INTERNATIONAL STANDARD

ISO 15064

Second edition
2010-12-01

Plastics — Aromatic isocyanates for use in the production of polyurethanes — Determination of the isomer ratio in toluenediisocyanate

Plastiques — Isocyanates aromatiques pour utilisation dans la production de polyuréthannes — Détermination du rapport des isomères dans le diisocyanate de toluène

Reference number
ISO 15064:2010(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 15064:2010

COPYRIGHT PROTECTED DOCUMENT

© ISO 2010

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15064 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 15064:2004), of which it constitutes a minor revision making the following changes:

- the introduction has been deleted;
- the titles of Table 2 and Table 3 have been corrected;
- the repeatability limit given in 9.4.1 has been modified;
- in both the repeatability and the reproducibility statements in 10.4.1, “2,4-TDI” has been replaced by “2,6-TDI”;
- the clarity of the key to Figure A.2 has been improved;
- the clarity of the title of Figure A.3 has been improved.

Plastics — Aromatic isocyanates for use in the production of polyurethanes — Determination of the isomer ratio in toluenediisocyanate

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions prior to use.

1 Scope

This International Standard specifies methods for the measurement of toluene-2,6-diisocyanate in mixtures of the 2,4- and 2,6-isomers. Two methods based on infrared spectroscopy are required to give accurate results over a broad range of isomer concentrations. Method A is applicable to TDI samples containing 5 % to 95 % of the 2,6-isomer. Method B is applicable to TDI samples containing 0 % to 5 % of the 2,6-isomer. Both 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 cm^{-1} and 782 cm^{-1} (12,3 µm and 13,8 µm).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
isomer
compound having the same percentage composition and molecular mass as another compound, but differing in chemical structure and properties

3.2
isomer content
amount of an isomer expressed as a mass percentage of the total isomer amount

3.3
TDI
toluenediisocyanate

3.4

polyurethane

polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

4 Sampling

Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods (for example, sampling an open drum with a thief), even when conducted rapidly, can cause contamination of the sample with insoluble ureas; therefore, blanket the sample with a dry inert gas (e.g. nitrogen, argon or dried air) at all times.

WARNING — Organic isocyanates are hazardous when absorbed through the skin or when the vapours are breathed in. Provide adequate ventilation and wear protective gloves and eyeglasses.

5 Principle

5.1 Method A

In method A (5 % to 95 % 2,6-isomer), the infrared spectrum of a cyclohexane solution of the sample is recorded in the 770 cm^{-1} to 840 cm^{-1} (12 µm to 13 µm) region. The absorbance ratio of the 810 cm^{-1} and 782 cm^{-1} bands is measured and converted to % toluene-2,6-diisocyanate from a previously established calibration curve.

5.2 Method B

In method B (0 % to 5 % 2,6-isomer), the absorbance of the 782 cm^{-1} band is measured from an infrared spectrum of an undiluted sample and then converted to % 2,6-isomer from a previously established calibration curve.

6 Reagents

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that the reagents shall conform to the specifications of ISO 6353-2. Other grades may be used, provided that it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.1 Cyclohexane, distilled and stored over silica gel to remove traces of moisture.

6.2 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:

for 2,4-TDI: freezing point = 22,0 °C; n_D^{20} = 1,567 81; ρ_4^{20} = 1,218 6;

for 2,6-TDI: freezing point = 18,2 °C; n_D^{20} = 1,571 11; ρ_4^{20} = 1,227 0.

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

7 Apparatus

7.1 Spectrophotometer: any single- or double-beam recording infrared spectrophotometer, or FTIR spectrophotometer, accurate to 0,2 % transmission and capable of resolving the two peaks of the 2,4-isomer doublet at 810 cm^{-1}.

7.2 Sealed sodium chloride (NaCl) liquid absorption cells, with 0,2 mm (method A) and 0,1 mm (method B) path lengths. The actual path lengths of the cells shall be known to ±0,002 mm.

7.3 Glassware: 25 ml glass-stoppered volumetric flasks, 0,80 ml pipette and an all-glass syringe conforming to ISO 648 or ISO 4787.

7.4 Laboratory balance, capable of weighing to ±0,1 mg.

8 Test conditions

Since isocyanates react with moisture, keep laboratory humidity low, preferably under 50 % relative humidity. Thoroughly dry all laboratory ware. Store cells (7.2) in a dessicator and use thin rubber or plastic gloves while handling.

9 Method A — Samples containing 5 % to 95 % of 2,6-TDI

9.1 Calibration

9.1.1 Weigh the amounts of pure 2,4- and 2,6-TDI given in Table 1, 2 or 3 as appropriate for the calibration range desired. Calibration over a narrow range gives more accurate results than a wide-range calibration.

9.1.2 Prepare standard solutions and calibration curves as follows:

9.1.2.1 Using a pipette, transfer 0,80 ml (0,98 g) of each standard isomer mixture into dry, 25 ml glass-stoppered volumetric flasks (see 7.3). Dilute each to volume with cyclohexane (6.1) and mix thoroughly.

9.1.2.2 Fill two 0,2 mm sealed, liquid absorption cells (one for a single-beam instrument) with cyclohexane and record the spectrum from 770 cm^{-1} to 840 cm^{-1} (12 µm to 13 µm). Refill the sample cell with a solution from 9.1.2.1 and record the spectrum, superimposing it over the previously recorded solvent spectrum. Repeat the process for each solution in 9.1.2.1.

9.1.2.3 Using the solvent spectrum as the baseline, measure the absorbance of each standard solution at 810 cm^{-1} (2,4-TDI) and 782 cm^{-1} (2,6-TDI) and calculate the 810/782 cm^{-1} absorbance ratio. See Figure A.4 in Annex A for an illustrative spectrum. Construct a calibration curve (see Figure A.1) by plotting absorbance ratio (ordinate) versus mass ratio of 2,4- to 2,6-TDI (abscissa).

9.1.2.4 For convenience in narrow-range calibrations, the absorbance ratio may be plotted against the concentration (expressed in mass %) of each isomer (see Figure A.2 and Figure A.3). 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.

Table 1 — Approximate standard mixtures for wide-range 2,4-/2,6-TDI calibration

Mass 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 % 2,4-/20 % 2,6-TDI samples

Mass 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 % 2,4-/35 % 2,6-TDI samples

Mass 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

9.2 Procedure

Using a pipette (see 7.3), transfer 0,80 ml (0,98 g) of sample into a dry, glass-stoppered volumetric flask (see 7.3). Dilute to volume with cyclohexane (6.1) and mix thoroughly. Fill a 0,2 mm cell with the solution and record the spectrum from 770 cm^{-1} to 840 cm^{-1} (12 µm to 13 µm) and, without changing the instrument settings, refill the sample cell with pure solvent and record its spectrum superimposed on the sample spectrum.

9.3 Expression of results

9.3.1 Using the solvent spectrum as the baseline, measure the absorbance of the sample at 810 cm^{-1} (2,4-TDI) and 782 cm^{-1} (2,6-TDI) and calculate the 810/782 cm^{-1} absorbance ratio. Read from the appropriate calibration curve the isomer mass ratio (Figure A.1) or percentage composition (Figures A.2 and A.3) that corresponds to the measured absorbance ratio.

9.3.2 When using the isomer mass ratio, calculate the percentage of each isomer as follows:

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

and

$$\% \text{ 2,4-TDI} = 100 - \% \text{ 2,6-TDI}$$

where R is the isomer mass ratio from Figure A.1.

9.3.3 Use of Figure A.2 or A.3 gives mass % of 2,4-TDI directly from the calibration curve. The 2,6-TDI content is calculated as follows:

$$\% \text{ 2,6-TDI by mass} = 100 - \% \text{ 2,4-TDI}$$

9.3.4 Record the results to one decimal place.

9.4 Precision and bias

9.4.1 Precision

Use the following criteria to judge the acceptability of results. Values were obtained in a round robin involving two samples (80:20 and 65:35 TDI) tested by eight laboratories. Each laboratory obtained ten test results for each material on a given day.

Repeatability: Duplicate results obtained by the same analyst using the same equipment on the same day shall only be considered suspect if they differ by more than ±0,23 % of isomer (narrow-range calibration).

Reproducibility (multilaboratory): Results, each the mean of duplicates, obtained on identical material in separate laboratories shall only be considered different if they differ by more than ±0,39 % of isomer (narrow-range calibration).

9.4.2 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. The bias for this test method has not been determined.

9.5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary to identify the product analysed (such as manufacturer, product type, lot or notebook numbers, date of manufacture, as required);

c) the results obtained, expressed as % isomer to the nearest 0,1 %;

d) the date of the analysis;

e) any incident or detail not stipulated in this International Standard which might have influenced the result.

10 Method B — Samples containing 0 % to 5 % of 2,6-TDI

10.1 Calibration

10.1.1 Using pure isomers, prepare the series of calibration mixtures given in Table 4.

Table 4 — Approximate standard mixtures for 2,4-TDI samples

Mass of 2,4-TDI g	Mass of 2,6-TDI g	2,6-TDI %
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

10.1.2 Using a 0,1 mm sealed liquid absorption cell (see 7.2), record the spectrum of each of the above seven mixtures from 770 cm^{-1} to 840 cm^{-1}.

10.1.3 For each of the calibration samples, measure the absorbance of the 2,6-isomer band at 782 cm^{-1} from a baseline-drawn tangent to the band shoulders. Draw a calibration curve by plotting absorbance versus concentration of the 2,6-isomer.

10.2 Procedure

10.2.1 Fill a 0,1 mm cell (see 7.2) with the sample and obtain the spectrum from 770 cm^{-1} to 840 cm^{-1}.

10.2.2 Measure the absorbance of the 2,6-isomer band at 782 cm^{-1} and read the % 2,6-isomer content from the calibration curve.

10.3 Expression of results

10.3.1 The 2,6-isomer content, expressed as mass % 2,6-TDI, is read directly from the calibration curve and reported to the nearest 0,1 % 2,6-TDI.

10.3.2 The 2,4-TDI isomer content can be calculated as follows:

% 2,4-TDI by mass = 100 − % 2,6-TDI (from 10.3.1 above)

10.4 Precision and bias

10.4.1 Precision

Use the following criteria to judge the acceptability of results:

Repeatability: Duplicate results obtained by the same analyst using the same equipment on the same day shall only be considered suspect if they differ by more than ±0,15 % 2,6-TDI (narrow-range calibration).

Reproducibility (multilaboratory): Results, each the mean of duplicates, obtained on identical material in separate laboratories shall only be considered different if they differ by more than ±0,25 % 2,6-TDI (narrow-range calibration).

10.4.2 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. The bias for this test method has not been determined.

10.5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary to identify the product analysed (such as manufacturer, product type, lot or notebook numbers, date of manufacture, as required);

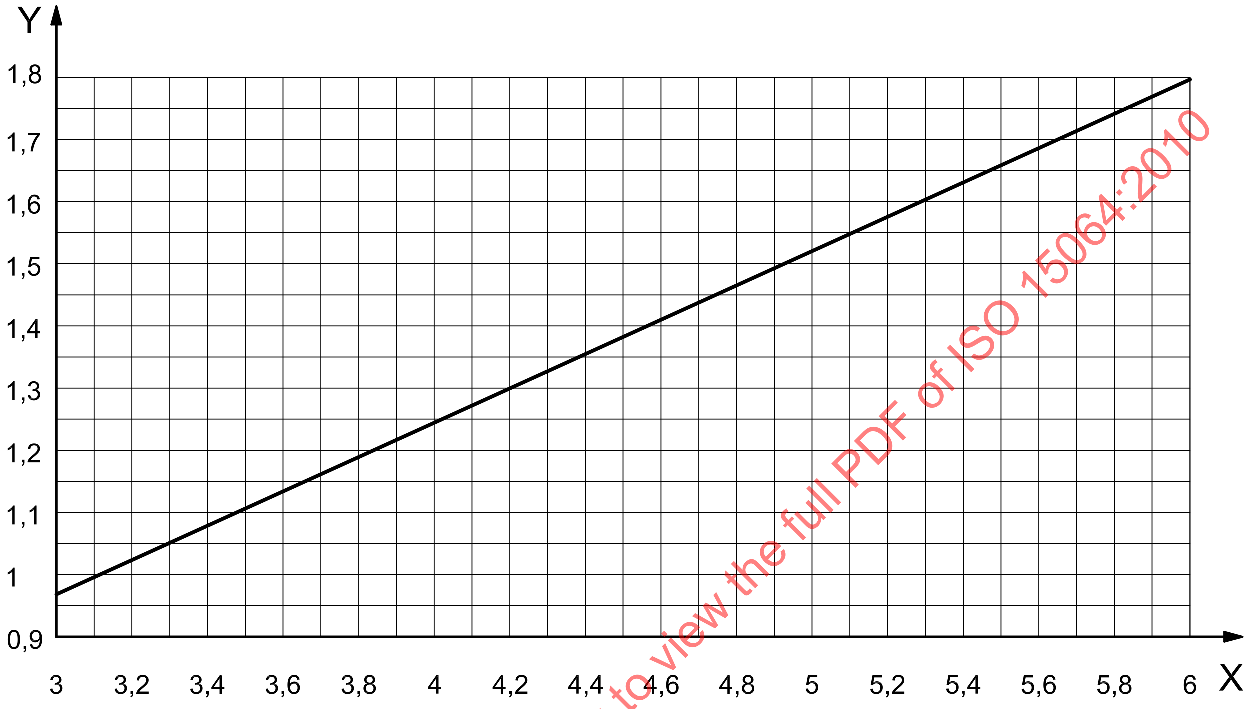
c) the results obtained, expressed as % isomer to the nearest 0,1 %;

d) the date of the analysis;

e) any incident or detail not stipulated in this International Standard which might have influenced the result.

Annex A
(normative)

Calibration curves



Key

X mass ratio (2,4-TDI/2,6-TDI)

Y absorbance ratio (810 cm^{-1}/782 cm^{-1})

Figure A.1 — Calibration curve for 80:20 toluenediisocyanate (mass ratio as abscissa)