
**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

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.

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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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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.

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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)

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 ^{TMa}																																							
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	<table border="1"> <thead> <tr> <th>Time (min)</th> <th>A %</th> <th>B %</th> <th>C %</th> </tr> </thead> <tbody> <tr> <td>-4,00</td> <td>55</td> <td>0</td> <td>45</td> </tr> <tr> <td>0,00</td> <td>55</td> <td>0</td> <td>45</td> </tr> <tr> <td>3,25</td> <td>45</td> <td>0</td> <td>55</td> </tr> <tr> <td>5,70</td> <td>35</td> <td>0</td> <td>65</td> </tr> <tr> <td>5,80</td> <td>0</td> <td>35</td> <td>65</td> </tr> <tr> <td>6,00</td> <td>0</td> <td>35</td> <td>65</td> </tr> <tr> <td>7,00</td> <td>0</td> <td>5</td> <td>95</td> </tr> <tr> <td>10,00</td> <td>0</td> <td>5</td> <td>95</td> </tr> </tbody> </table>				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
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																																							
<p>^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.</p> <p>^b 1 bar = 0,1 MPa = 10⁵ Pa; 1 MPa = 1 N/mm².</p>																																								

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 H₂SO₄, $c = 1$ 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.