Designation: ~~D4660 – 18~~ D4660 – 23

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E456 Terminology Relating to Quality and Statistics

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E2935 Practice for Evaluating Equivalence of Two Testing Processes

[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**

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~~Terms used in this standard are defined in accordance with Terminology D883, unless otherwise specified. For terms relating to precision and bias and associated issues, the terms used in this standard are defined in accordance with Terminology E456.

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~~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 are suitable 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).

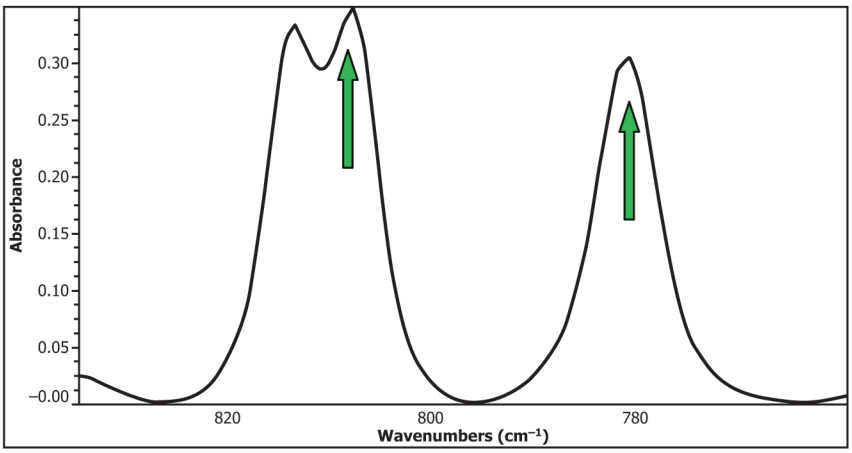

FIG. 1 IR Scan of TDI Showing 2,4-TDI Isomer Doublet at 810 cm^{-1} and ~~2,6 TDI~~ 2,6-TDI Isomer at 782 cm^{-1}

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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 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 are acceptable, 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—**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, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, 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 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).

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).

[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.

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

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

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~~ is plotted against the concentration, expressed in

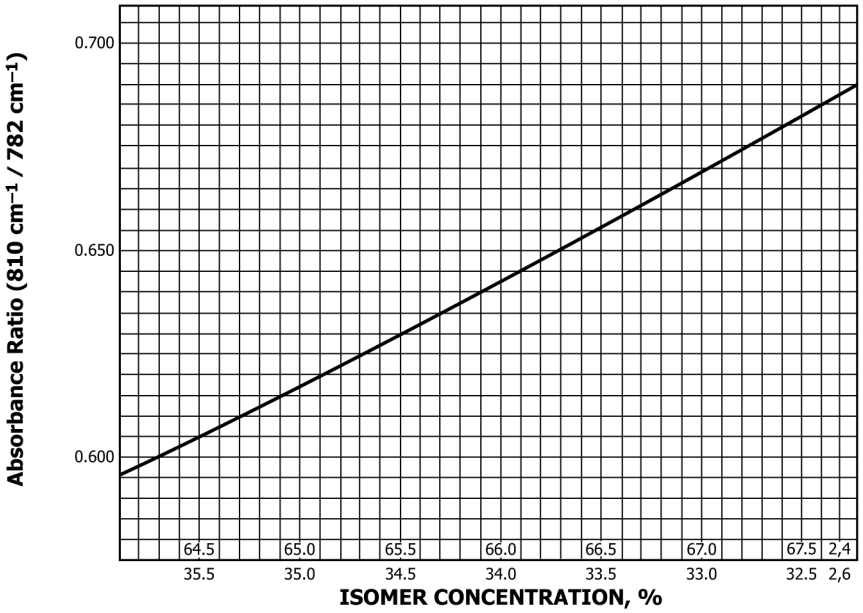

FIG. 2 Calibration Curve Toluene Diisocyanate 65:35 (2,4-TDI : 2,6-TDI)

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.

NOTE 4—All scans of the solvent, standards, and samples ~~should~~ are to be ratioed against an open beam background.

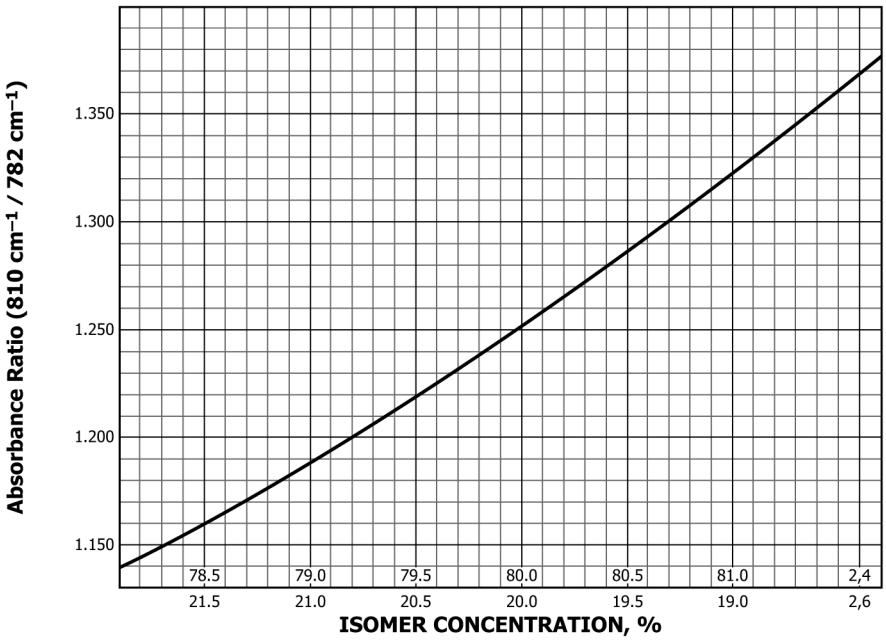

FIG. 3 Calibration Curve Toluene Diisocyanate 80:20 (2,4-TDI : 2,6-TDI)