TECHNICAL REPORT

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Plastics — Basic materials for polyurethanes — Determination of the amounts of 2,4- and 2,6-isomers in toluenediisocyanate by infrared spectroscopy

Plastiques — Matières de base pour polyuréthannes — Détermination des teneurs en isomères 2,4 et 2,6 du toluylène diisocyanate par spectroscopie infrarouge

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Foreword

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ISO/TR 9372, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 61, *Plastics*, Sub-Committee SC 12, *Thermosetting materials*.

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Plastics — Basic materials for polyurethanes — Determination of the amounts of 2,4- and 2,6-isomers in toluenediisocyanate by infrared spectroscopy

WARNING — SAFETY PRECAUTIONS

Handle isocyanates with care, and limit inhalation as much as possible. The operator should wear safety glasses and disposable gloves. The workplace should be well ventilated.

1 Scope

This Technical Report describes the determination of toluene-2,4-diisocyanate (2,4-isomer) and toluene-2,6-diisocyanate (2,6-isomer) in toluenediisocyanate.

This method is applicable to mixtures containing 5 % to 95 % of the 2,4-isomer.

NOTES

1 The method does not take into account the presence of other isomers. Purified toluenediisocyanates may contain trace amounts of the 2,5-isomer. This isomer interferes slightly in the determination of the 2,4-isomer at 810 cm^{-1}. For example, 1 % of the 2,5-isomer exhibits approximately the same absorbance as 0,5 % of 2,4-isomer at 810 cm^{-1}.

2 This note does not concern the English text.

2 Principle

Preparation of a cyclohexane solution of the sample to be analysed.

Measurement of the absorbance for the 810 cm^{-1} and 782 cm^{-1} bands which are characteristic of the 1,2,4- and 1,2,6-positions on the aromatic ring.

Calculation of the absorbance ratio (5.3).

Conversion of the absorbance ratio into a ratio of the percentages by mass of the 2,4- and 2,6-isomers (5.1.2). For this, a calibration is carried out using standard solutions. The calibration is checked before each analysis series by means of a reference solution.

3 Reagents

3.1 Cyclohexane, spectroscopy grade.

3.2 Toluene-2,4-diisocyanate, to the following specifications (see note 3):

Crystallization temperature (°C)	21,95
Refractive index (at 20 °C)	1,567 8
Density at 23 °C (kg/m^3)	1 218,6

3.3 Toluene-2,6-diisocyanate, to the following specifications (see note 3):

Crystallization temperature (°C)	18,15
Refractive index (at 20 °C)	1,571 1
Density at 23 °C (kg/m^3)	1 227,0

NOTE 3 In the absence of a pure toluene-2,6-diisocyanate (or toluene-2,4-diisocyanate) sample, a sample as pure as possible, with a known concentration of toluene-2,6-diisocyanate (or toluene-2,4-diisocyanate), and exhibiting no interfering impurity at the measurement wavelengths, should be selected as reference toluene-2,6-diisocyanate (or toluene-2,4-diisocyanate).

3.4 Reference sample (see note 4).

Commercial toluenediisocyanate containing $X \pm 1,5$ % (*m/m*) of the 2,4-isomer. The concentration of the 2,4-isomer in this reference sample shall have been measured 10 times by means of the method described in this Technical Report just after calibration of the spectrometer. (X is the assumed concentration of the 2,4-isomer in the sample) of toluene-diisocyanate to be analysed. This value of X must be known or determined by preliminary tests.)

NOTE 4 To use the same reference sample as long as possible, it is best to have a relatively large amount of this reference solution divided up and kept under argon atmosphere in low-capacity sealed flasks or ampoules.

4 Apparatus

4.1 Single-beam[1] or double-beam infrared spectrometer, equipped with a recorder, offering sufficient resolution to display the doublet exhibited by toluene-2,4-diisocyanate at 810 cm^{-1} and 814 cm^{-1} (see figure 1) and achieving a precision of 0,2 % in transmission.

4.2 Optical cells for infrared spectrometry, with a path length between 0,19 mm and 0,21 mm, known to within ± 0,002 mm, and having sodium chloride or potassium bromide windows.

4.3 Volumetric flasks, of 25 ml capacity, with stopper.

4.4 Conical flasks, of 10 ml capacity, with stopper.

4.5 Syringes, of 1 ml capacity.

4.6 Syringes, of 5 ml capacity.

4.7 Analytical balance, accurate to within 0,1 mg.

5 Calibration

All glassware used shall be completely dry.

5.1 Calibration solutions

5.1.1 Prepare successively seven calibration solutions containing mixtures of the 2,4- (3.2) and 2,6- (3.3) isomers with 2,4-isomer concentrations equal to $X - 1{,}5$; $X - 1$; $X - 0{,}5$; X; $X + 0{,}5$; $X + 1$; $X + 1{,}5$; where X is the assumed value of the concentration to be determined, expressed as a percentage by mass. For this, take the appropriate amounts of isomers by means of syringes (4.6) and weigh out 5 g of the isomer mixture, weighed to the nearest 0,1 mg, into 10 ml conical flasks (4.4).

5.1.2 For each mixture, calculate the ratio (R_n) of the percentages by mass of the isomers in the following manner:

$$R_n = \frac{\text{mass of 2,6-isomer}}{\text{mass of 2,4-isomer}}$$

where n is a number from 1 to 7.

5.1.3 Transfer 0,8 ml of each mixture by means of syringes (4.5) into 25 ml volumetric flasks (4.3), then make up to 25 ml with cyclohexane (3.1) and mix thoroughly.

5.2 Absorbance measurements

5.2.1 Procedure on a double-beam spectrometer:

a) Fill the measurement and reference cells (4.2) with cyclohexane, and record the spectrum from 850 cm^{-1} to 750 cm^{-1}.

b) Empty and dry the measurement cell (4.2); fill the cell with a solution prepared in 5.1.3, leaving the reference cell (4.2) filled with cyclohexane. Record the spectrum from 850 cm^{-1} to 750 cm^{-1}, superimposing it over the previously measured solvent-differential spectrum [5.2.1 a)]. Repeat the operation for each calibration solution (5.1.3).

c) On the spectrum obtained in 5.2.1 b), the doublet for the 2,4-isomer is observed at 810 cm^{-1} and 814 cm^{-1}, and the band for the 2,6-isomer at 782 cm^{-1}. Measure the absorbances $A_{2,4}$ at 810 cm^{-1} and $A_{2,6}$ at 782 cm^{-1} from the solvent-differential spectrum obtained in 5.2.1 a).

5.2.2 Procedure on a single-beam spectrometer:

a) Fill the measurement cell (4.2) with cyclohexane and record the spectrum from 850 cm^{-1} to 750 cm^{-1}.

b) Empty and dry the measurement cell (4.2). Fill the cell with a solution prepared in 5.1.3 and record the spectrum from 850 cm^{-1} to 750 cm^{-1}.

c) Plot the differential spectrum of the calibration solution [5.2.2 b)] versus the spectrum of the solvent [5.2.2 a)]. Repeat the operation for each calibration solution (5.1.3).

d) On the spectrum obtained in 5.2.2 c), the doublet for the 2,4-isomer is observed at 810 cm^{-1} and 814 cm^{-1}, and the band for the 2,6-isomer at 782 cm^{-1}. Measure the absorbances $A_{2,4}$ and $A_{2,6}$ at 810 cm^{-1} and 782 cm^{-1}, respectively.

1) For example, a Fourier Transform infrared (FT-IR) spectrometer.

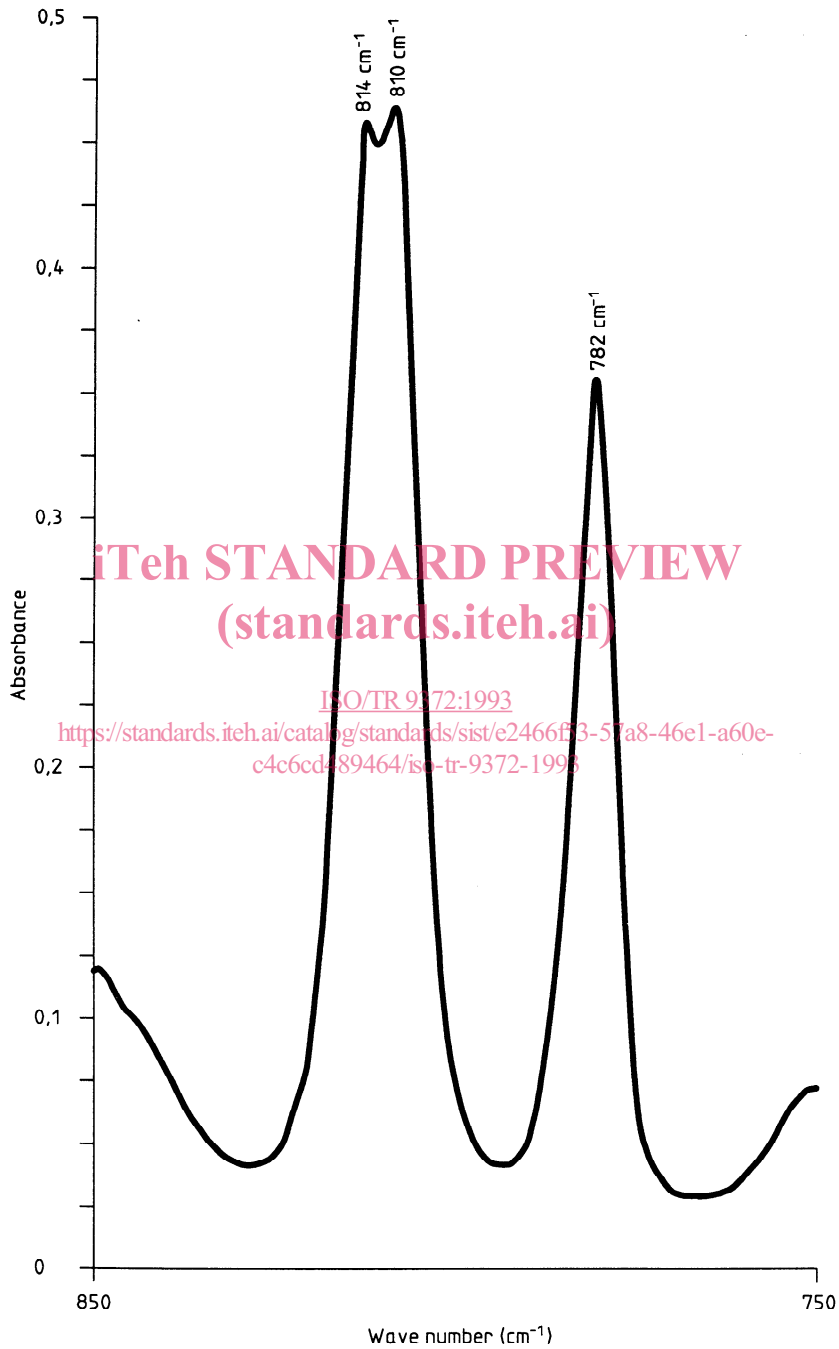

Figure 1

5.3 Absorbance ratio

5.3.1 For each calibration mixture, calculate the ratio (K_n) of the absorbances in the following manner:

$$K_n = \frac{A_{2,6}}{A_{2,4}}$$

where n is a number from 1 to 7.

5.3.2 Draw the calibration curve by plotting the absorbance ratio K_n obtained in 5.3.1 along the ordinate versus the corresponding values of R_n calculated in 5.1.2 along the abscissa.

6 Procedure

6.1 Transfer 0,8 ml of the toluenediisocyanate to be analysed into a 25 ml volumetric flask (4.3), dilute to the mark with cyclohexane (3.1) and mix thoroughly. This is the test solution.

Transfer 0,8 ml of the reference toluenediisocyanate (3.4) into a 25 ml volumetric flask, dilute to the mark with cyclohexane (3.1) and mix thoroughly. This is the reference solution.

6.2 For both solutions prepared in 6.1, record the spectrum from 850 cm^{-1} to 750 cm^{-1} and measure the absorbances $A_{2,4}$ at 810 cm^{-1} and $A_{2,6}$ at 782 cm^{-1}, as described in 5.2.1 or 5.2.2.

6.3 Calculate the ratio of the absorbances for the test solution and the reference solution as described in 5.3.1.

7 Calculation and expression of results

7.1 Plot the absorbance ratio values (as defined in 6.3) on the calibration curve (described in 5.3.2).

7.2 Calculate the ratios for the percentages by mass of the isomers:

R' in the case of the test sample;

R'_0 in the case of the reference sample.

7.3 By means of R' and R'_0, calculate the ratio, R, of the percentage by mass of the isomers in the test sample, taking into account any shift of the calibration curve using the following equation:

$$R = R' + (R_0 - R'_0)$$

where

R_0 is the average value of the ratio of the percentages by mass of the isomers in the case of the reference sample (3.4) determined after calibration and as described in clause 6;

R' and R'_0 are as defined in 7.2.

If $(R_0 - R'_0)$ is at a level less than the method precision (clause 8), no correction is required. In this case, $R = R'$.

7.4 Calculate the 2,4-isomer content, $c_{2,4}$, expressed as a percentage by mass, of the test sample by means of the equation

$$c_{2,4} = \frac{100}{1 + R}$$

Calculate the 2,6-isomer content, $c_{2,6}$, expressed as a percentage by mass, of the test sample by means of the equation

$$c_{2,6} = 100 - c_{2,4}$$

8 Precision

8.1 Repeatability

The 95 % confidence limits for the average value of duplicate measurements are ± 0,3 % (m/m) for a toluenediisocyanate sample containing about 80 % (m/m) of the 2,4-isomer.

8.2 Reproducibility

The 95 % confidence limits for the average value of duplicate measurements are ± 0,6 % (m/m) for a toluenediisocyanate sample containing about 80 % (m/m) of the 2,4-isomer.

9 Test report

The test report shall include the following information:

a) a reference to this Technical Report;

b) all information necessary for the complete identification of the sample;

c) expression of the results;

d) any deviation from the specified procedure and all circumstances which may have affected the results.

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Descriptors: plastics, cellular plastics, polyurethane, chemical analysis, determination of content, isocyanates, infrared spectroscopy.

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