BRITISH STANDARD

BS EN ISO 10283:2007

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

The European Standard EN ISO 10283:2007 has the status of a British Standard

ICS 87.060.20

British Standards

National foreword

This British Standard is the UK implementation of EN ISO 10283:2007. It supersedes BS EN ISO 10283:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee STI/3, Paints, media and related products.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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English Version

Binders for paints and varnishes - Determination of monomeric diisocyanates in isocyanate resins (ISO 10283:2007)

Liants pour peintures et vernis - Détermination des diisocyanates monomères dans les résines isocyanates (ISO 10283:2007)

Bindemittel für Beschichtungsstoffe - Bestimmung von monomeren Diisocyanaten in Isocyanatharzen (ISO 10283:2007)

This European Standard was approved by CEN on 21 August 2007.

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Foreword

This document (EN ISO 10283:2007) has been prepared by Technical Committee ISO/TC 35 "Paints and varnishes" in collaboration with Technical Committee CEN/TC 139 "Paints and varnishes", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2008, and conflicting national standards shall be withdrawn at the latest by March 2008.

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Endorsement notice

The text of ISO 10283:2007 has been approved by CEN as a EN ISO 10283:2007 without any modification.

INTERNATIONAL STANDARD

ISO 10283

Second edition
2007-09-01

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

Reference number
ISO 10283:2007(E)

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Foreword

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

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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 diisocyanate[1)], hexamethylene diisocyanate, isophorone diisocyanate[2)], diphenylmethane diisocyanate[3)] 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 µl or 10 µl.

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

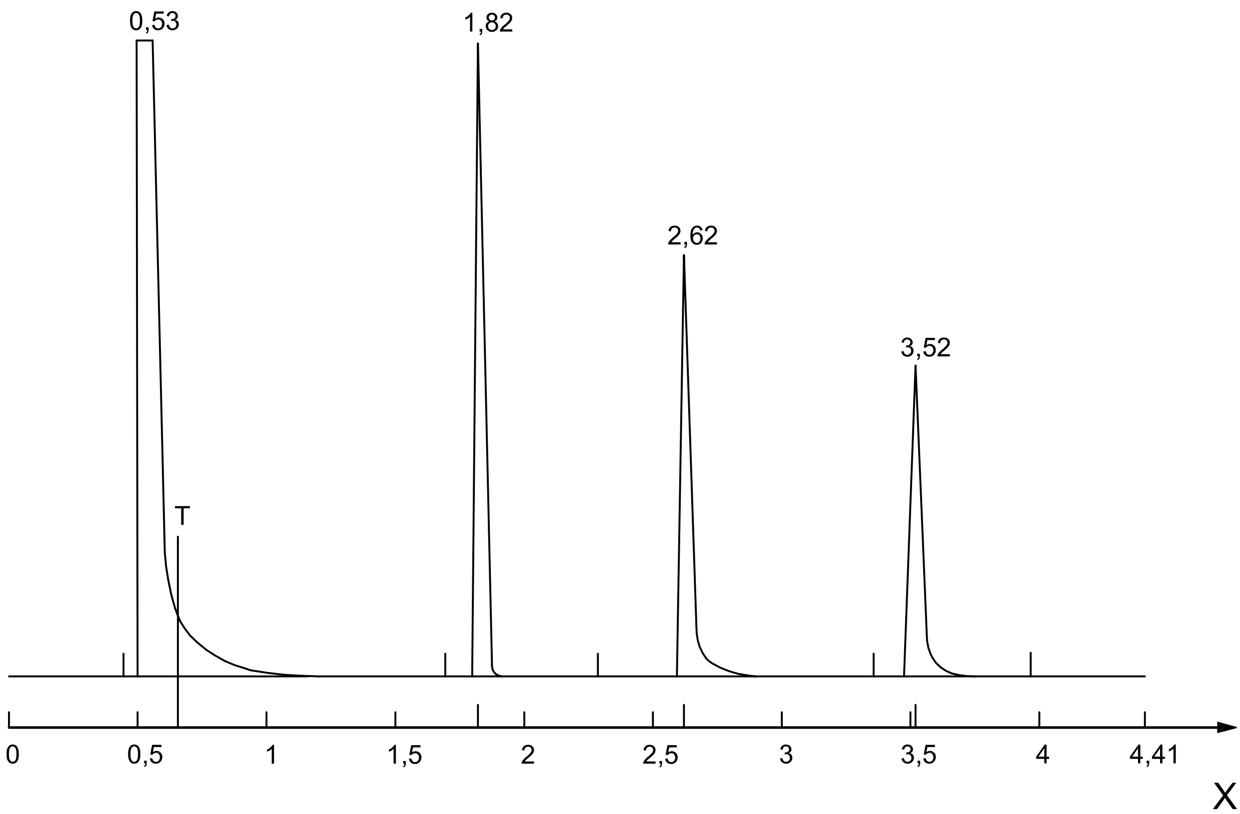
8.1 Operating conditions

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



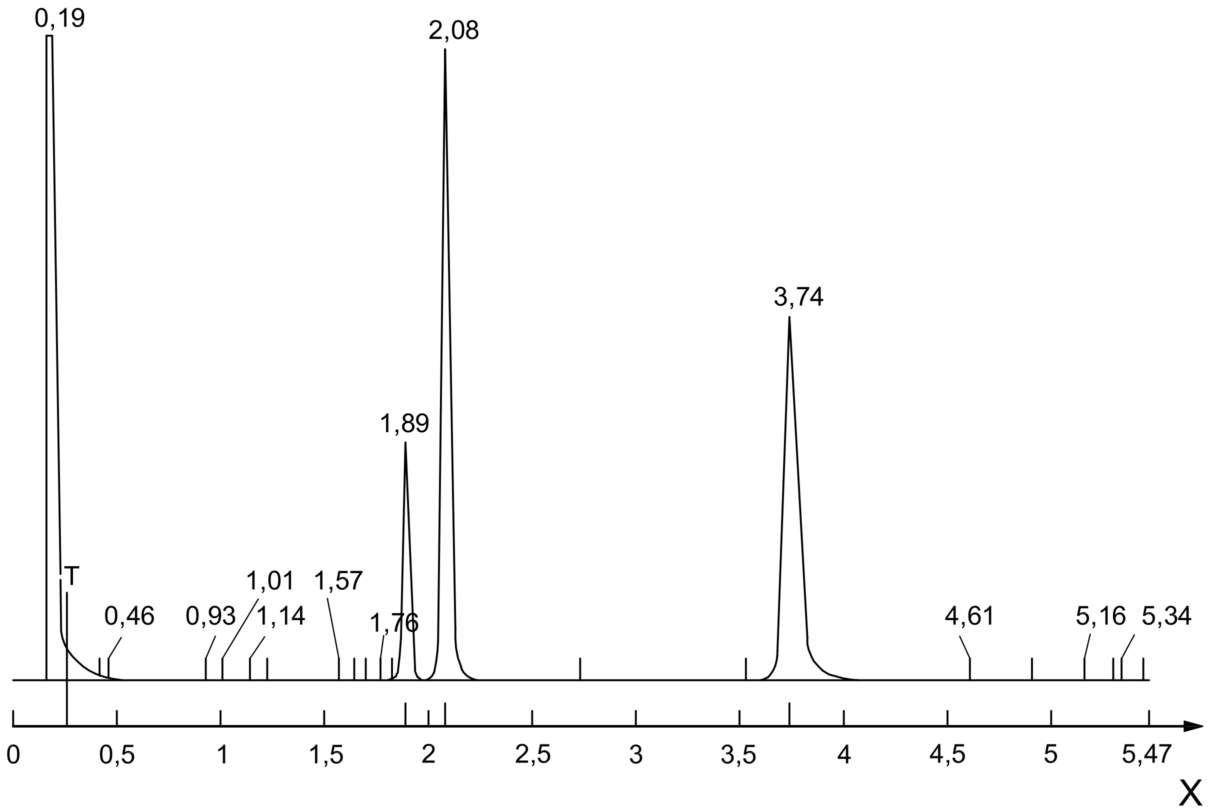
Key

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



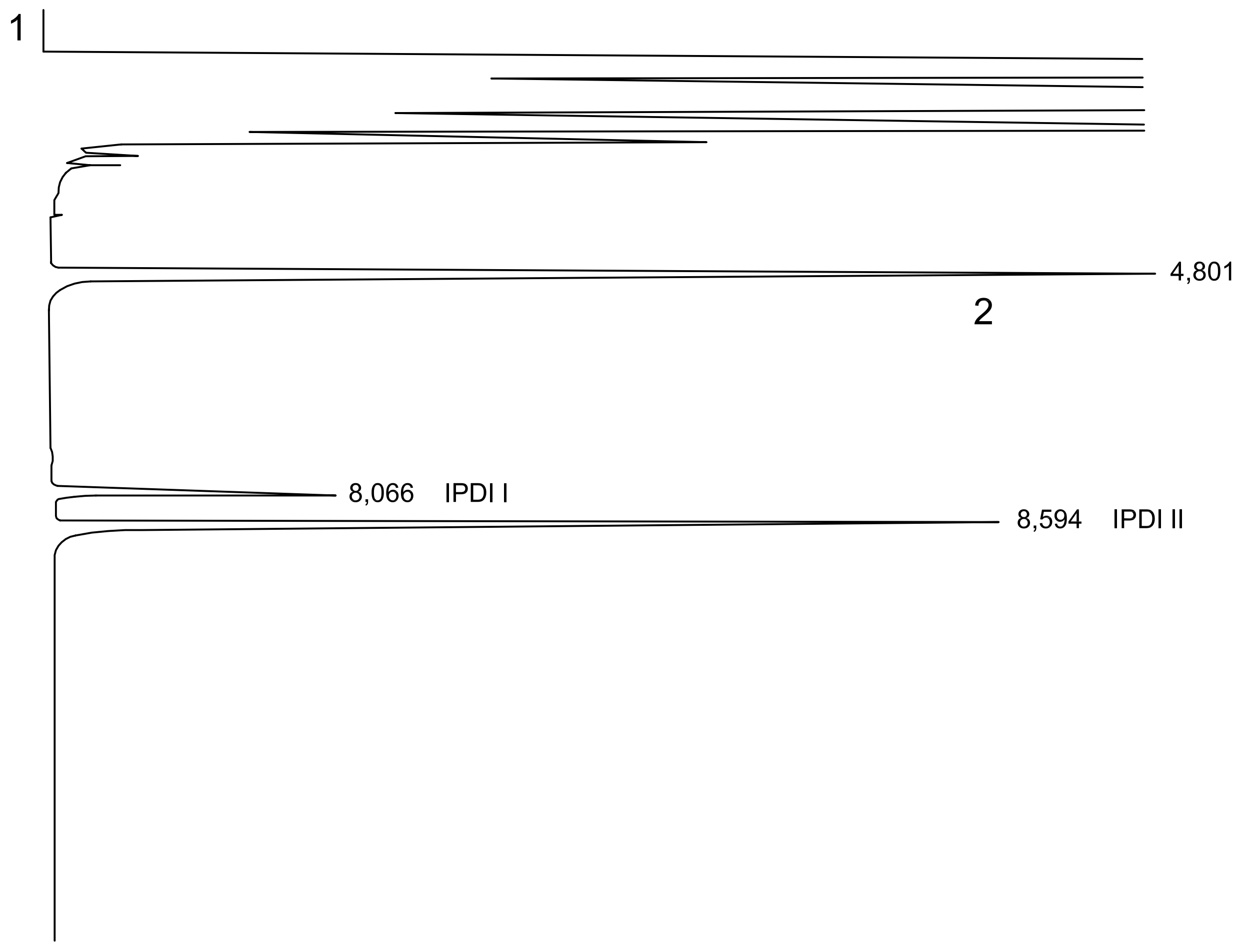
Key

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

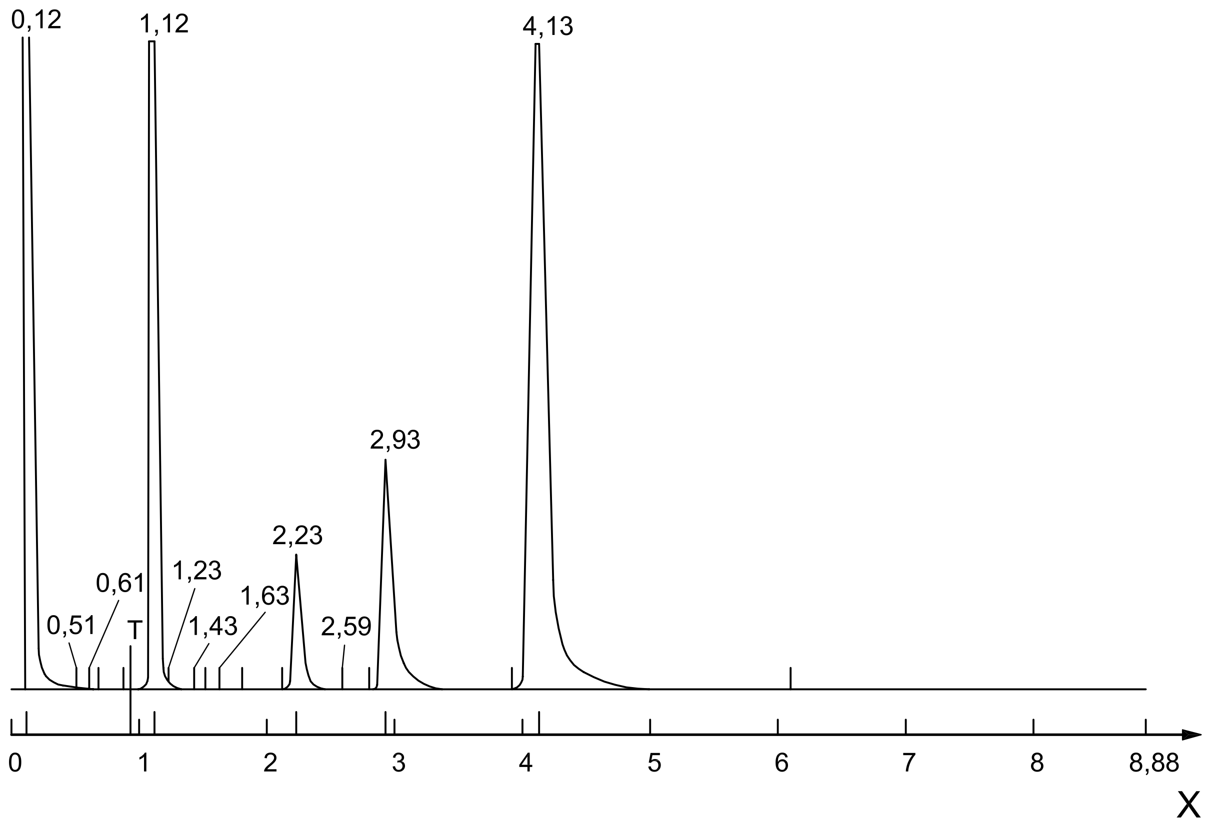
1 start

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
$\leqslant$ 0,5	2
> 0,5 but $\leqslant$ 1	1
> 1 but $\leqslant$ 2	0,5
> 2 but $\leqslant$ 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:

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

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:

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

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 ± 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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