~~Designation:D4660–06~~ 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 ~~required~~provided to give accurate results over ~~a~~the broad range of isomer concentrations possible.

1.1.1 *Test Method A*~~—Applicable to TDI samples containing 5 to 95% 2,6–isomer (95 to 5% 2,4–isomer).~~ —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% 2,6–isomer (95 to 100% 2,4–isomer).~~ —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.* ~~For specific warning and precautionary statements see Note 3.~~

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

2.2 *ISO Standard:*[3]

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

~~4.1Both 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~~

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} ~~(12.3 and 13.8 µm).~~

~~4.2In Test Method A, the infrared spectrum of a cyclohexane solution of the sample is recorded in the 770 to 840-cm~~region. The

---

[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.

Current edition approved ~~Sept.~~May 1, ~~2006.~~2012. Published ~~September 2006.~~June 2012. Originally approved in 1959. Last previous edition approved in 2006 as ~~D4660-00(2006)$^{\varepsilon1}$.~~D4660 - 06. DOI: ~~10.1520/D4660-06.~~10.1520/D4660-12.

[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] 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.**

absorbance ratio of the 805 cm^{-1} ~~(12 to 13-μm) region. The absorbance ratio of the 810 and 782-cm^{-1} bands is measured and converted to percent toluene-2,6-diisocyanate from a previously established calibration curve.~~ 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-isomer~~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 ~~ratios~~content of toluene diisocyanates.

5.2 The isomer ~~ratio~~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 ~~810~~805-815 cm^{-1}~~.~~

~~6.2~~*(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 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.[4] 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~~*, anhydrous, stored over molecular sieve.*

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:~~

~~2,4–TDI—freezingpoint=22.0°C,n^{20}_{D}=1.56781,*D*4660-06_1~~ ~~(1)~~

~~d^{20}_{4}=1.2186,and2,6–TDI—freezingpoint*D*4660-06_1~~

~~=18.2°C,n^{20}_{D}=1.57111,d^{20}_{4}=1.2270.*D*4660-06_1~~

~~NOTE2—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.~~ —Pure samples of 2,4-TDI and 2,6-TDI are required for calibration. The following criteria can be used to judge purity:

---

[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.

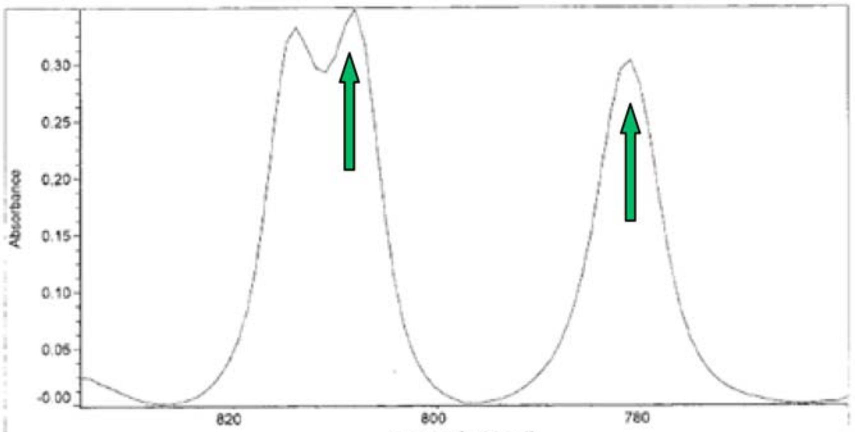

FIG. 1 IR Scan of TDI Showing 2,4-TDI Isomer Doublet at 810 cm^{-1} and 2,6 TDI Isomer at 782 cm^{-1}

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

~~8.1Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. 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.~~

~~8.1.1~~

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—**~~Organic isocyanates are toxic when they are absorbed through the skin, or when the vapors are breathed. Provide adequate ventilation and wear protective gloves and eyeglasses.~~ Many diisocyanates are known or suspected sensitizers. Over-exposure 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

~~10.1Weigh the amounts of pure 2,4- and 2,6-TDI given in~~

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~~into dry, 10-mL, glass-stoppered flasks (Note 3). For convenience, a dry pipet may be used. The total weight of each mixture is to 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.~~ . 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~~3—Dry carefully~~ 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 ~~short-range~~narrow-range calibrations (see Note ~~4~~3) are given in ~~Tables 2 and~~ Table 2 (15-25 % 2,6-TDI) and Table 3 ~~3 (see Figs. 1 and 2).~~ (30-40 % 2,6-TDI).

NOTE ~~4~~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}~~(12 to 13 µm). Refill the sample cell with a solution from~~ . 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 ~~samples~~ the blank and the standards of a given series. Repeat the process for each standard solution from 10.2.

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 ~~80/~~ Narrow-Range Calibration, 15–2~~0~~5 % 2,6-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/~~ Narrow-Range Calibration, 3~~5~~0–40 % 2,6-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

10.4 Using the solvent spectrum as the baseline, measure the absorbance of each standard solution sample at ~~810~~805 cm^{-1} (2,4-TDI) and 782 cm^{-1}(2,6-TDI) and calculate the 8~~1~~05/782-cm^{-1} absorbance ratio. Construct a calibration curve (see Fig. ~~3~~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. ~~1~~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 ~~solution~~cyclohexane and record the blank solvent

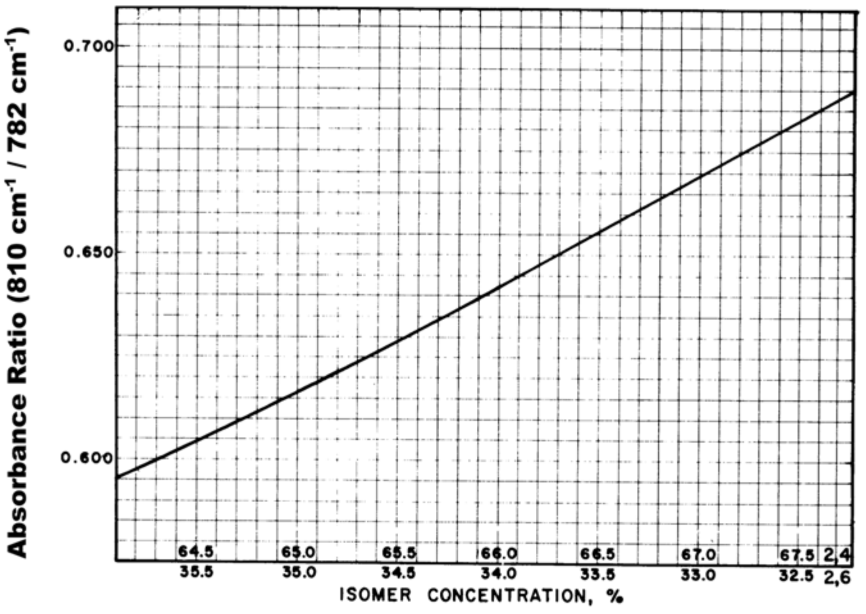

FIG. 2 Calibration Curve Toluene Diisocyanate 65:35 (2,4-TDI : 2,6-TDI)