INTERNATIONAL STANDARD

ISO 10283

First edition
1997-12-01

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

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

Reference number
ISO 10283:1997(E)

Foreword

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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.

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

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Printed in Switzerland

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 polyisocyanate 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 reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 842 : 1984 Raw materials for paints and varnishes - Sampling.

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 Isocyanate resin: A synthetic resin, with or without solvent, based on aromatic, aliphatic or cycloaliphatic isocyanates containing isocyanate (NCO) groups.

NOTE 1: 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), 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 1000 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 1000 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 2: 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 3: Instead of preparing a calibration solution, the internal standard and the monomeric diisocyanate can be weighed directly with 40 ml 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 1000 ml.

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

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

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 842. 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

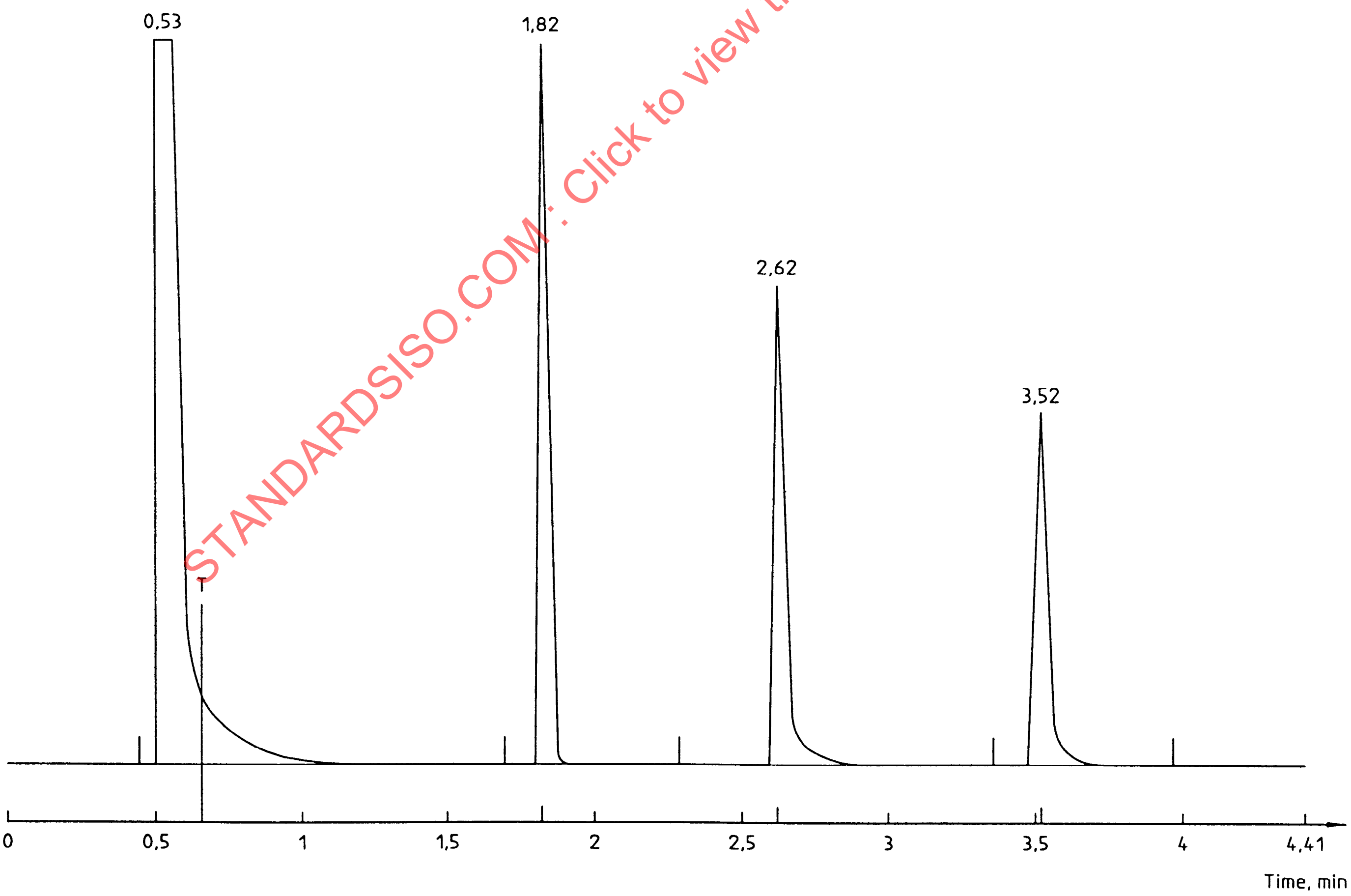

Figure 1: Gas chromatogram for hexamethylene diisocyanate and toluene diisocyanate

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

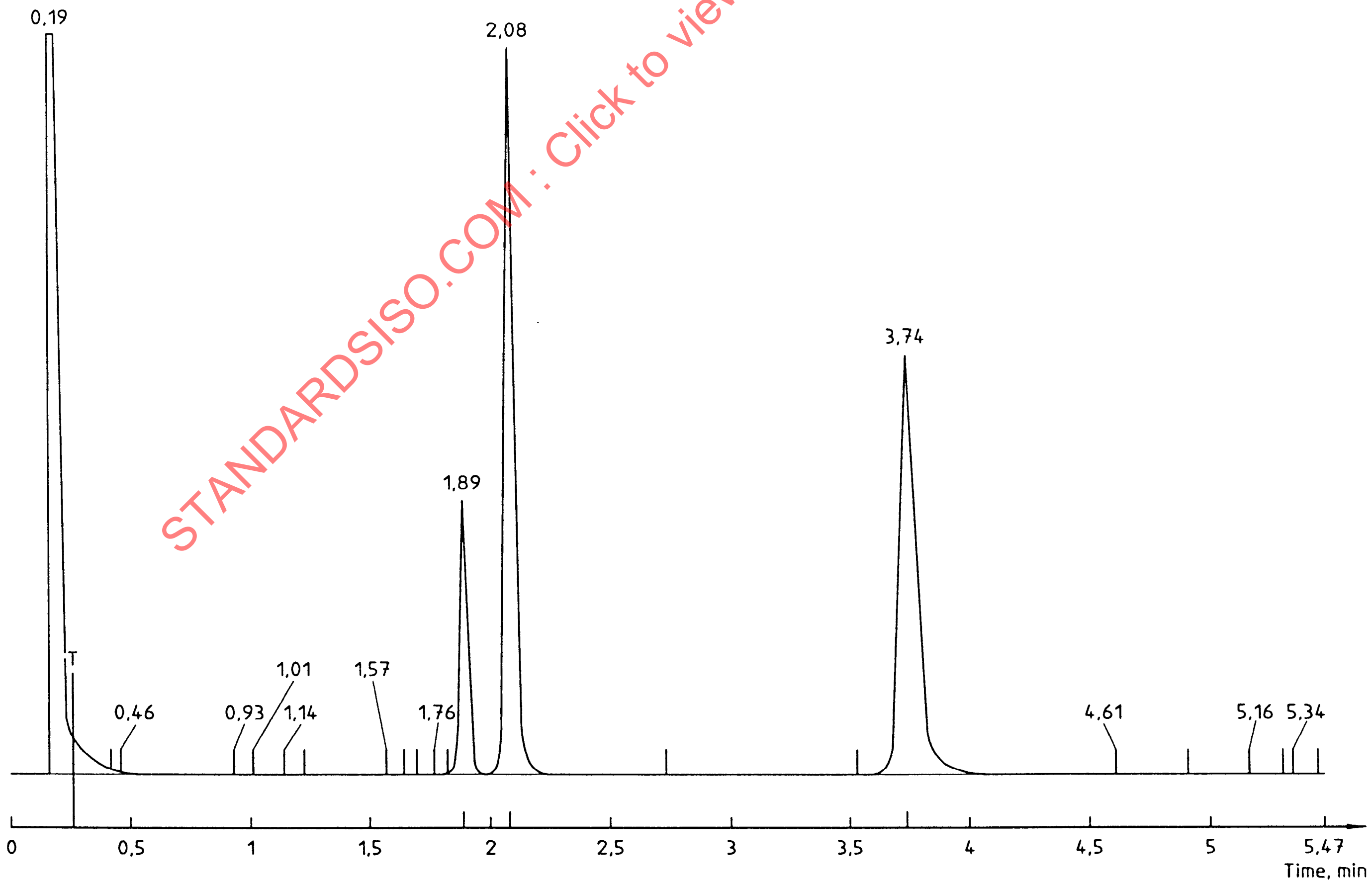

Figure 2: Gas chromatogram for isophorone diisocyanate (first example)

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

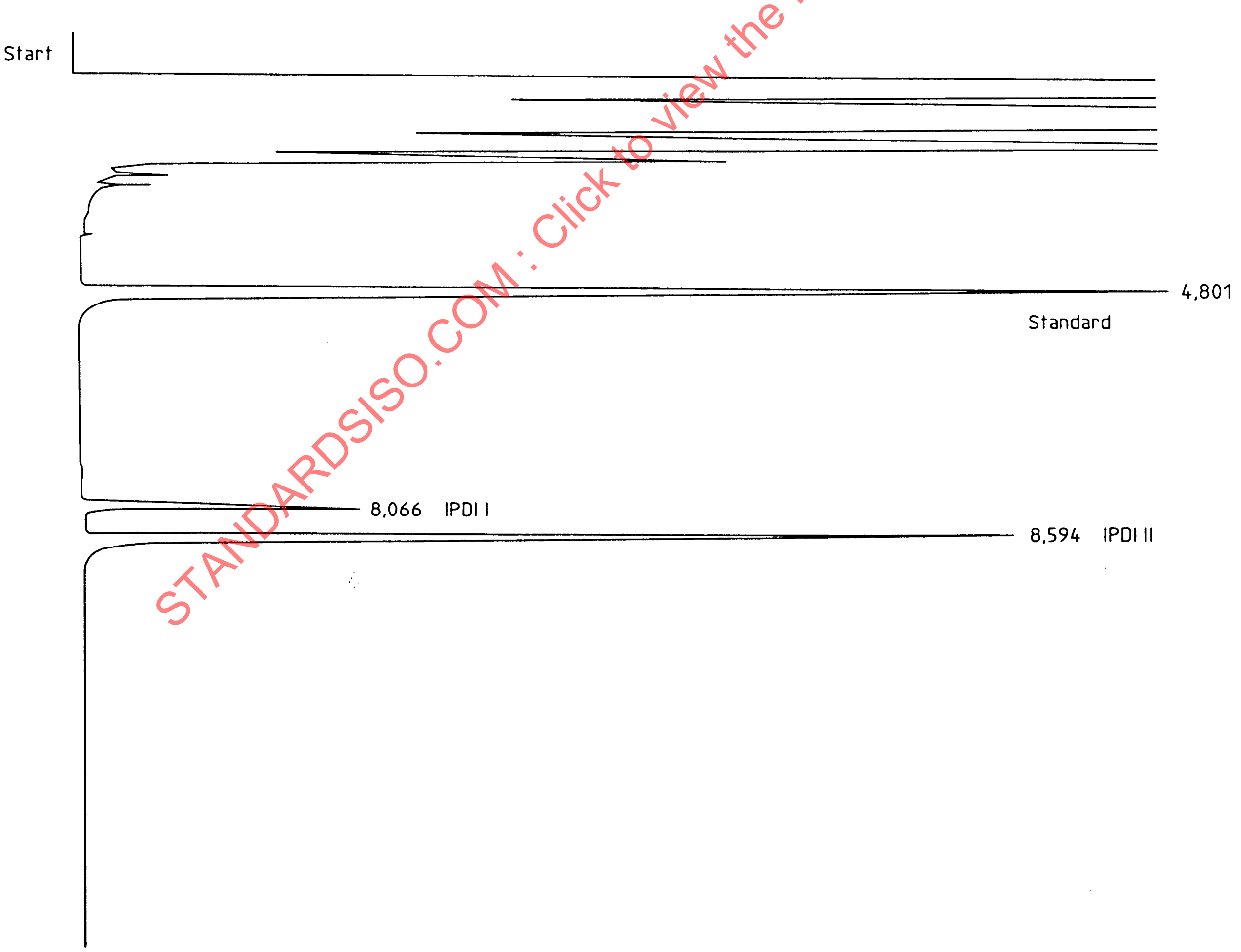

Figure 3: Gas chromatogram for isophorone diisocyanate (second example)

8.1.4 Example: diphenylmethane diisocyanate (MDI)

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

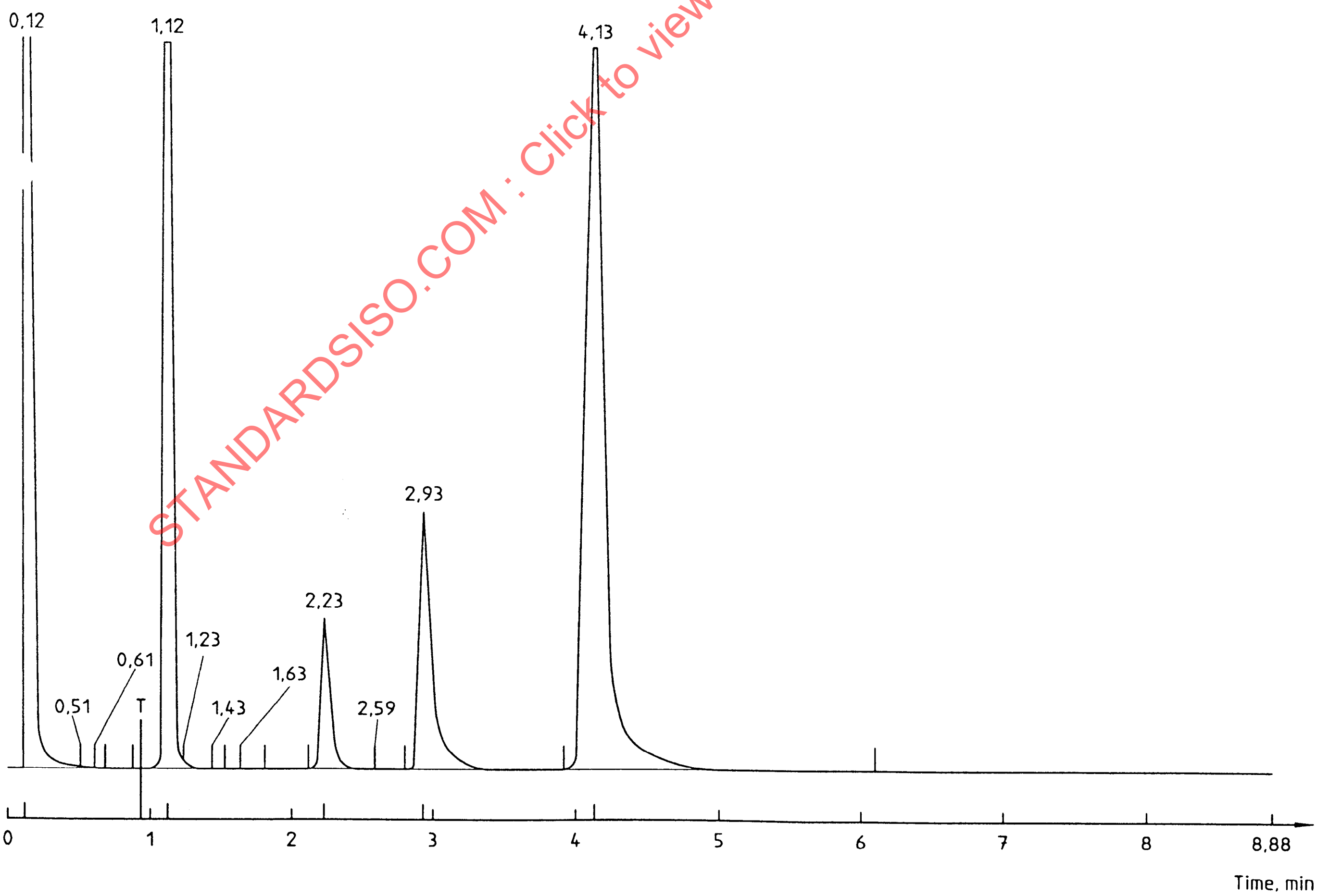

Figure 4: Gas chromatogram for diphenylmethane diisocyanate

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).

Expected Diisocyanate content % (m/m)	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 4: 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.