International Standard

ISO 16702

Workplace air — Determination of total organic isocyanate groups in air using 1-(2-methoxyphenyl) piperazine and liquid chromatography

Air des lieux de travail — Dosage des groupements isocyanates organiques totaux dans l'air par dérivatisation avec la 1-(2-méthoxyphényl)pipérazine et par chromatographie en phase liquide

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Contents

Page

Foreword ..... **v**
Introduction ..... **vi**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Principle **2**
5 Reagents **3**
6 Apparatus **3**
7 Reagent and calibration solutions **5**
7.1 Reagent solutions 5
7.1.1 Absorbing solution 5
7.1.2 Preparation of solution for impregnating filters (solution A) 5
7.1.3 Stability of reagent solutions 5
7.2 Calibration standards 5
7.2.1 Preparation of monomer derivatives 5
7.2.2 Alternative procedure for the less soluble isocyanate derivatives 5
7.2.3 Preparation of standard solutions of recrystallised isocyanate monomer derivatives 5
7.2.4 Stability of isocyanate ureas and their solutions 6
7.3 HPLC mobile phase 6
7.3.1 General 6
7.3.2 Preparation of "slow" mobile phase 6
7.3.3 Preparation of "fast" mobile phase 6
7.4 Calibration blend atmosphere 6
8 Sampling **7**
8.1 Calibration of pump 7
8.2 Sampling duration 7
8.3 Preparation of sampling equipment 7
8.3.1 General 7
8.3.2 Preparation of impregnated filters 7
8.3.3 Preparation of sampling devices (filters) 7
8.3.4 Preparation of impingers 7
8.4 Collection of filter samples (vapour phase samples) 7
8.4.1 Set-up of filter samplers 7
8.4.2 Collection of filter samples 8
8.5 Collection of impinger backed by filter samples (isocyanate aerosols) 8
8.5.1 Rationale for impinger backed by filter sampling 8
8.5.2 Recommended sampling rate for impinger backed by filter 8
8.6 Measurements to be made at the end of the sampling period 8
8.7 Sample logging and field desorption of samples 8
8.8 Transportation 9
8.8.1 Transportation of filter samples 9
8.8.2 Transportation of impinger samples 9
8.9 Field blanks 9
9 Analytical methods **9**
9.1 Safety precautions 9
9.2 Cleaning of glassware 9
9.3 Prereaction of impinger samples before HPLC analysis 9
9.4 Prereaction of filter samples before HPLC analysis 9
9.5 HPLC conditions 10
9.5.1 Choice of HPLC conditions 10

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9.5.2 Optimising the HPLC analysis 10
9.6 Determination of airborne isocyanate for monomeric isocyanates (UV detection) 11
9.7 Identification of polymeric isocyanates: EC:UV ratio approach 11
9.8 Confirmation of identification for polymeric isocyanates 12
9.8.1 Analysis of a bulk sample 12
9.8.2 Confirmation of identity using a diode array detector 12
9.8.3 Confirmation of identity using other techniques 12
9.9 Quantification of airborne isocyanate for polymeric isocyanates (EC detection) 13
9.10 Sampling efficiency 13
10 Calculations **13**
11 Interferences **14**
12 Uncertainty of measurement **14**
12.1 Overview 14
12.1.1 General 14
12.1.2 Summary of approach 14
12.1.3 Summary of calculated uncertainty data 14
12.2 Assessment of performance characteristics of the method — Sampling considerations (detailed ISO/IEC Guide 98-3:2008 approach) 15
12.2.1 Collection efficiency relative to particle size distribution 15
12.2.2 Sampled volume of air 15
12.2.3 Sampling time 15
12.2.4 Variations in flow rate during sampling 16
12.2.5 Concentration conversion to other specified temperature and pressure conditions 16
12.2.6 Combined uncertainty of sample volume 16
12.3 Assessment of performance characteristics of the method — Other considerations (detailed approach) 17
12.3.1 Mass of compound in sample 17
12.3.2 Analyte stability 17
12.3.3 Reaction and extraction efficiency 17
12.3.4 Uncorrected analytical mass of compound 18
12.3.5 Calibration standards 18
12.3.6 Lack-of-fit of calibration function 19
12.3.7 Drift in detector response 19
12.3.8 Precision of the analysis 19
12.3.9 Analytical selectivity 20
12.3.10 Combined uncertainty in the analytical mass of compound 20
12.3.11 Combined uncertainty in the sampled mass of compound 20
12.4 Mass of compound in field sample blank 20
12.5 Between-laboratory uncertainty contributions 21
12.6 Combined uncertainty 21
12.7 Expanded uncertainty 21
13 Stability **21**
14 Test report **21**
15 Quality control **22**
Annex A (informative) **Determination of sampling efficiency** **23**
Annex B (informative) **Data used for uncertainty estimates** **24**
Annex C (informative) **Combined uncertainties for isocyanate formulations** **25**
Annex D (informative) **Sample chromatograms** **27**
Bibliography **32**

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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 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).

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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 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

This third edition cancels and replaces the second edition (ISO 16702:2007), which has been technically revised.

The main changes are as follows:

— the references have been reviewed and updated, and obsolete references have been removed or replaced where appropriate;

— the Introduction and the Scope have been revised to conform with current ISO editorial requirements and to improve clarity on the applicability of the method;

— minor technical changes have been made, including the harmonization of common names of chemical compounds;

— additional information has been added on the use of impingers for sampling isocyanates (Clause 4);

— a note on the requirement to record the final volume of toluene has been introduced (8.8.2);

— examples of suitable internal standards have been added (9.9).

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.

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Introduction

Isocyanates are organic compounds containing the isocyanate functional group (-NCO) and are widely used in industrial applications such as the manufacture of polyurethanes, paints, coatings, foams, plastics and adhesives. They are highly reactive substances and are well-established respiratory sensitisers, representing a major cause of chemically induced occupational asthma. Occupational exposure can occur primarily by inhalation and, potentially, by skin contact.

Occupational exposure limits for isocyanates have been established in several countries and are generally expressed in terms of total isocyanate, defined as the sum of monomeric and polymeric isocyanates, including oligomeric and prepolymeric forms. These limits are specified as long-term (8 h time-weighted average) and short-term (15 min) exposure limits and require analytical methods capable of determining total isocyanate groups in workplace air.

The sampling and analysis of airborne isocyanates present particular challenges due to the diversity of chemical structures, molecular masses and physical forms encountered in workplace atmospheres. Isocyanates can be present as vapours, aerosols or liquids and often occur as mixtures of monomers, oligomers and polymers. Other airborne substances, such as water vapour, dust, amines and alcohols, can also be present and can interfere with analytical determination. In addition, reference standards for many polymeric isocyanates are currently not available, despite their contribution to total isocyanate exposure.

Because of the high reactivity of the isocyanate functional group, workplace air monitoring is commonly based on derivatisation techniques that convert isocyanates into more stable compounds suitable for analysis. The method described in this document is based on derivatisation with 1-(2-methoxyphenyl) piperazine (MP), forming stable urea derivatives that are analysed by liquid chromatography with electrochemical and ultraviolet and visible detection. The analytical approach was established[1] using widely used industrial diisocyanates, such as methylene diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI), and toluene diisocyanate (TDI), together with their associated oligomeric and polymeric forms. It has subsequently been applied to a broader range of organic isocyanates containing free isocyanate groups e.g. phenylisocyanate (PI), isophoronediisocyante (IPDI), naphthyldiisocyante (NDI), hydrogenated methylene diphenyl diisocyanate (H12MDI) and butylisocyanate.

If both isocyanates and amines are present and need to be determined, a standard capable of simultaneous determination of both classes of compounds can be more appropriate (see ISO 17734-2[2]). This method has also been modified for the determination of monoisocyanates produced during thermal degradation,[3] for the use of mass spectrometric detection,[4] and for alternative sampling equipment, such as 37 mm filters and other filter holders; however, these modifications are not covered by this document. When using a modified version of this method, it is the responsibility of the user to demonstrate the validity of the modifications.

Sampling approaches depend on the physical form of the isocyanates present. Filters are suitable for the collection of vapour-phase isocyanates, while combined impinger and filter arrangements are used for aerosol sampling. The method has been applied to commonly occurring mono- and diisocyanates and to polymeric isocyanates derived from these monomers.

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Workplace air — Determination of total organic isocyanate groups in air using 1-(2-methoxyphenyl)piperazine and liquid chromatography

1 Scope

This document specifies a test method for the sampling and analysis of airborne organic isocyanate (NCO) compounds in workplace air. The method covers organic compounds containing free isocyanate functional groups, including monomeric, oligomeric, prepolymeric and polymeric isocyanates, and addresses the measurement of total isocyanate groups in air samples collected for the assessment of occupational exposure.

The method is suitable for personal air sampling in the breathing zone for the determination of time-weighted average concentrations over sampling periods ranging from approximately 10 min to 8 h, although it can be applied to shorter sampling periods with high isocyanate air levels. It can also be used for background or fixed-location air sampling; however, due to aerodynamic effects, samplers designed for personal sampling do not necessarily exhibit the same collection characteristics when used for other purposes. It covers the measurement of airborne organic isocyanates over a concentration range of approximately 0,1 $\mu g/m^3$ to 140 $\mu g/m^3$ for a nominal air sample volume of 15 l; under the conditions specified in this document, typical qualitative and quantitative detection limits correspond to approximately 0,07 $\mu g/m^3$ and 0,3 $\mu g/m^3$, respectively, for a 15 l air sample.

This document does not apply to the simultaneous determination of isocyanates and amines, nor to modified methods employing alternative sampling devices or detection techniques not described in this document.

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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 13137, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

EN 1540, *Workplace exposure – Terminology*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158, EN 1540 and the following 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/

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3.1
bulk isocyanate material
isocyanate (3.3) based product supplied in bulk form and used in a manufacturing or processing operation

3.2
diisocyanate
chemical compound with two *isocyanate* (3.3) functional groups

3.3
isocyanate
chemical compound with one or more isocyanate (nitrogen carbon oxygen) functional groups

3.4
monomer
chemical compound that joins with other identical compounds to form dimers, trimers, *oligomers* (3.5) or polymers

Note 1 to entry: Classes of isocyanate monomers include: monoisocyanates, containing one isocyanate functional group, e.g. methyl isocyanate; *diisocyanates* (3.2), e.g. di(4-isocyanatophenyl)methane (MDI); and triisocyanates, e.g. tri(4-isocyanatophenyl)methane.

3.5
oligomer
compound of low relative molecular mass with multiple *isocyanate* (3.3) functional groups, formed by the combination of isocyanate *monomers* (3.4)

3.6
prepolymer
isocyanato-terminated reaction product of a *diisocyanate* (3.2) or polyisocyanate with a stochiometric deficiency of a hydroxyl-terminated polyol

Note 1 to entry: When used in the workplace, these prepolymers then react further to form polyurethanes or similar compounds

3.7
uncertainty
parameter, associated with the result of a measurement, that characterises the dispersion of the values that can reasonably be attributed to the measurand

Note 1 to entry: The parameter can be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

Note 2 to entry: Uncertainty of measurement comprises, in general, many components. Some of these components can be evaluated from the statistical distribution of the results of series of measurements and can be characterised by standard deviations. The other components, which can also be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information. This is often referred to as type A and type B evaluations of uncertainty, respectively.

4 Principle

The selection of the sampling arrangement in this method is determined by the physical state of the isocyanate being monitored. When sampling isocyanate aerosols, air is drawn through a glass impinger containing a solution of 1-(2-methoxyphenyl)piperazine (MP), followed by an MP-impregnated backup filter. In contrast, for isocyanates present in the vapour phase, sampling may be carried out using an MP-impregnated filter alone.

Impingers provide more efficient collection than filters when isocyanates are present in the aerosol phase. Nevertheless, very fine particles, particularly those smaller than 1 µm, might not be fully retained by an impinger,[5,6] and a so a treated downstream filter is required.[7] Sampling methods based solely on filters can lead to underestimation of exposure where larger particles (greater than 10 µm) are present or under

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