



# SLOVENSKI STANDARD SIST ENV 13999-4:2003

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Adhesives - Short term method for measuring the emission properties of low-solvent or solvent-free adhesives after application - Part 4: Determination of volatile diisocyanates

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Klebstoffe - Kurzzeit-Verfahren zum Messen der Emissionseigenschaften von lösemittelfarmen oder lösemittelfreien Klebstoffen nach der Applikation - Teil 4: Bestimmung flüchtiger Diisocyanate

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Adhésifs - Méthode de courte durée de mesurage des propriétés d'émission des adhésifs a faible teneur en solvants ou exempts de solvants apres application - Partie 4: Dosage des diisocyanates volatils

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ICS 83.180

English version

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This European Prestandard (ENV) was approved by CEN on 16 October 2002 as a prospective standard for provisional application.

The period of validity of this ENV is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the ENV can be converted into a European Standard.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

**Management Centre: rue de Stassart, 36 B-1050 Brussels**

## Contents

Foreword.....	3
1 Scope .....	4
2 Normative references .....	4
3 Principle .....	4
4 Safety .....	5
5 Reagents and materials.....	5
6 Apparatus .....	5
6.1 Sampler .....	5
6.1.1 Filter holder .....	5
6.1.2 Filter .....	5
6.2 Filtration equipment .....	5
6.3 Sampling pump .....	5
6.4 Tubing .....	5
6.5 Flow meter calibrator.....	6
6.6 High performance liquid chromatograph (HPLC).....	6
7 Procedure .....	6
7.1 Preparation of sampling devices.....	6
7.2 Test chamber air sampling .....	6
7.3 Storage of loaded sampling filters.....	6
7.4 Blanks .....	6
7.5 Analysis .....	7
7.5.1 Cleaning of glassware .....	7
7.5.2 Sample desorption and pre-reaction before HPLC analysis .....	7
7.5.3 Preparation of calibration standards .....	7
7.5.4 Calibration of liquid chromatograph.....	7
7.5.5 Analysis of pre-reacted sample solutions.....	8
8 Identification and calculation .....	8
8.1 Identification of isocyanates.....	8
8.2 Concentration of analytes in the sampled air .....	8
9 Interferences.....	9
10 Precision and bias .....	9
11 Test report .....	9
12 Quality control.....	10
Bibliography .....	11

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SIST ENV 13999-4:2003

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## Foreword

This document ENV 13999-4:2002 has been prepared by Technical Committee CEN/TC 193, "Adhesives", the secretariat of which is held by AENOR.

This document includes a Bibliography.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this European Prestandard : Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

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## 1 Scope

This European Prestandard specifies a procedure for the determination of volatile organic isocyanates in the exhaust air of an emission test chamber after application of an adhesive.

The method is based on chemisorption of volatile isocyanates with 1-(2-methoxyphenyl)piperazine (in the following: 1-2MP) impregnated filters with subsequent desorption and liquid chromatographic analysis. The method permits measurement of a wide range of organic compounds containing isocyanate functional groups (NCO), including isocyanate monomers. For testing of adhesives emissions mainly toluene diisocyanate (TDI) and methylene bis (4-phenyl isocyanate) (4,4-diisocyanato-diphenylmethane, MDI) are of concern. The method as described in this Prestandard can be used for other isocyanates too, such as isophorone diisocyanate (IPDI) and 1,6-hexamethylene diisocyanate (HDI) - see ISO 16702. Isocyanate oligomers or prepolymers are not volatile enough to be detected in emission test chambers at room temperature.

## 2 Normative references

This European Prestandard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Prestandard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 1232, *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods.*

ENV 13999-1, *Adhesives - Short term method for measuring the emission properties of low-solvent or solvent-free adhesives after application - Part 1: General procedure.*

ENV 13419-1, *Building products - Determination of the emission of volatile organic compounds - Part 1: Emission test chamber method.*

EN ISO 16017-1, *Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 1: Pumped sampling (ISO 16017-1:2000).*

prEN ISO 16017-2, *Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 2: Diffusive sampling (ISO/DIS 16017-2:1999).*

ISO 16702, *Workplace air quality - Determination of total isocyanate groups in air using 2-(1-methoxyphenyl) piperazine and liquid chromatography.*

## 3 Principle

An emission test chamber as described in ENV 13999-1 or ENV 13419-1 shall be used.

A sufficient volume of test chamber air is drawn with an appropriate flow through a glass fibre filter impregnated with 1-(2-methoxyphenyl)piperazine (1-2MP) reagent. Any volatile isocyanates present will react and form non-volatile isocyanate urea derivatives. Desorption is done with acetic anhydride and a 1-2MP solution in toluene. The resultant solution is concentrated and analysed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. Isocyanate-derived peaks are identified on the basis of their UV responses at more than one wavelength and/or by diode array detection (DAD) and comparison with a derivative standard. Quantification is by comparison with the relevant isocyanate monomer standard.

## 4 Safety

This Prestandard does not purport to address all of the safety concerns, if any, associated with its use. The user of this Prestandard should be familiar with common laboratory practice including general safety measures. It is the responsibility of the user of this Prestandard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

When handling reagents and chemical solutions always wear disposable gloves to reduce the possibility of contamination. If contamination of a glove occurs substitute it within a maximum of 1 min as the solvents and solutions applied will permeate through disposable gloves within a very short time.

## 5 Reagents and materials

**5.1 Acetonitrile**, of HPLC grade.

**5.2 1-(2-methoxyphenyl) piperazine (1-2 MP)** purity > 98 %.

**5.3 Reagent solvent**

The reagent solvent, commonly toluene, shall be of chromatographic quality. It shall be free from compounds co-eluting with the substances of interest. Before use for the preparation of standards it is advisable to dry the solvent with anhydrous calcium chloride or magnesium sulphate.

**5.4 HPLC mobile phase**

Dissolve 5 g of anhydrous sodium acetate in 1 l distilled water. Adjust the pH of this solution to 6,0 with glacial acetic acid. Add 550 ml of this solution to acetonitrile (450 ml) to give a 45 % acetonitrile / 55 % sodium acetate buffer solution. Degas this solution by filtering under vacuum or by bubbling a stream of helium through it.

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## 6 Apparatus

**6.1 Sampler**

**6.1.1 Filter holder**

Use an appropriate filter holder.

NOTE Details of suitable sampling heads are given in MDHS14/2 [2]. A 25 mm head fitted with a stainless steel cassette as described in this reference is recommended for filter samples.

**6.1.2 Filter**

Commercially fabricated 1-2MP filters or prepared impregnated filters as described in ISO 16702.

**6.2 Filtration equipment**

A solvent resistant filter unit of < 0,5 µm pore size for filtration of HPLC solvents. Syringeless filters or < 0,5 µm syringe filters for filtration of the desorbed samples prior to HPLC analysis.

**6.3 Sampling pump**

The pump shall fulfil the requirements of EN 1232 or equivalent.

**6.4 Tubing**

Tubing of appropriate diameter to ensure a leak-proof fit to both pump and sample tube. PTFE tubes shall be used upstream of the sorbent to avoid loss of substance due to reaction with tubing walls.

## 6.5 Flow meter calibrator

Bubble meter or other appropriate device suitable for gas flow calibration.

## 6.6 High performance liquid chromatograph (HPLC)

A typical apparatus for HPLC, with ultraviolet (UV) detector.

# 7 Procedure

## 7.1 Preparation of sampling devices

Clean the samplers (filter cassette) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water, wipe with absorptive tissue and allow to dry thoroughly before reassembling. Alternatively, use a laboratory washing machine.

In an area free from isocyanates, load the filters into clean, dry samplers using clean flat-tipped tweezers. Connect each loaded sampling head to a sampling pump using plastic tubing ensuring that no leaks can occur. Switch on the pump, attach the calibrated flow-meter to the sampling head so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate with a limit deviation of  $\pm 5\%$ . Switch off the pump and seal the sampler with a protective cover to prevent contamination during transport to the sampling position.

## 7.2 Test chamber air sampling

Remove the protective cover from the sampler and assemble the sampling line. Always use two samplers in series with the downstream sampler serving as control filter. Prepare the test chamber sampling port as described in ENV 13999-1 or in ENV 13419-1.

If the sampling flow rate is determined with a calibrator, start the pump, note and record the sampling flow rate. Connect the sampler to the chamber sampling port, note and record the time the sampler was connected. Never use more than 50 % of the test chamber supply air flow rate as the combined sampling flow rates. At the end of the sampling period disconnect the sampler from the chamber sampling port, note and record the time of disconnection, repeat the sampling flow determination, and turn off the pump.

Disconnect the sampler or the samplers from the sampling line and seal both ends using inert caps.

**NOTE** When applying a sampling flow rate in the range of 2 l/min and a sampling air volume of 240 l then the method is suitable for the measurement of airborne organic isocyanates in the concentration range of approximately (0,01 to 10)  $\mu\text{g}$  isocyanate per  $\text{m}^3$ .

## 7.3 Storage of loaded sampling filters

Remove each filter from the sampler, place in a glass vial containing 2 ml 1-2MP absorbing solution and cap the vial.

## 7.4 Blanks

Take at least one blank sample which is an impregnated filter in samplers equivalent to the ones used for sampling. Subject blank samples to the same handling procedure in the laboratory as the actual samples except for the actual period of sampling, i.e. repeat the sampling procedure up to the point of actual sample collection. Do not perform sampling but repeat normal post-sampling activities for the filters. Mark, store, and analyse blank samples in sequence with the actual samples.

For blank control of the test chamber see ENV 13999-1.



## 7.5 Analysis

### 7.5.1 Cleaning of glassware

Before use, clean all glassware to remove any residual grease or chemicals by soaking overnight in laboratory detergent solution and then rinsing thoroughly with water. Alternatively, use a laboratory washing machine.

### 7.5.2 Sample desorption and pre-reaction before HPLC analysis

Pipette 100 µl acetic anhydride into each glass vial containing the 1-2MP solution and sampling filter and agitate well. Evaporate to dryness, redissolve the residue in 2 ml acetonitrile or mobile phase and agitate well. Filter this solution into an autosampler vial, using a syringeless filter or < 0,5 µm syringe filter. Analyse using liquid chromatography as described below.

### 7.5.3 Preparation of calibration standards

#### 7.5.3.1 Preparation of isocyanate urea derivatives

Add the appropriate isocyanate 0,1 g to 0,6 g of 1-2MP dissolved in dry toluene (10 ml) and leave to stand for one hour. A white crystalline isocyanate urea derivative will be precipitated. Collect this on a filter and wash several times with dry toluene to remove excess reagent.

Recrystallise the isocyanate urea derivative from toluene by warming to about 60°C and slowly adding methanol to dissolve the isocyanate urea derivative. Allow to cool and filter the resulting crystals, washing with cold, dry toluene. Dry the solid in air. The isocyanate urea derivatives are only slightly soluble in toluene but readily soluble in methanol or acetonitrile.

MDI is less soluble in toluene. For MDI the alternative method of preparation given below shall be used.

Slowly add a solution of the appropriate isocyanate (0,5 g) in dichloromethane (25 ml) to a solution of 1-(2-methoxyphenyl)piperazine (0,7 g) in dichloromethane (50 ml). A white suspension will form. Add this dropwise to a beaker of hexane (500 ml) with stirring. Filter the resultant precipitate and redissolve it in a minimum volume of dichloromethane. Add hexane to re-precipitate the solid, filter this and wash with hexane. Dry the isocyanate urea derivative in air.

#### 7.5.3.2 Preparation of standard solutions of recrystallised isocyanate urea derivatives

Weigh a known mass of the isocyanate urea derivative, place in a 100 ml volumetric flask and fill to volume with acetonitrile or methanol. Take aliquots of this solution and dilute volumetrically in acetonitrile or HPLC mobile phase to create a series of standard solutions over the concentration range (0,01 to 1,0) µg isocyanate per ml. Prepare further standard solutions if the concentration range of the samples exceeds that of the standards.

#### 7.5.3.3 Stability of isocyanate urea derivatives and their solutions

Pure isocyanate urea derivatives shall be stored below – 10 °C

Stock solutions of isocyanate monomer derivatives shall be stored below 10 °C.

NOTE Isocyanate monomers (TDI) on filters and toluene solution have been found to be stable up to 90 days (73 % and 81% recoveries respectively) [1].

### 7.5.4 Calibration of liquid chromatograph

Pre-react the samples and the blanks. Analyse by injecting a known fixed volume (10 to 20) µl of each standard solution into the liquid chromatograph using UV detection as described below. A standardised injection technique is required to obtain reproducible peak heights/areas. Prepare a calibration graph of UV response (height or area) versus analyte concentration in the standard solutions.