SLOVENSKI STANDARD
SIST ISO 17735:2019

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Zrak na delovnem mestu - Določevanje skupin izocianatov v zraku z reagentom 1-(9-antracenilmetil)piperazin (MAP) in s tekočinsko kromatografijo

Workplace atmospheres - Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl)piperazine (MAP) reagent and liquid chromatography

Air des lieux de travail - Dosage des groupements isocyanates totaux dans l'air par réaction avec la 1-(9-anthracénylméthyl)pipérazine (MAP) et par chromatographie en phase liquide

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Workplace atmospheres — Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl)piperazine (MAP) reagent and liquid chromatography

Air des lieux de travail — Dosage des groupements isocyanates totaux dans l'air par réaction avec la 1-(9-anthracénylméthyl)pipérazine (MAP) et par chromatographie en phase liquide

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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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

This second edition cancels and replaces the first edition (ISO 17735:2009), which has been technically revised. The main changes compared to the previous edition are as follows.

— Additional limit of detection information has been provided (Clause 1).

— The method has been used in high air concentrations successfully with a higher reagent concentration in an impinger (5.3.1).

— During processing of impinger samples, rinsing the SPE cartridge with 6 ml dichloromethane has been changed to rinsing with two consecutive 3 ml aliquots. This is more effective in removing all of the butyl benzoate impinger solvent (7.8).

— The liquid chromatographic system has been adapted to use a smaller diameter analytical column (6.7.3).

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

This document specifies the use of 1-(9-anthracenylmethyl)piperazine (MAP) to measure monomeric and oligomeric isocyanate species in workplace atmospheres. MAP was designed to improve the reliability of identification of isocyanate species in sample chromatograms and to improve the accuracy of quantification of these species relative to established reagents. The high performance liquid chromatography (HPLC) analysis uses a pH gradient to selectively accelerate the elution of MAP derivatives of oligomeric isocyanates that might be unobservable in an isocratic analysis. The performance of MAP has been compared to other reagents used for total isocyanate analysis[8], MAP has been found to react with phenyl isocyanate (used as a model isocyanate) as fast as or faster than other reagents commonly used for isocyanate analysis. The UV response of MAP derivatives is comparable to that of 9-(methylaminomethyl)anthracene (MAMA) derivatives and considerably greater than other commonly used reagents [approximately three times greater than 1-(2-methoxyphenyl)piperazine (1-2MP) derivatives of aromatic isocyanates and 14 times greater than 1-2MP derivatives of aliphatic isocyanates]. The compound-to-compound variability of UV response per isocyanate group for MAP derivatives is smaller than the variability of any other commonly used reagent/detector combination (the coefficient of variation is 3,5 % for five model isocyanates). This results in more accurate quantification of detectable non-monomeric isocyanate species based on a calibration curve generated from analysing standards of monomeric species. The monomeric species used for calibration is generally the one associated with the product being analysed, but others could be used due to the very small compound-to-compound response variability of the MAP derivatives. The intensity of fluorescence response of MAP derivatives is comparable to that of MAMA derivatives and considerably greater than other reagents (e.g. approximately 30 times more intense than that of tryptamine derivatives). The compound-to-compound variability in fluorescence response has been found to be smaller than that of MAMA derivatives but larger than that of tryptamine derivatives (MAMA = 59 % coefficient of variation, MAP = 33 % coefficient of variation, and tryptamine = 16 % coefficient of variation for 5 model isocyanates). The compound-to-compound fluorescence variability of MAP derivatives is considered too great for accurate quantification of non-monomeric isocyanate species based on calibration with monomer standards. However, the sensitivity of the fluorescence detection makes it especially suitable for quantification of low levels of monomer, and the selectivity is very useful to designate an unidentified HPLC peak as a MAP derivative. MAP derivatives also give a strong response by electrochemical detection. The pH gradient used in the HPLC analysis selectively accelerates the elution of amines (MAP derivatives are amines) and is very strong (it accelerates MDI more than 100-fold). Re-equilibration to initial conditions is almost immediate. Many oligomeric species can be measured in the 30 min MAP analysis that may be unobservable in a much longer isocratic analysis.

MAP has been used in several studies comparing it side-by-side with other methods. Reference [9] found MAP impingers and NIOSH 5521 impingers (comparable to MDHS 25) to give comparable results in spray painting environments. Reference [9] used MAP reagent, but the pH gradient was not employed. Reference [10] compared MAP impingers with several other impinger methods (NIOSH 5521 and NIOSH 5522) and the double filter method. The average MAP oligomer value was substantially higher than the other impinger methods and slightly higher than the double filter method. The pH gradient was used in these MAP analyses. Reference [11] found that the MAP oligomer results compared favourably against several other methods for measurement of oligomeric isocyanates in the collision repair industry, and agreed well with the reference values.

The MAP method is currently available as NIOSH Method 5525[12]. The performance characteristics of the method have been evaluated in Reference [13].

Workplace atmospheres — Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl) piperazine (MAP) reagent and liquid chromatography

1 Scope

This document specifies a method for the sampling and analysis of airborne organic isocyanates in workplace air.

This document is applicable to a wide range of organic compounds containing isocyanate groups, including monofunctional isocyanates (e.g. phenyl isocyanate), diisocyanate monomers [e.g. 1,6-hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4′-diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI)], prepolymers (e.g. the biuret and isocyanurate of HDI), as well as chromatographable intermediate products formed during production or thermal breakdown of polyurethane.

In mixed systems of HDI and IPDI products, it is impossible to identify and quantify low levels of IPDI monomer using this document, due to coelution of IPDI monomer with HDI-uretidinedione.

It is known that the method underestimates the oligomer in MDI-based products. Total isocyanate group (NCO) is underestimated in MDI-based products by about 35 % as compared to dibutylamine titration.

The method has been successfully modified to be used with LC-MS-MS for TDI monomer using an isocratic 70 % acetonitrile/30 % 10 mM ammonium formate mobile phase.

The useful range of the method, expressed in moles of isocyanate group per species per sample, is approximately 1×10^{-10} to 2×10^{-7}. The instrumental detection limit for the monomers using both ultraviolet (UV) detection and fluorescence (FL) detection is about 2 ng monomer per sample. The useful limit of detection for the method using reagent impregnated filters is about 10 ng to 20 ng monomer per sample for both UV and FL detection. For a 15 l sample, this corresponds to 0,7 µg/m^{-3} to 1,4 µg/m^{-3}. For impinger samples, which require solid phase extraction, experience has shown that the useful limit of detection is about 30 ng to 80 ng monomer per sample.

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.

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

3 Terms and definitions

No terms and definitions are listed in this document.

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

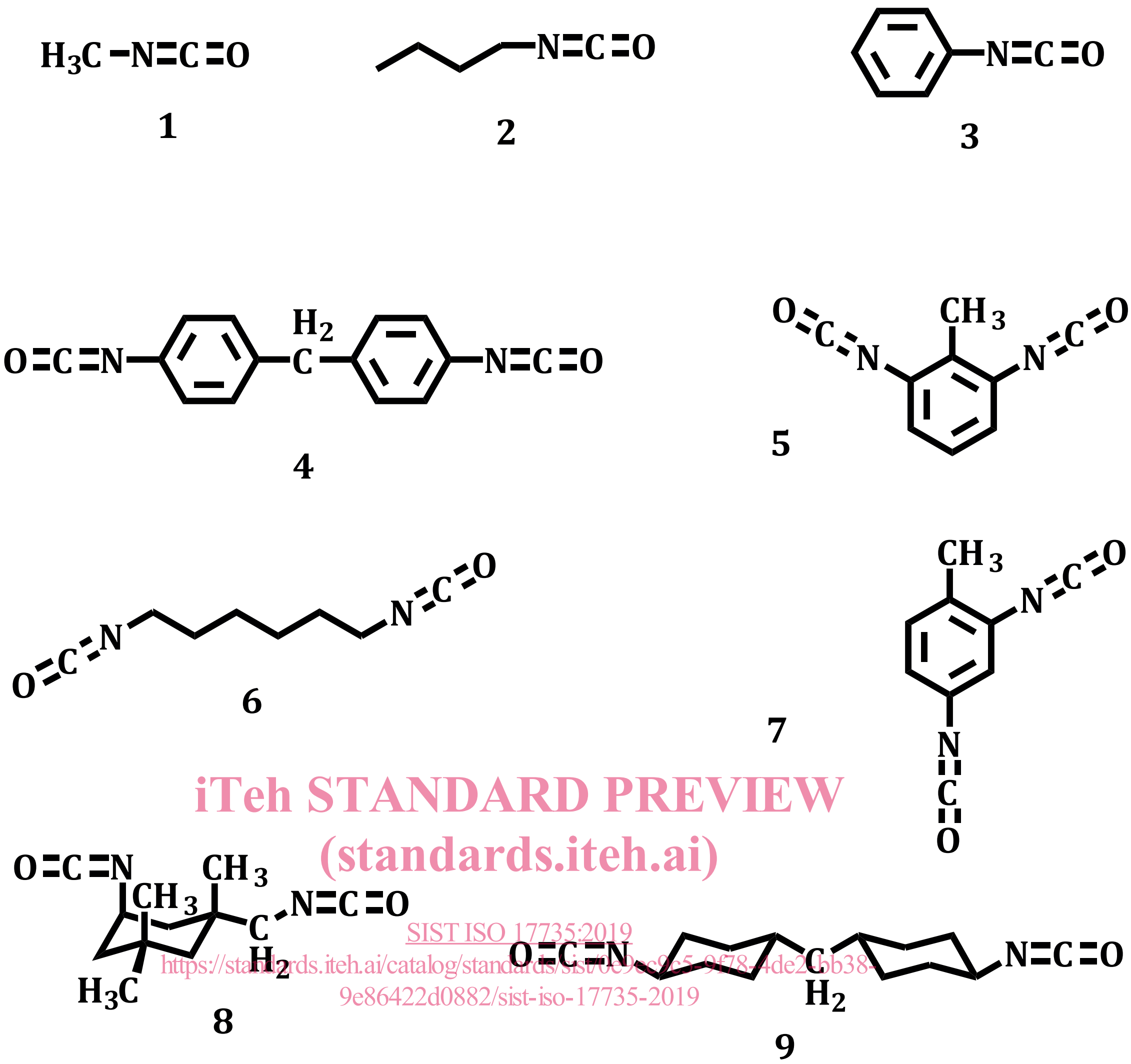
— ISO Online browsing platform: available at https://www.iso.org/obp

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

4 Principle

A measured volume of air is drawn through either an impinger containing a solution of 1-(9-anthracenylmethyl)piperazine (MAP), a filter impregnated with MAP, or a sampling train consisting of an impinger followed by an impregnated filter. The choice of sampler depends on the chemical and physical characteristics of the airborne isocyanate[14]. If an impinger is used, the solution is subjected to solid-phase extraction (SPE) and the eluate is concentrated and analysed by reverse phase high performance liquid chromatography (HPLC) with ultraviolet (UV) absorbance and fluorescence (FL) detection in series. If an impregnated filter is used for sampling, it is extracted with solvent either in the field after completion of sampling or in the laboratory. Waiting to extract the filter until after the sample has been received by the analytical laboratory is acceptable only for analysis of isocyanates collected as vapour. This solution is filtered and analysed by HPLC/UV/FL. Isocyanate-derived peaks are identified based on their UV and FL responses and by comparison with the chromatogram of a derivatized bulk isocyanate product if available. Quantification of compounds for which analytical standards are available (generally monomers) is achieved by comparison of the FL peak height of the sample peak with the FL peak height of standard matching solutions. Quantification of compounds for which analytical standards are not available is achieved by comparison of the UV area of the sample peak with the UV area of the appropriate monomer standard (i.e. the monomer from which the isocyanate product is derived).

Structures of some common diisocyanate monomers are shown in Figure 1.



Key

1	methyl isocyanate	6	HDI
2	butyl isocyanate	7	2,4-TDI
3	phenyl isocyanate	8	IPDI
4	4,4′-MDI	9	hydrogenated MDI (HMDI)
5	2,6-TDI		

Figure 1 — Structures of some common isocyanates

5 Reagents and materials

CAUTION — Observe appropriate safety precautions when preparing reagents. Carry out preparations under a fume hood to avoid exposure to solvents, isocyanates or other volatile reagents. Wear chemical protective gloves when manipulating reagents and solvents.

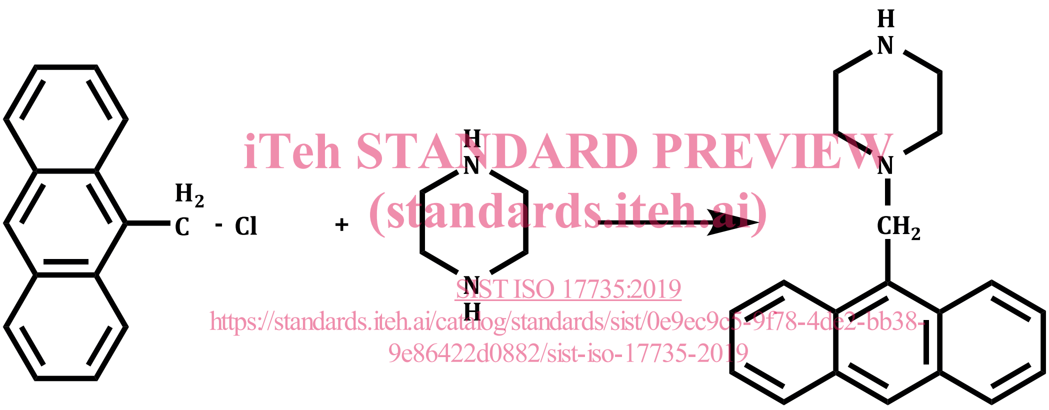
5.1 General

During the analysis, unless otherwise stated, use only reagents of HPLC grade or better, and water of HPLC grade. The following list of reagents are used for the below procedures and for the procedures in Clauses 6 and 7: 9-(chloromethyl)anthracene, 1,6-hexamethylene diisocyanate, 4,4′-methylenebis(cyclohexyl isocyanate), 4,4′-methylenebis(phenyl isocyanate), acetic anhydride, acetonitrile, butyl benzoate, dichloromethane, dimethyl formamide, ethyl acetate, formic acid, hexane, hydrochloric acid, isophorone diisocyanate, methanol, nitric acid, non-chromate/concentrated sulfuric acid-based cleaning solution, phosphoric acid, piperazine, prepurified nitrogen compressed gas, toluene, tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, and triethylamine.

The following materials are used for the below procedures and for the procedures in Clauses 6 and 7: amber jars with polytetrafluoroethylene (PTFE)-lined caps, Büchner funnel, cool packs, cooler, disposable glass vials (7 ml and 20 ml, PTFE-lined caps), dropping funnel, filter holder (open- or closed-face 37 mm polystyrene cassettes, 13 mm polypropylene cassettes), filter paper, glass chromatography column (short), glass fibre filter (37 mm or 13 mm, binder-free), magnetic stirring bar, nylon filter (0,45 µm), round-bottomed flasks (250 ml two-necked; 100 ml one-necked; 1 000 ml one-necked), separating funnel, silica gel (high-purity grade, 60 Å, 70-230 mesh), SPE tubes (normal phase silica gel, 6 ml/500 mg), syringe barrel (empty, polypropylene), syringe filter (0,45 µm PTFE), TLC plates (green fluorescing F_{254} or blue fluorescing F_{254s}), tubing (fluoroelastomer and plastic, rubber, or other suitable material 900 mm long), volumetric flask (10 ml one-mark, ISO 1042:2004, Class A), wax bath.

5.2 MAP reagent

5.2.1 MAP is prepared by the reaction of 9-(chloromethyl)anthracene with piperazine as shown in Figure 2. The procedure is as shown in 5.2.2 to 5.2.12.



1 2 3

Key

1 9-(chloromethyl)anthracene

2 piperazine

3 MAP

Figure 2 — Preparation of MAP

5.2.2 Dissolve 10,8 mmol (2,47 g) of 9-(chloromethyl)anthracene (98 % mass fraction) in 25 ml dichloromethane. Place this solution in a dropping funnel.

5.2.3 Dissolve 54,4 mmol (4,69 g) of piperazine (99 % mass fraction) and 21,8 mmol (3,04 ml) of triethylamine (99,5 % mass fraction) in 37 ml dichloromethane. Place this solution in a 250 ml two-necked round-bottomed flask with a magnetic stirring bar.

5.2.4 While stirring this solution, add the 9-(chloromethyl)anthracene solution dropwise over a 30 min period. Rinse down the dropping funnel with an additional 10 ml of dichloromethane. Allow the reaction to continue while stirring for at least 2 h.

5.2.5 Using a separating funnel, wash the reaction mixture three times with 130 ml water by shaking vigorously for 1 min. Discard the emulsion that forms after the first wash, which contains primarily an impurity and not MAP. Discard the aqueous washings.

