyanate (2,4-TDI) isomer in mixtures of the 2,4- and 2,6-isomers of toluenediisocyanate (TDI). Two different test methods are provided to give accurate results over the broad range of isomer concentrations possible.

1.1.1 *Test Method A*—Applicable to TDI samples containing 5 to 95 % of 2,6-TDI isomer (5 to 95 % 2,4-TDI isomer).

1.1.2 *Test Method B*—Applicable to TDI samples containing 0 to 5 % of 2,6-TDI isomer (95 to 100 % 2,4-TDI isomer).

NOTE 1—These test methods are equivalent to ISO 15064.

1.2 The values stated in SI units are to be regarded as 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

2.2 *ISO Standard:*[4]

ISO 15064 Plastics—Aromatic Isocyanates for Use in the Production of Polyurethanes—Determination of the Isomer Ratio in Toluenediisocyanate

3. Terminology

3.1 Terminology in these test methods is in accordance with Terminology D883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *isomer*—a compound having the same molecular formula (percentage composition and molecular weight) as another compound but differs in chemical or physical properties.

3.2.2 *isomer content*—the amount of an isomer expressed as a percentage of total 2,4 and 2,6-TDI isomer amount.

4. Summary of Test Methods

4.1 Both test methods are based on the quantitative measurement of absorption bands arising from out-of-plane C-H deformation vibrations of the aromatic ring.

4.2 In Test Method A, the infrared spectrum of a cyclohexane solution of the sample is recorded in the 770 to 840-cm^{-1} region. The absorbance ratio of the 805 cm^{-1} to the 782 cm^{-1} band is measured and converted to percent 2,6-TDI, or percent 2,4-TDI, or both, from a previously established calibration curve.

4.3 In Test Method B, the absorbance of the 782-cm^{-1} band is measured from an infrared spectrum of an undiluted sample and then converted to percent 2,6-TDI from a previously established calibration curve.

5. Significance and Use

5.1 These test methods can be used for research or for quality control to determine the isomer content of toluene diisocyanates.

5.2 The isomer content of a toluene diisocyanate relates to its reactivity.

6. Apparatus

6.1 *Spectrophotometer*—Any single- or double-beam recording infrared spectrophotometer accurate to 0.2 % transmission and capable of resolving the two peaks of the 2,4-TDI isomer doublet at 805-815 cm^{-1} (see Fig. 1).

6.2 *Cells,* sealed sodium chloride (NaCl) liquid absorption cells with 0.2-mm (Test Method A) and 0.1-mm (Test Method

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[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.

[4] 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**

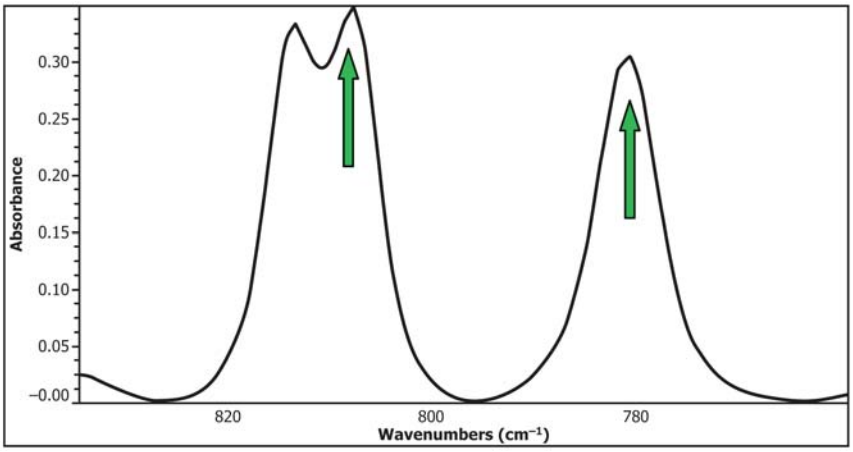

FIG. 1 IR Scan of TDI Showing 2,4-TDI Isomer Doublet at 810 cm^{-1} and 2,6 TDI Isomer at 782 cm^{-1}

B) path lengths. The actual thicknesses of the cells are to be known to ±0.002 mm.

6.3 *Glassware,* 25-mL, glass-stoppered, volumetric flasks, 10-mL, glass-stoppered, flasks, 0.80-mL volumetric pipet, and an all-glass syringe.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise noted, all reagents 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 ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Cyclohexane,* anhydrous, stored over molecular sieve.

7.3 *Diisocyanate Standards*—Pure samples of 2,4-TDI and 2,6-TDI are required for calibration. The following criteria can be used to judge purity:

Pure Isomer	Freezing point	Refractive Index @ 20C $n^{20}D$	Density @ 20C/4C
2,4-TDI	22.0°C	1.56781	1.2186
2,6-TDI	18.2°C	1.57111	1.2270

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. Overexposure 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 Safety Data 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. Test Conditions

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

TEST METHOD A—SAMPLES CONTAINING 5 TO 95 % 2,6-TDI

10. Calibration

10.1 Weigh amounts of pure 2,4-TDI and 2,6-TDI into dry, 10-mL, glass-stoppered flasks (Note 2) to obtain the weight ratios given in 10.1.1 or 10.1.2. Carefully shake the mixtures. From the weights of pure 2,4-TDI and 2,6-TDI, calculate the weight ratios (2,4-TDI to 2,6-TDI), or the weight percent composition of the mixtures, or both, expressed to four significant figures.

NOTE 2—Carefully dry all glassware since the diisocyanates react readily with moisture.

10.1.1 Approximate standard mixtures for wide-range calibration are given in Table 1 (5-95 % 2,6-TDI).

TABLE 1 Approximate Standard Mixtures for Wide-Range Calibration, 5–95 % 2,6-TDI

	Weight Ratio	
%, 2,4-TDI	%, 2,6-TDI	2,4-/2,6-TDI
5.0	95.0	0.05
10.0	90.0	0.11
20.0	80.0	0.25
30.0	70.0	0.43
40.0	60.0	0.67
50.0	50.0	1.00
60.0	40.0	1.50
70.0	30.0	2.33
80.0	20.0	4.00
90.0	10.0	9.00
95.0	5.0	19.00

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[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.

10.1.2 Approximate standard mixtures for narrow-range calibrations (see Note 3) are given in Table 2 (15-25 % 2,6-TDI) and Table 3 (30-40 % 2,6-TDI).

NOTE 3—Calibration over a narrow range covering the expected isomer ratio gives more accurate results than a wide-range calibration.

10.2 *Preparation of Standard Solutions*— Using a pipet, transfer 0.80 mL (0.98 g) of standard mixture into a dry, 25-mL glass-stoppered, volumetric flask. Dilute to volume with cyclohexane and mix thoroughly.

10.3 Fill two 0.2-mm sealed, liquid absorption cells (one for a single-beam instrument) with cyclohexane and record its spectrum from 770 to 840 cm^{-1}. Refill the sample cell with a standard solution from 10.2 and record the spectrum superimposing it over the previously recorded solvent spectrum. The instrument controls must remain unchanged between the blank and the standards of a given series. Repeat the process for each standard solution from 10.2.

10.4 Using the solvent spectrum as the baseline, measure the absorbance of each standard solution sample at 805 cm^{-1} (2,4-TDI) and 782 cm^{-1} (2,6-TDI) and calculate the 805/782-cm^{-1} absorbance ratio. Construct a calibration curve (see Fig. 2) by plotting absorbance ratio (ordinate) versus weight ratio of 2,4-TDI to 2,6-TDI (abscissa).

10.5 For convenience in short-range calibrations, the absorbance ratio may be plotted against the concentration, expressed in weight percent, of each isomer (see Figs. 3 and 2). This allows direct determination of composition without equations, however, the relationship is not linear and the shape of the calibration curve must be carefully determined.

11. Procedure

11.1 Using a dry pipet, transfer 0.8 mL (0.98 g) of sample into a dry, 25-mL, glass-stoppered, volumetric flask. Dilute to volume with anhydrous cyclohexane and mix thoroughly. Fill the 0.2-mm cell with the cyclohexane and record the blank solvent spectrum from 770 to 840 cm^{-1}. Without changing instrument settings, refill the sample cell with the sample solution and record its spectrum superimposed on the blank solvent spectrum.

12. Calculation

12.1 Using the solvent spectrum as the baseline, measure the absorbance of the sample at 805 cm^{-1} (2,4-TDI) and 782 cm^{-1} (2,6-TDI) and calculate the 805/782-cm^{-1} absorbance ratio. From the appropriate standard curve, obtain the percentage composition (Figs. 3 and 2), or isomer weight ratio (*R*), (Fig. 4), or both, that corresponds to the measured absorbance ratio.

TABLE 2 Approximate Standard Mixtures for Narrow-Range Calibration, 15–25 % 2,6-TDI

Weight Ratio		
%, 2,4-TDI	%, 2,6-TDI	2,4-/2,6-TDI
75.0	25.0	3.00
78.5	21.5	3.65
79.0	21.0	3.76
79.5	20.5	3.88
80.0	20.0	4.00
80.5	19.5	4.13
81.0	19.0	4.26
81.5	18.5	4.40
85.0	15.0	5.67

TABLE 3 Approximate Standard Mixtures for Narrow-Range Calibration, 30–40 % 2,6-TDI

Weight Ratio		
%, 2,4-TDI	%, 2,6-TDI	2,4-/2,6-TDI
60.0	40.0	1.50
63.5	36.5	1.74
64.0	36.0	1.77
64.5	35.5	1.82
65.0	35.0	1.86
65.5	34.5	1.90
66.0	34.0	1.94
66.5	33.5	1.98
70.0	30.0	2.33

12.2 When using the isomer weight ratio, (*R*), calculate the percentage of each isomer as follows:

$$\text{Percent } 2{,}6 - \text{TDI} = \frac{100}{(R+1)} \quad (1)$$

and

$$\text{Percent } 2{,}4 - \text{TDI} = 100 - \text{percent } 2{,}6 - \text{TDI} \quad (2)$$

12.3 Express the result to one decimal place.

13. Precision and Bias

13.1 *Precision*—Table 4 is based on a round robin conducted in 1994 involving two samples tested by eight laboratories. For each material, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each laboratory obtained ten test results for each material on a given day. Narrow-range calibrations were used.

13.1.1 The following explanations of *r* and *R* (13.1.2 – 13.1.4) are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 4 are not to be rigorously applied to the acceptance or rejection of material, as these data apply only to the materials tested in the round robin and are unlikely to be rigorously representative of other lots, conditions, materials and laboratories. Users of this test method should apply the principles outlined in Practice E180 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 13.1.2 – 13.1.4 would then be valid for such data.

13.1.2 *Repeatability, r*—Two results obtained within one laboratory shall be judged not equivalent if they differ by more than the *r* value for that material where *r* is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

13.1.3 *Reproducibility, R*—Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the *R* value for that material where *R* is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

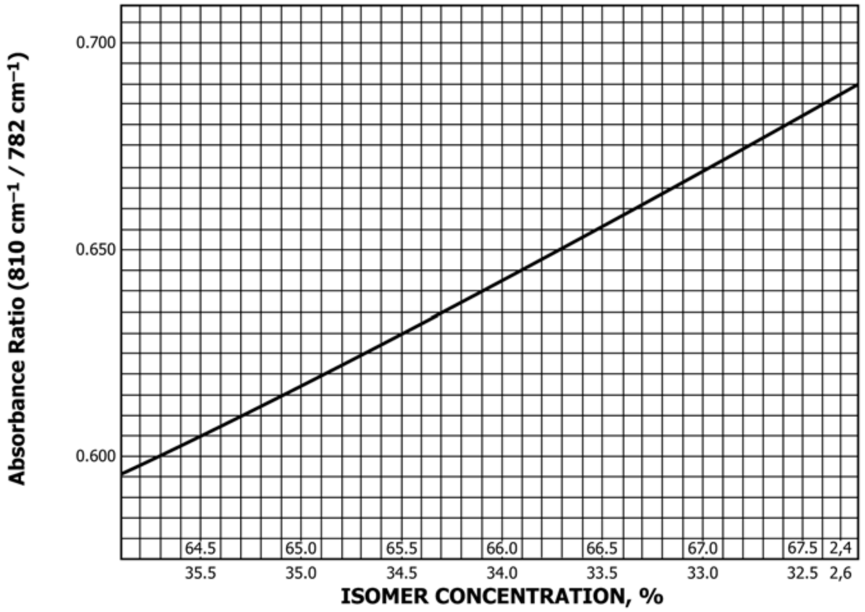

FIG. 2 Calibration Curve Toluene Diisocyanate 65:35 (2,4-TDI : 2,6-TDI)

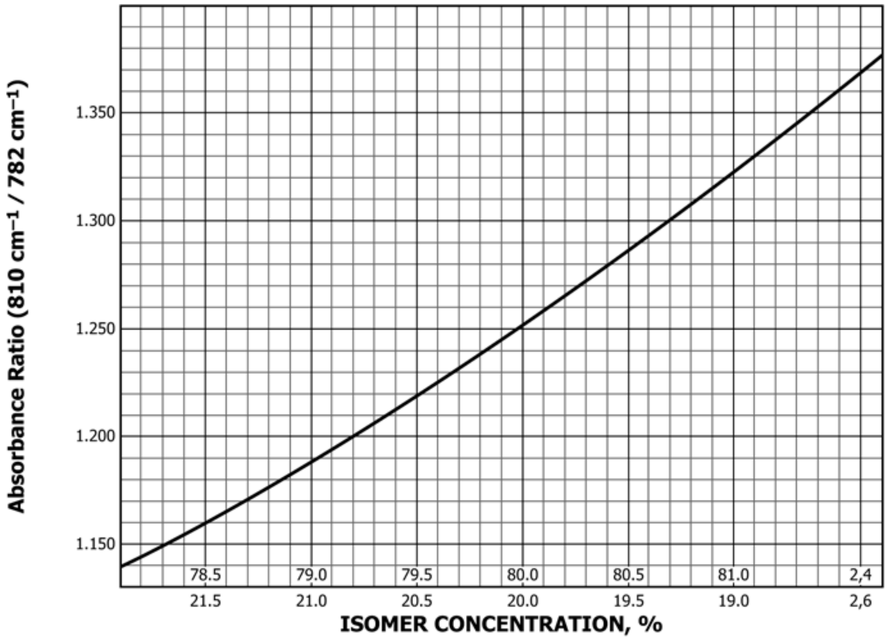

FIG. 3 Calibration Curve Toluene Diisocyanate 80:20 (2,4-TDI : 2,6-TDI)

13.1.4 Any judgment in accordance with 13.1.2 and 13.1.3 would have an approximate 95 % (0.95) probability of being correct.

13.2 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

13.3 It has also been estimated that the results reported by laboratories are to be considered suspect if they differ from one another by more than ±0.34 % isomer (narrow-range calibration).

TEST METHOD B—SAMPLES CONTAINING 0 TO 5 % 2,6-TDI

14. Calibration

14.1 Using pure 2,4- and 2,6-TDI and dry, 10-mL, glass-stoppered flasks, prepare a series of calibration mixtures as given in Table 5.

FIG. 4 Calibration Curve Toluene Diisocyanate 80:20 (2,4-TDI : 2,6-TDI)

TABLE 4 Round Robin Isomer Content of TDI (Data Values in Units of Percent 2,4-TDI)

Sample	Avrage	S_r[A]	S_R[B]	r[C]	R[D]	n[E]
TD-80	80.5	0.08	0.16	0.21	0.45	8
TD-65	67.3	0.09	0.11	0.26	0.31	4
Pooled		0.08	0.14	0.23	0.39	8

[A] S_r = within-laboratory standard deviation of the replicates.
[B] S_R = between-laboratory standard deviation of the average.
[C] r = within-laboratory repeatability limit = 2.8*S_r.
[D] R = between-laboratory reproducibility limit = 2.8*S_R.
[E] n = number of laboratories contributing valid data for this material.

TABLE 5 Approximate Standard Mixtures for Calibration, 0–5 % 2,6-TDI

Weight of 2,4-isomer, g	Weight of 2,6-isomer, g	2,6-isomer, %
5.000	0.000	0.00
4.975	0.025	0.50
4.950	0.050	1.00
4.900	0.100	2.00
4.850	0.150	3.00
4.800	0.200	4.00
4.750	0.250	5.00

14.2 From the weights of pure 2,4- and 2,6-TDI, calculate the concentration of 2,6-TDI in each of the mixtures, expressed to four significant figures.

14.3 Using a 0.1-mm sealed liquid absorption cell, record the spectrum of each of the calibration mixtures from 770 to 840 cm^{-1}.

14.4 For each of the calibration mixtures, measure the absorbance of the 2,6-TDI isomer band at 782 cm^{-1} from a baseline-drawn tangent to the band shoulders.

14.5 Construct a calibration curve by plotting the absorbance (ordinate) versus the concentration of 2,6-TDI (abscissa) expressed in weight percent, (see Fig. 4). This allows direct determination of composition without equations.

15. Procedure

15.1 Fill the 0.1-mm cell with the sample and record the spectrum from 770 to 840 cm^{-1}.

16. Measurement

16.1 Measure the absorbance of the 2,6-TDI isomer band at 782 cm^{-1} and obtain the percentage of 2,6-TDI from the calibration curve.

17. Precision and Bias

17.1 Attempts to develop a full precision and bias statement for this test method have not been successful. For this reason, data on precision and bias cannot be given. Because this test method does not contain a round-robin-based numerical precision and bias statement, it shall not be used as a referee test method in case of dispute. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.00 (Section 20.00.00), ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428

17.2 It has been estimated that duplicate results by the same operator are to be considered suspect if they differ by more than ±0.15 % 2,6-TDI (narrow-range calibration).

17.3 It has also been estimated that the results reported by laboratories are to be considered suspect if they differ from one another by more than ±0.25 % 2,6-TDI (narrow-range calibration).

18. Keywords

18.1 FTIR; infrared; IR; isomer; polyurethane raw material; TDI; toluene diisocyanate

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D4660 - 06) that may impact the use of this standard. (May 1, 2012)

(1) Added Typical Scan as Fig. 1 with arrows indicating the peaks of interest, also referenced in 6.1.
(2) Corrected ordinate scale label for Fig. 3 and Fig. 2.
(3) Removed all references to wavelength in units of µm.
(4) Removed from 4.1 specific peaks from the general description. Method A uses two peaks and method B only uses one.
(5) Specified which peak of the doublet it to be used in 4.2, 10.4, and 12.1.
(6) Specified the location of each peak in the doublet 6.1.
(7) Added required glassware to 6.3.
(8) Updated quality requirements for cyclohexane to store over molecular sieve rather than silica gel in 7.2.
(9) Reformatted information in 7.3 into table.
(10) Updated Warning statement in 8.1.
(11) Updated Section 11 to specify the measurement of blank solvent followed by sample measurement.
(12) All other changes editorial in nature.

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