



Designation: **D 4660 – 9500**

An American National Standard

## Standard Test Methods for Polyurethane Raw Materials: Determination of the Isomer Content of Toluenediisocyanate <sup>1</sup>

This standard is issued under the fixed designation D 4660; 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 amount of toluene-2,6-diisocyanate (TDI) or toluene-2,4-diisocyanate in mixtures of the 2,4- and 2,6-isomers. Two test methods are required to give accurate results over a broad range of isomer concentrations.

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

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

NOTE 1—There are no equivalent ISO standards.

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 3.

### 2. Referenced Documents

2.1 *ASTM Standards:*

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Plastics. Current edition approved Oct. 10, 1995. 2000. Published December 1995. February 2001. Originally published as part of D 1638 – 59 T. Last previous edition D 1638 – 905.

D 883 Terminology Relating to Plastics<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals<sup>3</sup>

### 3. Terminology

3.1 Terminology in these test methods is in accordance with Terminology D 883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *isomer*—a compound having the same 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 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 at 810 and 782 cm<sup>-1</sup> (12.3 and 13.8 μm).

4.2 In Test Method A, the infrared spectrum of a cyclohexane solution of the sample is recorded in the 770 to 840-cm<sup>-1</sup> (12 to 13-μm) region. The absorbance ratio of the 810 and 782-cm<sup>-1</sup> bands is measured and converted to percent toluene-2,6-diisocyanate from a previously established calibration curve.

4.3 In Test Method B, the absorbance of the 782-cm<sup>-1</sup> band is measured from an infrared spectrum of an undiluted sample and then converted to percent 2,6-isomer 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 ratios of toluene diisocyanates.

5.2 The isomer ratio 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-isomer doublet at 810 cm<sup>-1</sup>.

6.2 *Cells*, sealed sodium chloride (NaCl) liquid absorption cells with 0.2-mm (Test Method A) and 0.1-mm (Test Method B) path lengths. The actual thicknesses of the cells should be known to ±0.002 mm.

6.3 *Glassware*, 25-mL, glass-stoppered, volumetric flasks, 0.80-mL 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.<sup>4</sup> 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*, distilled and stored over silica gel to remove traces of moisture.

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

$$\begin{aligned}
 &2,4\text{-TDI—freezing point} = 22.0^\circ\text{C}, n_D^{20} = 1.56781, & (1) \\
 &d_{4}^{20} = 1.2186, \text{ and } 2,6\text{-TDI—freezing point} \\
 &= 18.2^\circ\text{C}, n_D^{20} = 1.57111, d_{4}^{20} = 1.2270.
 \end{aligned}$$

NOTE 2—The diisocyanates can be prepared by phosgenating the corresponding pure amines and vacuum-distilling the products. Since these diisocyanates will react with moisture and may discolor in the presence of air, store them under dry nitrogen.

### 8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. ~~(Warning: Precaution—Note 3).~~ See 8.1.1. Usual sampling methods (for example, sampling an open drum with a thief), even when carried out rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times.

NOTE 3—~~Warning: Organic~~

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>3</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 ASTM Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD; Vol 15.05.

<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.

**8.1.1 Warning:** Organic isocyanates are toxic when they are absorbed through the skin, or when the vapors are breathed.  
**Precaution—Provide** Provide adequate ventilation and wear protective gloves and eyeglasses.

## 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 the amounts of pure 2,4- and 2,6-TDI given in 10.1.1 ~~and~~ or 10.1.2 into dry, 10-mL, glass-stoppered flasks (Note 4); 3). For convenience, a dry pipet may be used. The total weight of each mixture should be 3.5 to 4.0 g. Carefully shake the mixtures. From the weights of pure 2,4- and 2,6-TDI, calculate the weight ratios (2,4-TDI to 2,6-TDI) of the mixtures, expressed to four significant figures.

NOTE 43—Dry carefully all glassware since the diisocyanates react readily with moisture.

10.1.1 Approximate standard mixtures for wide-range calibration are given in Table 1.

10.1.2 Approximate standard mixtures for short-range calibrations (see Note 5) 4) are given in Tables 2 and 3 (see Figs. 1 and 2).

NOTE 54—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  $\text{cm}^{-1}$  (12 to 13  $\mu\text{m}$ ). Refill the sample cell with a solution from 10.2 and record the spectrum superimposing it over the previously recorded solvent spectrum. The instrument controls must remain unchanged between samples of a given series. Repeat the process for each solution from 10.2.

10.4 Using the solvent spectrum as the baseline, measure the absorbance of each standard solution sample at 810  $\text{cm}^{-1}$  (2,4-TDI) and 782  $\text{cm}^{-1}$  (2,6-TDI) and calculate the 810/782- $\text{cm}^{-1}$  absorbance ratio. Construct a calibration curve (see Fig. 3) by plotting absorbance ratio (ordinate) versus weight ratio of 2,4- 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. 1 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 pipet, transfer 0.8 mL (0.98 g) of sample into a dry, 25-mL, glass-stoppered, volumetric flask. Dilute to volume with cyclohexane and mix thoroughly. Fill the 0.2-mm cell with the solution and record the spectrum from 770 to 840  $\text{cm}^{-1}$  (12 to 13  $\mu\text{m}$ ), and without changing instrument settings, refill the sample cell with pure solvent and record its spectrum superimposed on the sample spectrum.

## 12. Calculation

12.1 Using the solvent spectrum as the baseline, measure the absorbance of the sample at 810  $\text{cm}^{-1}$  (2,4-TDI) and 782  $\text{cm}^{-1}$  (2,6-TDI) and calculate the 810/782- $\text{cm}^{-1}$  absorbance ratio. Read from the appropriate standard curve the isomer weight ratio ( $R$ ), (Fig. 3) or percentage composition (Figs. 1 and 2) that corresponds to the measured absorbance ratio.

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

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

**TABLE 1 Approximate Standard Mixtures for Wide-Range Calibration**

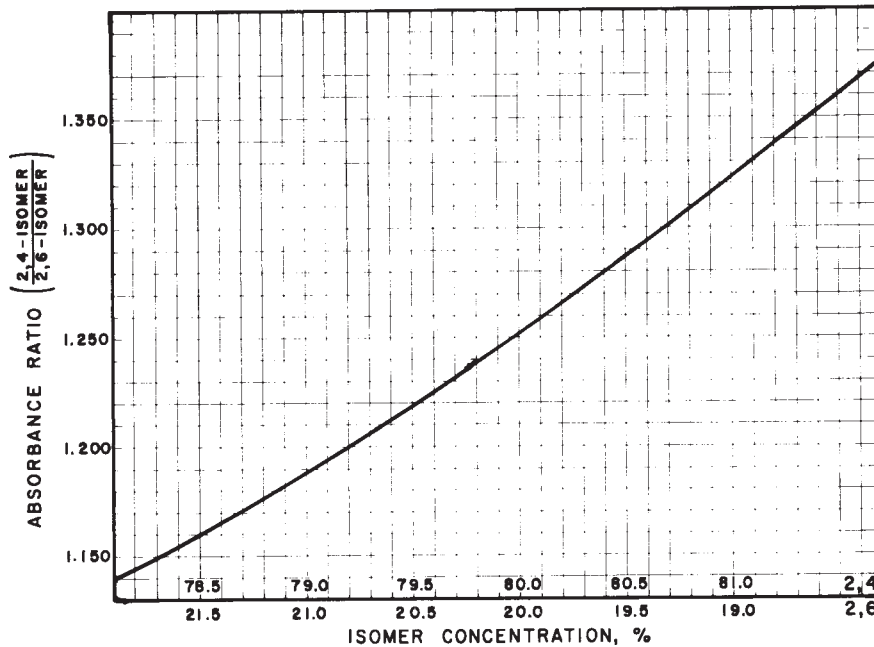
%, 2,4-TDI	Weight Ratio	
	%, 2,6-TDI	2,4-/2,6-TDI
5.0	95.0	0.05
10.0	90.0	0.11
20.0	80.0	0.25
30.0	70.0	0.43
40.0	60.0	0.67
50.0	50.0	1.00
60.0	40.0	1.50
70.0	30.0	2.33
80.0	20.0	4.00
90.0	10.0	9.00
95.0	5.0	19.00

**TABLE 2 Approximate Standard Mixtures for 80/20 TDI Samples**

	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 65/35 TDI Samples**

	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



**FIG. 1 Calibration Curve Toluene Diisocyanate 80:20**

$$\text{Percent 2,4-TDI} = 100 - \text{percent 2,6-TDI} \tag{3}$$

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. Each laboratory obtained ten test results for each material on a given day. Short-range calibrations were used.

13.1.1 **Warning**—The following explanations of *r* and bias *R* (13.1.2-13.1.4) are only intended to present a meaningful way of considering the approximate precision of this test method are under investigation by a task group method. The data in Table 1 should not be rigorously applied to the acceptance or rejection of Subcommittee D20.22. Anyone wishing material, as those data are specific to participate in this work the round robin and may contact Chairman, Subcommittee D20.22, through ASTM Headquarters.

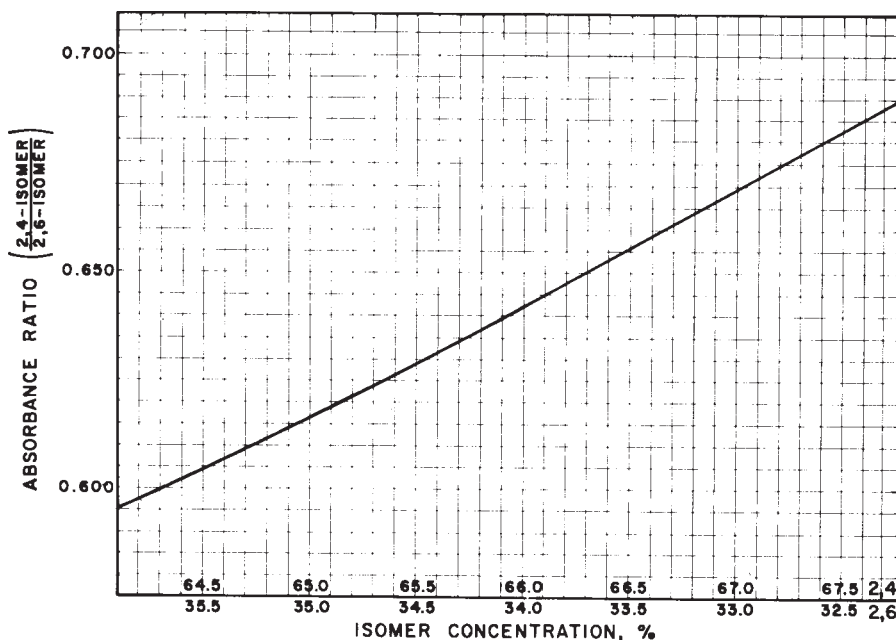


FIG. 2 Calibration Curve Toluene Diisocyanate 65:35

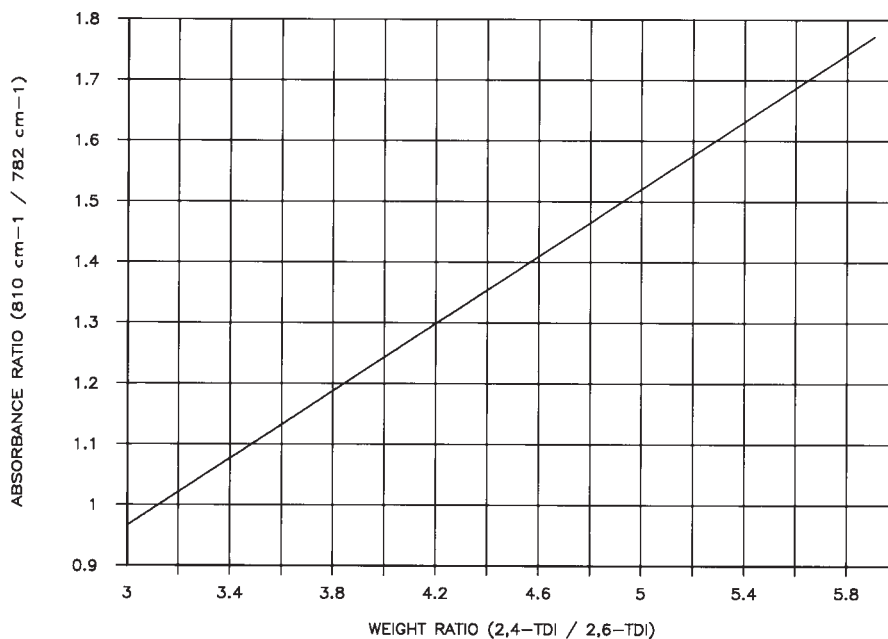


FIG. 3 Calibration Curve Toluene Diisocyanate 80:20

13.2 It has been estimated that duplicate not be representative of other lots, conditions, materials and laboratories. Users of this test method should apply the principles outlined in Practice E 180 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*—(Comparing two results for the same material, obtained by the same operator using the same equipment on the same day). The two results should be considered suspect judged not equivalent if they differ by more than  $\pm \theta$  the *r* value for that material.

13.1.3 *Reproducibility, R*—(Comparing two results for the same material, obtained by different operators using different equipment in different laboratories on different days). The two results should be judged not equivalent if they differ by more than the *R* value for that material.

13.1.4 Any judgment per 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 should be considered suspect if they differ from one another by more than  $\pm 0.34$  % isomer (short-range calibration).

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

Sample	Average	$S_r^A$	$S_R^B$	$C_r^C$	$R^D$	$n^E$
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

<sup>A</sup> $S_r$  = within-laboratory standard deviation of the replicates.  
<sup>B</sup> $S_R$  = between-laboratory standard deviation of the average.  
<sup>C</sup> $C_r$  = within-laboratory repeatability limit =  $2.8 \cdot S_r$ .  
<sup>D</sup> $R$  = between-laboratory reproducibility limit =  $2.8 \cdot S_R$ .  
<sup>E</sup> $n$  = number of laboratories contributing valid data for this material.

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

**14. Calibration**

- 14.1 Prepare the following series of calibration mixtures using samples of the pure isomers given in Table 4 5.
- 14.2 Using a 0.1-mm sealed liquid absorption cell, record the spectrum of each of the above seven mixtures from 770 to 840  $\text{cm}^{-1}$ .
- 14.3 For each of the calibration samples, measure the absorbance of the 2,6-isomer band at 782  $\text{cm}^{-1}$  (12.80  $\mu\text{m}$ ) from a baseline-drawn tangent to the band shoulders. Draw a calibration curve by plotting absorbance versus concentration of 2,6-isomer.

**15. Procedure**

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

**16. Measurement**

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

**17. Precision and Bias**

- 17.1 The precision and bias of this test method are under investigation by a task group of Subcommittee D20.22. Anyone wishing to participate in this work may contact Chairman, Subcommittee D20.22, through ASTM Headquarters.
- 17.2 It has been estimated that duplicate results by the same operator should be considered suspect if they differ by more than  $\pm 0.15\%$  2,6-TDI (short-range calibration).
- 17.3 It has also been estimated that the results reported by laboratories should be considered suspect if they differ from one another by more than  $\pm 0.25\%$  2,6-TDI (short-range calibration).

**18. Keywords**

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

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**TABLE 4 5 Approximate Standard Mixtures for 2,4-TDI Samples**

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