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Paints and varnishes — Determination of monomeric diisocyanate content in coating materials and similar products using high performance liquid chromatography with ultraviolet detection (HPLC-UV)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 16, *Chemical analysis*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The analytical method described in this document was developed in 2011. The validity of this method has been continuously tested until it was finalized in 2015 for the low content monomer diisocyanate under 0,20 % mass fraction. Several internal interlaboratory tests have clearly demonstrated its reproducibility. Moreover, under the framework of interlaboratory tests organized by the Association of the European Adhesive and Sealant Industry (FEICA), it has been shown that the described method is accurate in determining monomer diisocyanate content in various polyurethane (PU) matrices.

Paints and varnishes — Determination of monomeric diisocyanate content in coating materials and similar products using high performance liquid chromatography with ultraviolet detection (HPLC-UV)

1 Scope

This document specifies a method for the quantitative determination of monomeric diisocyanate content in coating materials, adhesives and other liquid or pasty materials.

This method is suitable for the quantification of the following monomeric diisocyanates: methylene diphenyl diisocyanate (MDI, 2,4'-MDI and 4,4'-MDI), toluene diisocyanate (TDI, 2,6-TDI, 2,4-TDI), (cis/trans) isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI,1,6-HDI) in various matrices for concentrations ranging from 0,01 % to 2,0 % mass fraction. For higher concentrations, a suitable dilution before the derivatization with p-nitrobenzyl-N-propylamine (PNBPA) is performed. The measurements are carried out using ultra high performance liquid chromatography (UHPLC) with a multiple wavelength detector.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 4618, *Paints and varnishes — Vocabulary*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The sample is directly weighed into a 10 ml measuring flask (the mass depends on the isocyanate content). The flask is filled with dry acetonitrile to the mark. Subsequently, in a vial, an aliquot of the solution is derivatised with PNBPA in dry acetonitrile (1+1 by volume). After filtration, the clear solution is injected directly into the HPLC.

5 Apparatus

Use ordinary laboratory apparatus and glassware together with the following.

5.1 HPLC/UV with the parameters given in Table 1.

Table 1 — Parameters

System	HPLC system with a pressure up to 600 bar[b] and a quaternary gradient pump, including a thermostat oven
Detector	Multiple wavelength detector
Column	HPLC column superficial porous particles, C18 100 Å, particle size 2,6 µm, column dimension 100 x 3 mm, e.g. Kinetex™[a]
Column oven	(30 ± 1) °C
Mobile phase A	40 mM sodium acetate (pH 4,5)
Mobile phase B	fresh deionised water
Mobile phase C	acetonitrile
Gradient	

Time (min)	A %	B %	C %
−4,00	55	0	45
0,00	55	0	45
3,25	45	0	55
5,70	35	0	65
5,80	0	35	65
6,00	0	35	65
7,00	0	5	95
10,00	0	5	95

Flow rate	1,40 ml/min
Detection	UV 275 nm 2,6-TDI, 2,4-TDI, c/t-IPDI, 1,6-HDI UV 250 nm 2,4'-MDI; 4,4'-MDI
Injection volume	2,5 µl

[a] Kinetex is the trade name of a product supplied by Phenomenex. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

[b] 1 bar = 0,1 MPa = 10^5 Pa; 1 MPa = 1 N/mm^2.

5.2 Balance

In the 60 g range, expect readability of 0,01 mg, repeatability of 0,015 mg, and linearity of ±0,08 mg.

5.3 Filter system, filtration glassware

5.4 Filter membranes, nylon, 0,20 µm pore size, 47 mm diameter.

5.5 Pipette, of capacity 200 µl, 1 000 µl and 10 000 µl.

5.6 Measuring flask, of capacity 10 ml.

5.7 Pipette tips, polypropylene, tip-rack, 50 µl to 1 000 µl.

5.8 Derivatisation vials, of capacity 5 ml with PE-lid.

5.9 HPLC vials, of capacity 2 ml.

5.10 Syringe filter, 0,2 µm syringe filter polyamide PA 66.

5.11 One-way syringe, of capacity 1 ml.

6 Reagents

6.1 Acetonitrile, HPLC, >99,9 % UV grade, dried over molecular sieve.

6.2 Deionised water, resistance >18 MΩ.

6.3 4-Nitro-N-propylbenzylamin-hydrochloride (PNBPA-HCl)

6.4 Petrol ether, 50 °C to 70 °C.

6.5 Sodium hydroxide pellets

6.6 Magnesium sulfate

6.7 Sodium acetate, water free, 99 % puriss.

6.8 Molecular sieves, 4 Å.

6.9 Mobile phase C: acetonitrile, gradient grade for liquid chromatography.

6.10 Sulfuric acid, c = 1 mol/l.

Fill a 500 ml measuring flask with 250 ml deionized water and add 27,5 ml concentrated sulfuric acid (97 %).

Complete the measuring flask with deionized water to the mark.

6.11 Mobile phase A: 40 mM sodium acetate, pH ~4,5.

Weigh 6,63 g of sodium acetate water free (99 %) in a 2 l Erlenmeyer flask.

Add 2 l of deionized water and 13 ml of H_2SO_4, c = 1 mol/l.

6.12 Derivatisation agent (PNBPA)

Weigh about 1,0 g PNBPA-HCl in an erlenmeyer flask and dissolve in 40 ml deionised water.

Add drop wise a solution of 2 N sodium hydroxide (about 30 drops). The solution will become milky.

Extract three times with 20 ml petrol ether (50 °C to 70 °C) in a separating funnel.

Dry the petrol ether phase over magnesium sulfate for 15 min.

Filter the petrol ether phase into a round bottomed flask.

Concentrate the solution in the rotary evaporator at 40 °C until a light-yellow oil is obtained.

Take up the yellow residue with 150 ml dry acetonitrile into a brown bottle filled with a molecular sieve.

Store the solution in the fridge for no more than two months at a temperature of less than or equal to 4 °C before use.

7 Reference standards

7.1 2,4'-/4,4'-Methylene diphenyl diisocyanates, ratio: 2,4' (51 %)/ 4,4' (49 %), purity at least 99,4 % (mass fraction) determined in accordance with this document using a standard 4,4'-MDI of at least 99,5 % (mass fraction).

7.2 1,6-Hexamethylendiisocyanat (1,6-HDI), purity at least 99 % (mass fraction).

7.3 2,6-Toluene diisocyanate (2,6-TDI), purity at least 97 % (mass fraction).

7.4 2,4-Toluene diisocyanate (2,4-TDI), purity at least 98 % (mass fraction).

7.5 IPDI cis/trans Isomers, purity at least 98 % (mass fraction).

8 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 shall 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.

Isocyanates are very toxic and react readily with moisture. Directly after weighing dry acetonitrile shall be added.

The sample shall be well suspended using a fast-rotating lab shaker and ultrasonic bath.

9 Procedure

9.1 Sample preparation

Weigh 30 mg to 250 mg of the sample in a clean 10 ml measuring flask (30 mg for prepolymers in a 20 ml flask, 200 mg for adhesives with <0,1 % residual monomer and 50 mg for other adhesives in a 10 ml flask).

Fill directly with dry acetonitrile up to the mark.

Suspend and homogenize the sample by mixing with a fast rotating lab shaker and with ultrasonic bath, each for 5 min. The time depends on the matrix of the sample.

In a 5 ml glass vial, derivatise an aliquot of 500 µl of the sample solution with 500 µl of the PNBPA solution.

Close the glass vial with a lid, mix by hand and let react for about 30 min at room temperature, in order to complete the derivatisation reaction.

Filter through a 0,2 µm polyamide PA 6.6 membrane.

Inject 2,5 µl in the HPLC.

NOTE For high concentration of residual monomer diisocyanate a dilution (1+9, 1+19 or 1+49 by volume with dry acetonitrile) before the derivatisation step can be necessary.

9.2 Calibration

9.2.1 Preparation of the standard

First bring the references, stored in the freezer at about –18 °C, to room temperature. MDI shall be warmed at 60 °C in the oven until a clear yellow solution is obtained.

Weigh about 50 mg from each reference (see Table 2) in a 50 ml measuring flask. For the reference MDI about 100 mg shall be weighed in.

Fill the measuring flask with dry acetonitrile up to the mark. This is the stock solution (SL).

Homogenize the solution with the fast rotating lab shaker and the ultrasonic bath.

Dilute the stock solution with dry acetonitrile 1+20 by volume, derivatise with the solution of PNBPA: STD 6; 2,5 ml (SL) + 30 ml PNBPA solution and complete to 50 ml with dry acetonitrile.

Table 2 — References

Standards	Volume (STD 6) ml	Flask ml	Concentration in acetonitrile [a] µg/ml
STD 1	0,50	25	1
STD 2	2,50	25	5
STD 3	7,00	25	14
STD 4	12,0	25	24
STD 5	17,0	25	34
STD 6	—	—	50

[a] Assumption: STD 6 corresponds to 50 µg/ml standard solution; the diluted solutions according to their dilutions of STD 6.

The standards shall be stored at 4 °C in the refrigerator.

NOTE 1 Two series (A;B) of the 6 concentration levels are prepared every 3 months. Both series are divided into 6 sets of 6 concentration levels in vials which are then labelled with their production date, series, and level.

NOTE 2 One set of 6 levels of each series is run and compared to the previous series of standards. The series which is best fitting is selected as calibration series and from the other series, two levels are selected to be check standards.

After running a sequence, the caps of the vials with the standards set used should be replaced.

To ensure quality, a set of 6 concentration levels may be run up to 3 times within 2 to 3 weeks.

9.2.2 Quantification

The quantification is performed by external standards by integrating the peak area by using a linear fit and adding the origin. See the demonstration in the validation shown in Annex A.

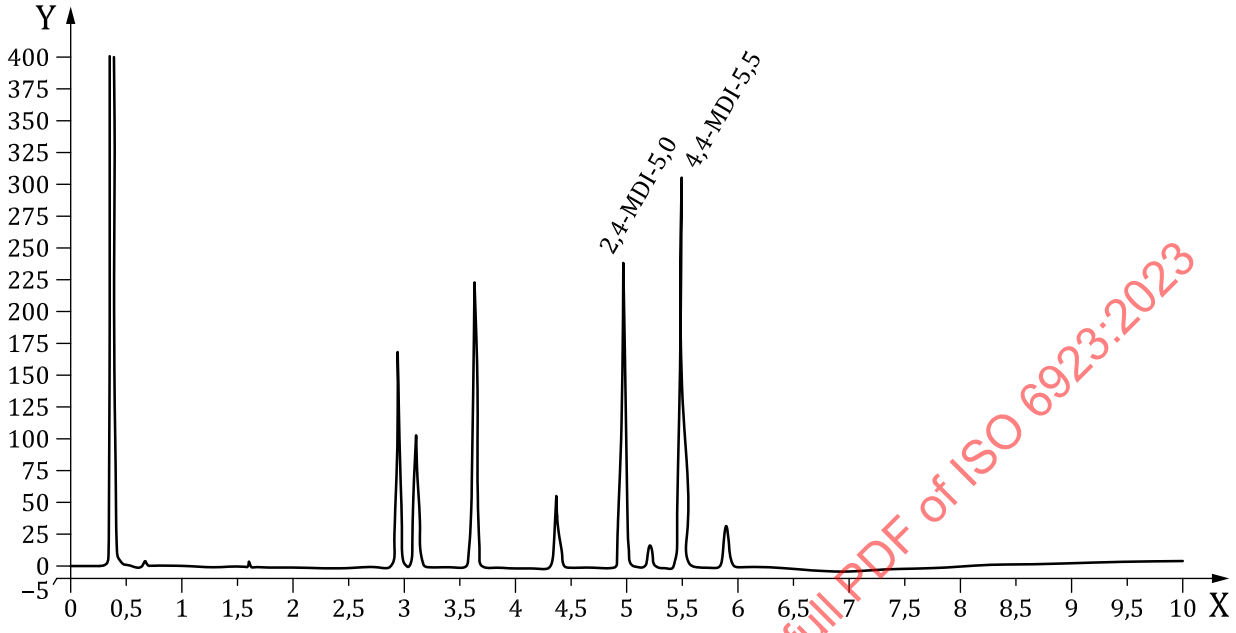
For c/t-IPDI, both isomers are integrated as a group (both areas are summed up and integrated as one).

During the recovery study for IPDI in the range of 0,01 % mass fraction to 0,15 % mass fraction, it was noticed that ageing PNBPA solution gave rise to disturbing peaks, which are eluting near 2,4-TDI and c/t-IPDI. These peaks can artificially increase the amount of 2,4-TDI and c/t-IPDI. Therefore, it is necessary to inject the solution of PNBPA diluted with the solution acetonitrile (1+1 by volume), which are used for the preparation of the samples. The amounts of those peaks accountable for PNBPA shall be abstracted to the amounts obtained for 2,4-TDI and c/t-IPDI for the sample of analysis (see Annex A).

Figure 1 shows a chromatogram of a set of 6 concentration levels of standards at 250 nm.

Figure 2 shows a chromatogram of a set of 6 concentration levels of standards at 275 nm.

Figure 3 shows a calibration curve with 6 concentration levels of 4,4'-MDI with a confidence interval of 0,95.

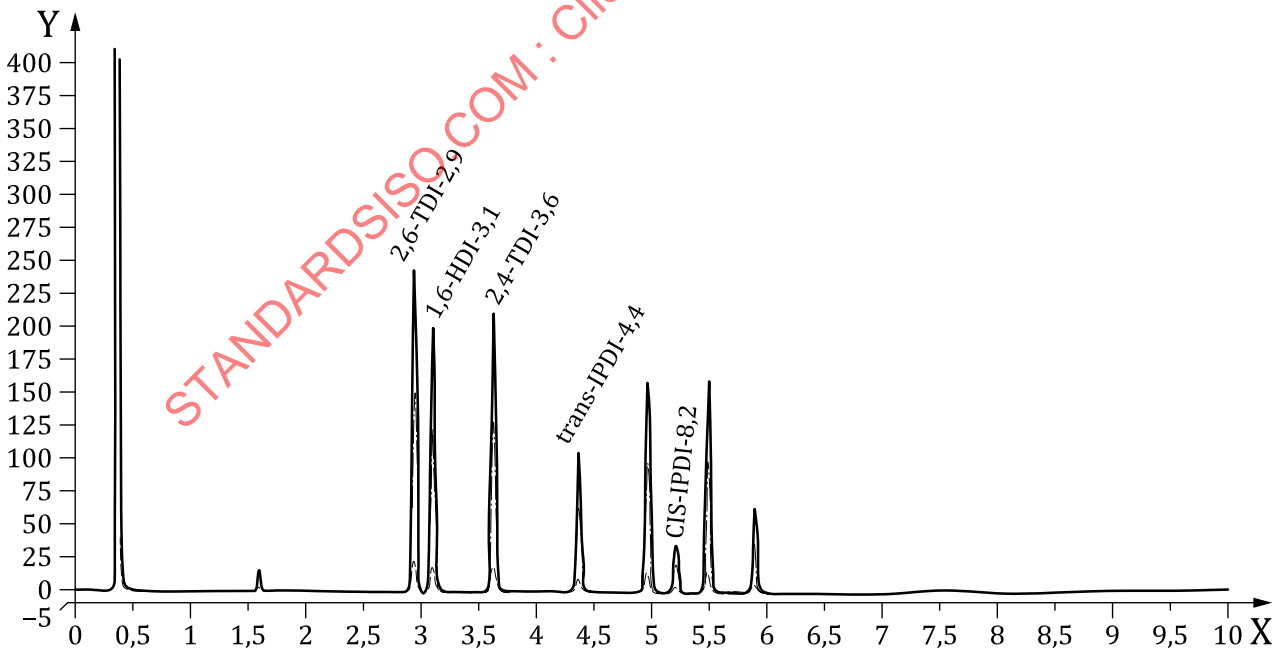


Key

X time, in minutes (min)

Y detector signal, in milli absorbance units (mAU)

Figure 1 — Chromatogram of a set of 6 concentration levels of standards at 250 nm



Key

X time, in minutes (min)

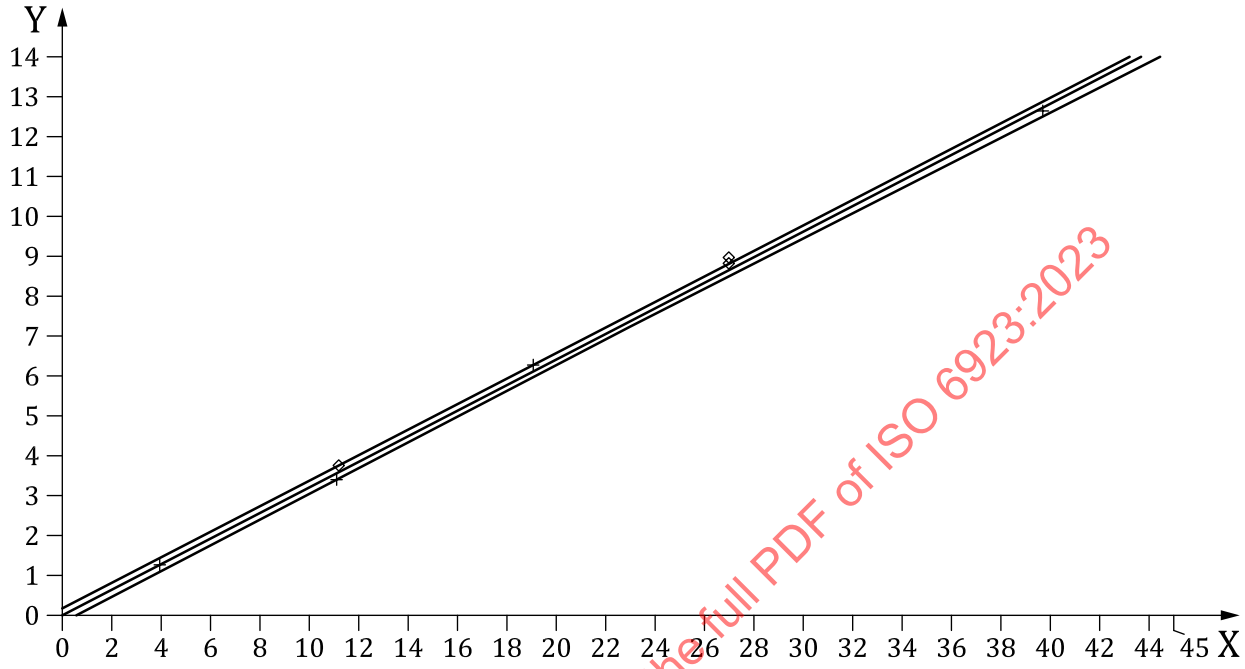
Y detector signal, in milli absorbance units (mAU)

_____ series A standard 1

_.__.__ series A standard 2

series A standard 3

Figure 2 — Chromatogram of a set of 6 concentration levels of standards at 275 nm



Key

X concentration of the standard solution, in micrograms per millilitre (µg/ml)

Y peak area, in milli absorbance units time minutes (mAU ·min)

Figure 3 — Calibration curve with 6 concentration levels of 4,4'-MDI with a confidence interval of 0,95

10 Calculation

Calculate the final result as a mass fraction in percent (%) for each monomer diisocyanate contained in the sample using Formula (1):

$$c = \frac{c_d}{c_s} \times 100 \quad (1)$$

where

c is the concentration of the diisocyanate, as mass fraction in percent (%);

c_d is the concentration of the diisocyanate, in milligrams per millilitre (mg/ml);

c_s is the concentration of the sample, in milligrams per millilitre (mg/ml).

An excel sheet can be used to calculate the final percentage using Formula (1).

11 Expression of results

The following results and parameters shall be reported:

— when two determinations are performed, i.e. the average calculated together with the excel sheet and its associated standard deviation;

— when one determination is performed, i.e. the single measurement result, if in agreement with the expectation. Otherwise, a second determination can be necessary.

A result of *c* that is under the determined limit of quantification (LOQ) with a confidence interval of 0,95 will be given also in Annex A down to 0,01 % mass fraction. The LOQ with a confidence interval of 0,95 for one determination will be clearly stated under Table A.1 as a reference.

A result of *c* under 0,01 % mass fraction will be given as <0,01 % mass fraction if the result of the monomer diisocyanate concentration in the solution is above 0,25 µg/ml. Otherwise the result will be given as not detected (n.d.).

12 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 document, i.e. ISO 6923:2023;

c) the results of the test, as indicated in Clause 11;

d) any deviations from the procedure specified;

e) any unusual features (anomalies) observed during the test;

f) the date of the test.