
**Binders for paints and varnishes —
Determination of monomeric
diisocyanates in isocyanate resins**

*Liants pour peintures et vernis — Détermination des diisocyanates
monomères dans les résines isocyanates*



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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 10283 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 10, *Test methods for binders for paints and varnishes*.

This second edition cancels and replaces the first edition (ISO 10283:1997), in which the normative references clause has been updated.

Introduction

It is well-known fact that, due to the production methods used, all the commercial isocyanate resins named in this standard contain a certain amount of volatile monomeric isocyanates. This amount is generally less than 0,5 % relative to the resin as supplied. In view of the regulations relating to the handling of hazardous substances, it has become a matter of special concern that a generally accepted and applicable method of determination should be available. This standard is not intended to present a method suitable for the analytical determination of volatile isocyanates in any form and in any quantity. The standard specifies a method confined to determining the amounts of volatile isocyanates which occur in practice in isocyanate resins, namely about 0,1 % to 0,4 %. A further objective of the standard was to develop a method for determining with adequate accuracy as many as possible of the monomeric isocyanates which occur in isocyanate resins. It detects the principle isocyanates, namely toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), diphenylmethane diisocyanate (MDI) and isophorone diisocyanate (IPDI), and is a method considered by industry, authorities and institutes alike to be the state of the art.

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Binders for paints and varnishes — Determination of monomeric diisocyanates in isocyanate resins

1 Scope

This International Standard specifies a gas-chromatographic method for determining monomeric diisocyanates such as toluene diisocyanate¹⁾, hexamethylene diisocyanate, isophorone diisocyanate²⁾, diphenylmethane diisocyanate³⁾ and other diisocyanates in isocyanate resins as defined in Clause 3 and in solutions prepared from such resins, insofar as these are used in the formulation of paints and similar coating materials.

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 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

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

3.1

isocyanate resin

synthetic resin, with or without solvent, based on aromatic, aliphatic or cycloaliphatic isocyanates containing isocyanate (NCO) groups

NOTE For the purposes of this International Standard, such isocyanate resins comprise:

- those which are manufactured from any diisocyanate, in particular toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or diphenylmethane diisocyanate (MDI), and which contain urethane and/or biuret and/or isocyanurate groups;
- those which are prepared from mixtures of the isocyanate resins given above.

1) The term “toluene diisocyanate” is used here and in the following text for 4-methyl-1,3-phenylene diisocyanate (2,4-toluene diisocyanate) and 2-methyl-1,3-phenylene diisocyanate (2,6-toluene diisocyanate).

2) The term “isophorone diisocyanate” is used here and in the following text for 2-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate. The stereoisomers are identified at the appropriate points in the text by (I) and (II).

3) The term “diphenylmethane diisocyanate” is used here and in the following text for 4,4-diisocyanatodiphenylmethane, 2,4-diisocyanatodiphenylmethane and 2,2-diisocyanatodiphenylmethane.

4 Principle

The content of monomeric diisocyanate in isocyanate resins is determined by gas chromatography, using tetradecane or, in the case of diisocyanates of low volatility, anthracene as the internal standard.

5 Reagents

During the analysis, use only reagents of recognized analytical grade.

5.1 Ethyl acetate, anhydrous (dried with 0,5 nm molecular sieve) and ethanol-free (ethanol content < 200 ppm).

5.2 Tetradecane or anthracene.

5.3 Toluene diisocyanate (isomeric mixture).

5.4 Hexamethylene diisocyanate.

5.5 Isophorone diisocyanate (isomeric mixture).

5.6 Diphenylmethane diisocyanate.

5.7 Solution of internal standard.

Weigh approximately 1,4 g of tetradecane or anthracene to the nearest 0,1 mg into a 1 000 ml volumetric flask and make up to the mark with ethyl acetate (5.1).

5.8 Reference solution of monomeric diisocyanate.

Weigh approximately 1,4 g of the relevant monomeric diisocyanate to the nearest 0,1 mg into a 1 000 ml volumetric flask and make up to the mark with ethyl acetate (5.1).

Protect the monomeric diisocyanate reference solutions from air and moisture.

NOTE If stored properly, they will remain stable for about two weeks.

5.9 Calibration solution.

Pipette 10 ml of the internal-standard solution (5.7) and 10 ml of the reference solution (5.8) into a sample bottle or conical flask (see 6.2). Using the 25 ml measuring cylinder, add 15 ml of ethyl acetate and mix.

NOTE Instead of preparing a calibration solution, the internal standard and the monomeric diisocyanate can be weighed directly with 40 ml of ethyl acetate into a 50 ml sample bottle fitted with a septum seal (dried free of water). Steps 5.7 and 5.8 are then no longer necessary.

6 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

6.1 Analytical balance.

6.2 Conical flask, of capacity 50 ml, fitted with a ground-glass stopper, or **sample bottle** of capacity 50 ml, fitted with a septum seal.

6.3 One-mark pipette, of capacity 10 ml.

6.4 Measuring cylinder, of capacity 25 ml.

6.5 One-mark volumetric flask, of capacity 1 000 ml.

6.6 Sample-injection syringe, of capacity 2 μ l or 10 μ l.

6.7 Gas-chromatography, with an exchangeable glass sample-evaporation tube, a flame ionization detector and an integrator.

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528. Store the sample in a cool, dry place and in the dark.

Under unfavourable storage conditions, reactions take place, particularly at elevated temperatures, which alter the monomeric isocyanate content of some isocyanate resins. In order to prevent these reactions as far as possible, samples must be stored in cool, dark conditions. However, it is then necessary to readjust the samples to room temperature before opening the containers so that ingressing atmospheric moisture cannot condense and thus change the monomeric isocyanate content. If there is any doubt, discard reference materials or samples which have been stored for prolonged periods.

8 Procedure

8.1 Operating conditions

The test conditions given in the examples are recommended as being suitable. Columns and test/operating conditions giving equivalent or superior performance may also be used.

The temperatures specified for the injector and the column depend on the thermal stability of the polyisocyanate resin under test. The monomeric diisocyanate content of many polyisocyanate resins, e.g. those with a biuret structure, may be altered at elevated temperatures. In such cases, the temperatures specified in the examples shall be used. The glass sample-evaporation tube shall be cleaned or changed as necessary, but at least at the start of each day's work.

8.1.1 Example: hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI)

Column: quartz capillary, length 15 m, internal diameter 0,32 mm

Column packing material: phenyl methyl silicone resin (OV[®] 1701), film thickness 0,25 µm

Temperatures: injector 125 °C
column 130 °C
detector 250 °C

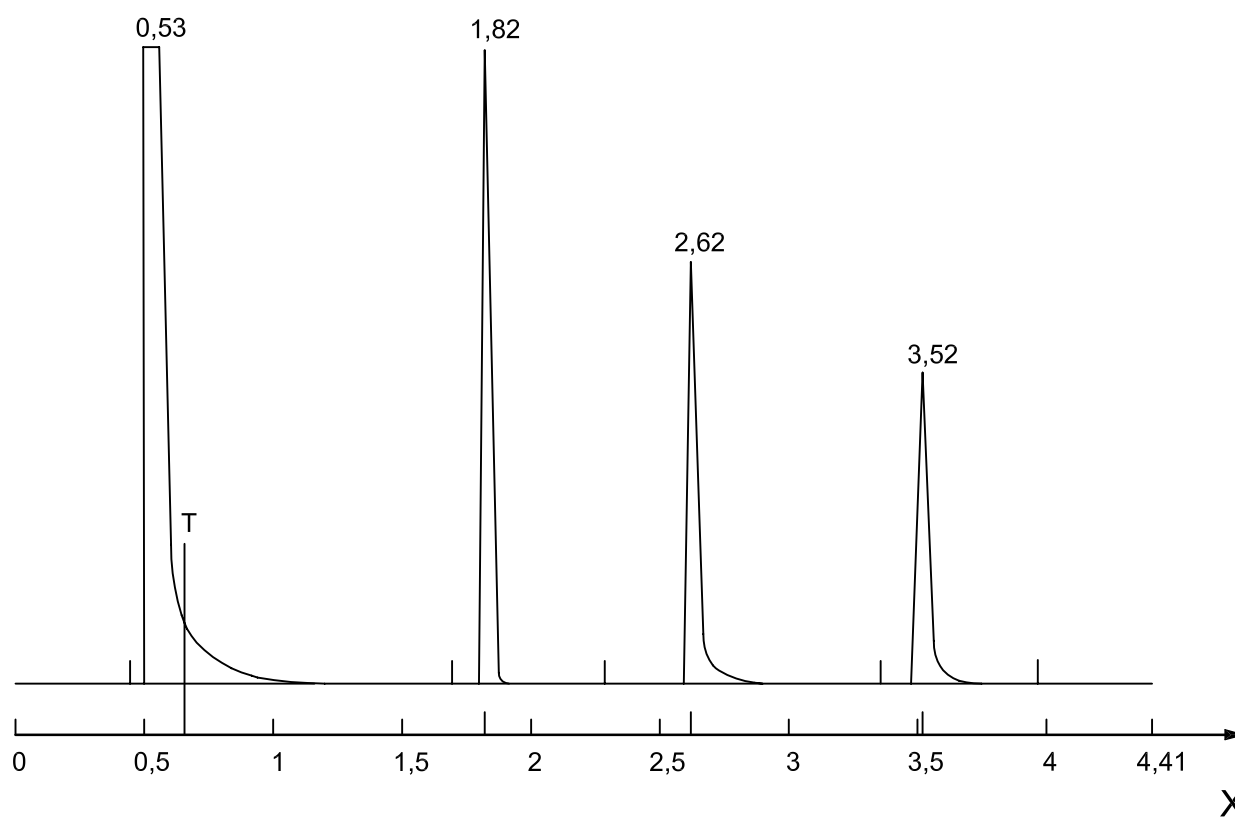
Carrier gas: helium
column head pressure approx. 100 kPa
column flow rate approx. 4 ml/min
split approx. 60 ml/min

Detector-flame gases: hydrogen approx. 35 ml/min
air approx. 400 ml/min

Flushing: approx. 25 ml nitrogen/min

Injection volume: approx. 1 µl

Retention times: tetradecane (internal standard) 1,82 min
TDI (2,4-) 2,62 min
HDI 3,52 min



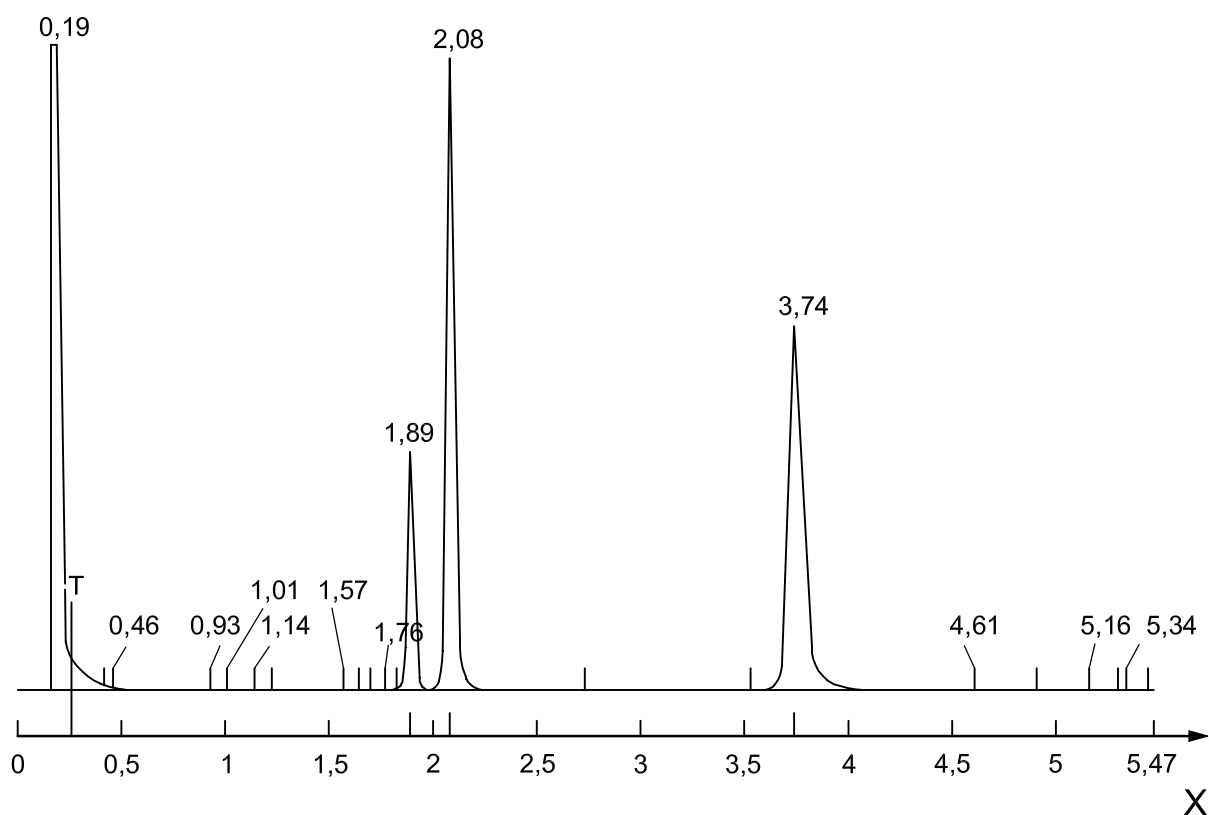
Key

X time (min)

Figure 1 — Gas chromatogram for hexamethylene diisocyanate and toluene diisocyanate

8.1.2 Example: isophorone diisocyanate (IPDI) (first example)

Column:	quartz capillary, length 15 m, internal diameter 0,32 mm	
Column packing material:	phenyl methyl silicone resin (OV [®] 1701), film thickness 0,25 µm	
Temperatures:	injector	160 °C
	column	140 °C
	detector	250 °C
Carrier gas:	helium	
	column head pressure	approx. 120 kPa
	column flow rate	approx. 6 ml/min
	split	approx. 60 ml/min
Detector-flame gases:	hydrogen	approx. 35 ml/min
	air	approx. 400 ml/min
Flushing:	approx. 25 ml nitrogen/min	
Injection volume:	approx. 1 µl	
Retention times:	IPDI I	1,89 min
	IPDI II	2,08 min
	anthracene (internal standard)	3,74 min



Key

X time (min)

Figure 2 — Gas chromatogram for isophorone diisocyanate (first example)

8.1.3 Example: isophorone diisocyanate (IPDI) (second example)

Column: quartz capillary, length 30 m, internal diameter 0,25 mm

Column packing material: SE 54 FS

Temperatures: injector 200 °C
 column 140 °C 0 min, 3 °C/min at 200 °C
 detector 250 °C

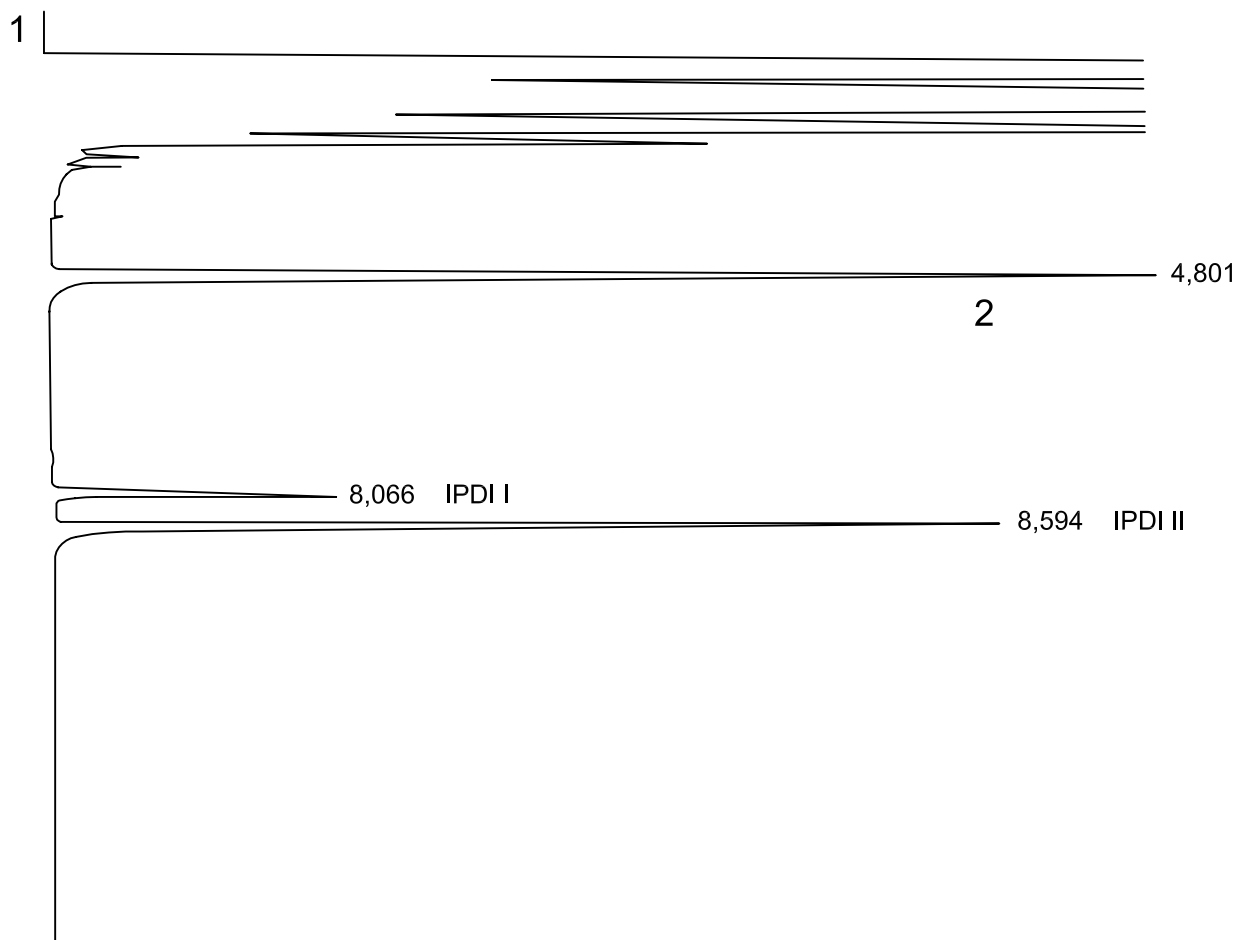
Carrier gas: helium
 column head pressure approx. 150 kPa
 split 1:200

Detector-flame gases: hydrogen approx. 35 ml/min
 air approx. 300 ml/min

Injection volume: 0,8 µl

Running time: approx. 10 min

Retention times: tetradecane (internal standard) 4,801 min
 IPDI I 8,066 min
 IPDI II 8,594 min

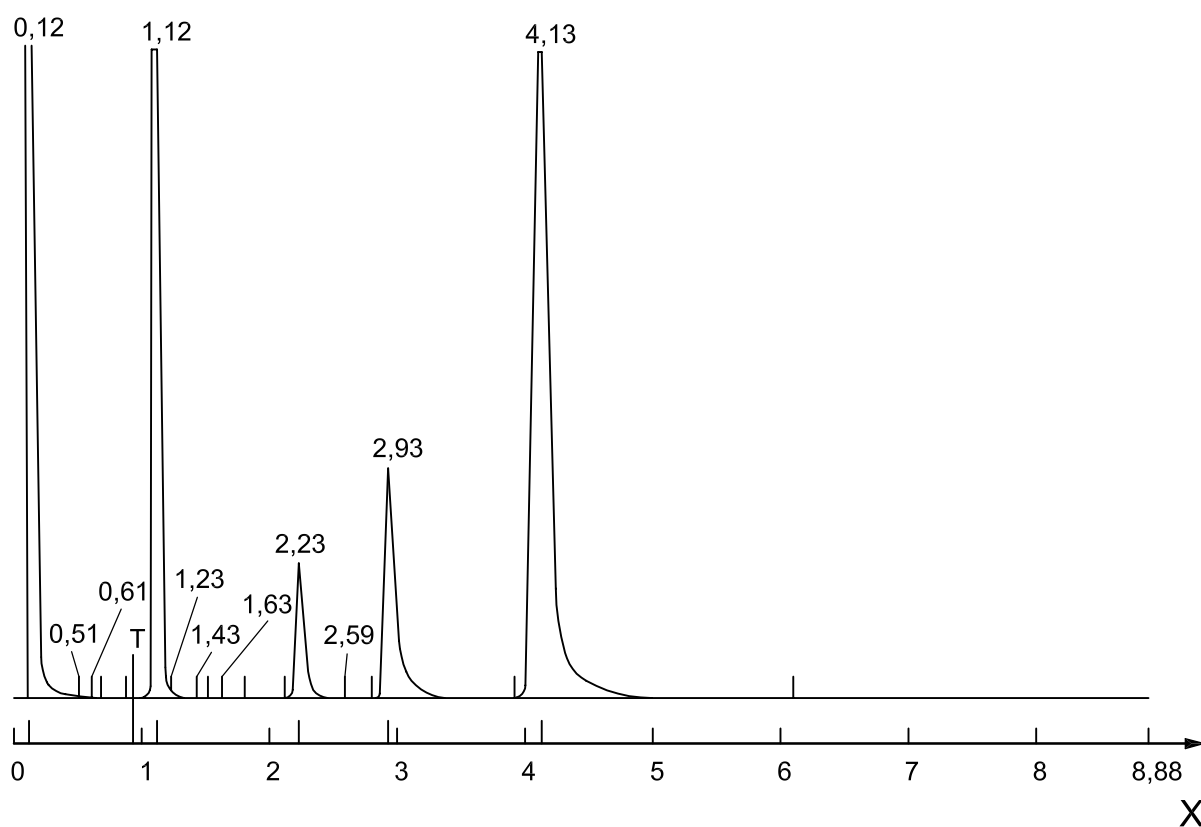


Key
 1 start
 2 internal standard

Figure 3 — Gas chromatogram for isophorone diisocyanate (second example)

8.1.4 Example: diphenylmethane diisocyanate (MDI)

Column:	quartz capillary, length 15 m, internal diameter 0,32 mm	
Column packing material:	phenyl methyl silicone resin (OV [®] 1701), film thickness 0,25 µm	
Temperatures:	injector	200 °C
	column	160 °C
	detector	250 °C
Carrier gas:	helium or hydrogen	
	column head pressure	approx. 200 kPa
	column flow rate	approx. 12 ml/min
	split	approx. 60 ml/min
Detector-flame gases:	hydrogen	approx. 35 ml/min
	air	approx. 400 ml/min
Flushing:	approx. 25 ml nitrogen/min	
Injection volume:	approx. 1 µl	
Retention times:	anthracene (internal standard)	1,12 min
	MDI (2,2'-)	2,23 min
	MDI (2,4'-)	2,93 min
	MDI (4,4'-)	4,13 min



Key

X time (min)

Figure 4 — Gas chromatogram for diphenylmethane diisocyanate

8.2 Column conditioning

Before each analysis, condition the column by repeated injection of the calibration solution until the ratio of the peak area for the monomeric diisocyanate to be determined to the peak area for the internal standard is constant.

In conditioning the separation column, the calibration solution shall be injected frequently until constancy of the peak area ratio is achieved. However, round-robin tests have shown that the approximate constancy achieved after the fifth injection of the calibration solution is adequate.

Select the carrier gas flow rate, the packing material and length of the column so that the duration of a run does not exceed 10 min.

8.3 Gas-chromatographic determination

To determine the calibration factor, inject 1 µl of the calibration solution at least twice under the conditions specified in 8.1.

The mass of the test sample depends on the expected diisocyanate content (see Table 1).

Table 1

Expected diisocyanate content % (by mass)	Mass of test sample g
≤ 0,5	2
> 0,5 but ≤ 1	1
> 1 but ≤ 2	0,5
> 2 but ≤ 4	0,2
> 4	0,1

Weigh the test sample to the nearest 0,1 mg (mass m_0) into a conical flask (6.2). Using the pipette (6.3), add 10 ml of the internal-standard solution (5.7)⁴. Add about 25 ml of ethyl acetate, close the conical flask and shake well to dissolve the test sample.

NOTE The test sample can also be weighed to the nearest 0,1 mg into a 50 ml sample bottle fitted with a septum seal. Add about (15 ± 0,1) mg of the internal standard to the sample bottle. Dissolve the sample in 40 ml of ethyl acetate.

Examine 1 µl of this solution (test solution) by gas chromatography.

The following sequence shall be observed for each determination:

- inject calibration solution at least twice;
- inject test solution twice.

4) Approx. 15 mg of the internal standard weighed to an accuracy of ± 0,1 mg can be used instead of the standard solution.

9 Expression of results

9.1 Determination of calibration factor

From each calibration chromatogram, calculate the calibration factor f , using the following equation:

$$f = \frac{m_{\text{DI}} \times A_{\text{St}}}{m_{\text{St}} \times A_{\text{DI}}}$$

where

m_{St} is the mass of internal standard (tetradecane or anthracene) in the internal-standard solution (5.7);

m_{DI} is the mass of monomeric diisocyanate in the reference solution (5.8);

A_{DI} is the peak area for the monomeric diisocyanate contained in the reference solution;

A_{St} is the peak area for the internal standard.

9.2 Calculation of the monomeric diisocyanate content

Calculate the content of monomeric diisocyanate w_{DI} from the peak areas, using the following equation:

$$w_{\text{DI}} = \frac{m_1 \times A_2 \times f}{m_2 \times A_1}$$

where

m_1 is the mass of internal standard in the test solution;

m_2 is the mass of test sample;

A_2 is the peak area for the monomeric diisocyanate in the test solution;

A_1 is the peak area for the internal standard in the test solution.

Calculate the mean of two determinations, this mean being corrected by the average value of the calibration factor f calculated for each determination.

Detection limit: 0,01 % (by mass) of the monomeric diisocyanate under the conditions specified in 8.1.

10 Precision

[for a content of monomeric diisocyanate of $(0,50 \pm 0,05)$ % (by mass)].

10.1 Repeatability (r)

The value below which the absolute difference between two single test results, each the mean of duplicates, obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method may be expected to lie with a 95 % probability is 0,02 %.

10.2 Reproducibility (*R*)

The value below which the absolute difference between two test results, each the mean of duplicates, obtained on identical material by operators in different laboratories using the standardized test method may be expected to lie with a 95 % probability is 0,05 %.

11 Test report

The test report shall contain at least the following information:

- a) all details necessary to identify the product tested;
- b) a reference to this International Standard (ISO 10283);
- c) the individual values and means of the content of monomeric diisocyanates (as indicated in 9.2);
- d) any deviation from the method specified;
- e) the date of the test.

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