



SLOVENSKI STANDARD
SIST ISO 17734-1:2013

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Določevanje organskih dušikovih spojin v zraku s tekočinsko kromatografijo in masno spektrometrijo - 1. del: Določevanje izocianatov preko derivatov dibutilamina

Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry - Part 1: Isocyanates using dibutylamine derivatives

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Détermination des composés organiques azotés dans l'air par chromatographie liquide et spectrométrie de masse - Partie 1: Isocyanates par les dérivés de la dibutylamine

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INTERNATIONAL STANDARD

ISO 17734-1

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2006-03-01

Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry —

Part 1: Isocyanates using dibutylamine derivatives

*Détermination des composés organiques azotés dans l'air par
chromatographie liquide et spectrométrie de masse —
Partie 1: Isocyanates par les dérivés de la dibutylamine*



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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 17734-1 was prepared by Technical Committee ISO/TC 146, *Air Quality*, Subcommittee SC 2, *Workplace Atmospheres*.

ISO 17734 consists of the following parts, under the general title *Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry*:

- Part 1: *Isocyanates using dibutylamine derivatives*
- Part 2: *Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives*

Introduction

Isocyanates have been used in industry for about 50 years. They are commercially important chemicals mainly used for the production of polyurethane (PUR). In spite of controls to limit exposures, there are adverse health effects such as asthma, contact dermatitis and hypersensitivity pneumonitis as a consequence of exposure to isocyanates in some industrial sectors.

The analytical method for the determination of isocyanates in workplace air must be sensitive due to the high irritation and sensitization properties of isocyanates. Extremely low occupational exposure limits (OELs) exist in many countries, and concentrations well below the OEL ($< 1/100$) often must be determined. Isocyanates are very reactive and therefore cannot be analysed directly. Derivatization during sampling is required in order to prevent interfering reactions. Hundreds of different isocyanates are used in industry, and many more are formed during thermal degradation of PUR. Therefore the analytical method must be highly selective.

The determination of isocyanates in the work environment using di-*n*-butylamine (DBA) as a reagent and liquid chromatography-mass spectrometric detection (LC-MS) has been demonstrated to be a robust method. The development of the method was initiated when difficulties using the “older” methods during sampling of isocyanates in complex atmospheres were encountered (e.g. thermal decomposition of PUR) [1], [2], [3]. The reaction rate between DBA and isocyanates was found to be fast, and high concentrations can be used to secure instantaneous reactions and eliminate problems with interfering compounds [4], [5]. Using impinger flasks containing a reagent solution and a filter in series efficiently collects and derivatizes isocyanates in both the gas and the particle phase [6]. LC-MS/MS of the isocyanate-DBA derivatives enables highly selective and precise determinations down to levels below 10^{-6} of the OEL [7].

Solvent-free sampling can also be performed by using a tube coated with a DBA-impregnated glass fibre filter followed by an impregnated filter. An impregnation solution containing DBA together with an acid is used, and the formed ion pair reduces volatility. DBA remains on the filter even after 8 h of sampling [8].

Monomeric isocyanates that are formed during thermal decomposition of polymers [typically PUR and phenol/formaldehyde/urea (PFU)-resins], such as isocyanic acid and methyl isocyanate, can also be determined [6], [7], [8], [9], [10]. Volatile isocyanate DBA derivatives can be determined using gas chromatography (GC)-MS [9]. Using the DBA-method and derivatization with ethyl chloroformate makes simultaneous determinations of amine, aminoisocyanates and isocyanates possible, as described in the companion method ISO 17734-2.

For quantification, reference compounds are necessary but are only available for a few monomeric isocyanates. Most of the isocyanates that are used in industry for the production of PUR can only be obtained in technical grade mixtures. Many isocyanates that are formed during thermal degradation are not available and are not easily synthesized. In this method, a nitrogen sensitive detector has been used for quantifying isocyanates in reference solutions. This technique has been demonstrated to be a useful tool, together with MS characterization, in greatly facilitating the production of reference solutions [10], [11], [12].

For quantifying isocyanates in complex mixtures, MS detection is necessary and provides a unique possibility of identifying unknown compounds. This method has enabled assessment of new areas for which exposure to isocyanates previously was not known and has identified new kinds of isocyanates in the work environment [6], [7], [8], [9], [10], [11], [12].

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Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry —

Part 1: Isocyanates using dibutylamine derivatives

1 Scope

This part of ISO 17734 gives general guidance for the sampling and analysis of airborne isocyanates in workplace air. When amines and aminoisocyanates are suspected to be emitted (e.g. from thermal degradation of PUR), it is recommended that in addition to isocyanates the amines and aminoisocyanates in air are determined, using DBA and ethyl chloroformate as reagents (ISO 17734-2).

The method is suitable for the determination of a wide range of different isocyanates in both the gas and particle phases. Typical monofunctional isocyanates that can be determined are isocyanic acid (ICA), methyl isocyanate (MIC), ethyl isocyanate (EIC), propyl isocyanate (PIC), butyl isocyanate (BIC), and phenyl isocyanate (PhI). Typical monomeric diisocyanates include 1,6-hexamethylene- (HDI), 2,4- and 2,6-toluene- (TDI), 4,4'-diphenylmethane- (MDI), 1,5-naphthyl- (NDI), isophorone- (IPDI), and 4,4'-dicyclohexylmethane diisocyanate (HMDI). Multifunctional isocyanates that can be determined are typically oligomers in polymeric MDI, biuret-, isocyanurate-, and allophanate-adducts and prepolymeric forms of isocyanates.

The instrumental detection limit for aliphatic isocyanates is about 50 fmol and for aromatic isocyanates, it is 2 fmol. For a 15-l air sample, this corresponds to 0,6 ng·m⁻³ for HDI and 0,02 ng·m⁻³ for TDI.

The useful range, for a 5-l air sample, of the method is approximately 0,001 µg·m⁻³ to 200 mg·m⁻³ for TDI.

2 Normative references

The following referenced documents are indispensable for the application 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 16200-1:2001, *Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography — Part 1: Pumped sampling method*

ISO 5725-2:1994, *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* (including Technical Corrigendum 1:2002)

3 Principle

Samples are collected by drawing a known volume of air through a midjet impinger flask followed by a filter. The impinger contains 10 ml of 0,01 mol l⁻¹ of DBA in toluene and the filter is a glass fibre filter with no binder.

Solvent-free sampling can also be performed by drawing air through a tube coated with a DBA-impregnated glass fibre filter followed by an impregnated filter. An impregnation solution containing DBA together with acetic acid is used, the ion pair so formed reducing the volatility and enabling long-time sampling.

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After sampling, deuterium-labelled DBA-isocyanate derivatives (used as internal standard) are added to the sample solutions. The excess reagent and solvent are evaporated, and the samples are dissolved in acetonitrile. The samples are analysed using reversed-phase LC and electrospray (ESP)-MS detection, monitoring positive ions. Quantification is made by monitoring selected ions. See Figure 1.

Quantification and qualitative determinations can be performed using different LC-MS or LC-MS/MS techniques. LC-CLND (chemiluminescent nitrogen detection) or for aromatic isocyanates LC-UV (ultraviolet detection) can be used for the determination of higher concentrations of isocyanates.

Reference materials can be characterized using LC-MS/CLND. For characterization of volatile compounds, GC-thermionic specific detector (TSD) can also be used.

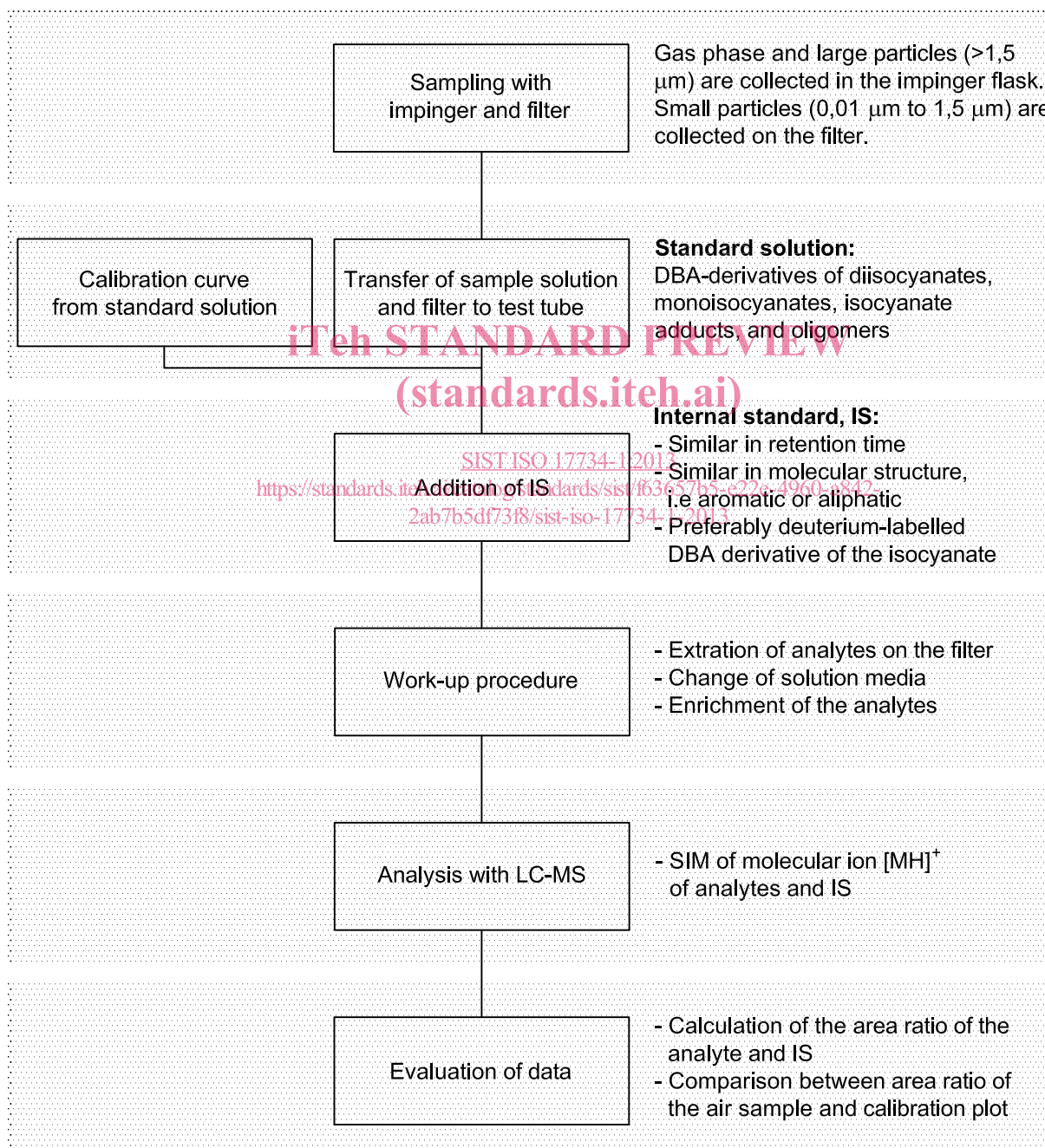


Figure 1 — Principle of the described method

4 Reagents and materials

4.1 DBA reagent.

Analytical grade di-*n*-butylamine is commercially available.

4.2 Solvents.

The reagent solvent, typically toluene, and other solvents, acetonitrile, isooctane and methanol, should be of liquid chromatographic quality.

4.3 Formic acid, concentrated formic acid, analytical grade.

4.4 Acetic acid, concentrated acetic acid, analytical grade.

4.5 Reagent solution.

In a 1-l volumetric flask, dilute 1,69 ml of DBA in toluene, and make up to the mark. The solution is stable and no special care during storage is necessary.

4.6 Reagent solution for solvent-free sampler.

4.6.1 Solution 1: 0,74 mol l⁻¹ DBA.

Mix 80 ml methanol and 12,5 ml DBA in a 100 ml volumetric flask. Then while stirring, slowly add 4,16 ml of acetic acid to the flask. Finally, add methanol to the flask, and make up to the mark.

4.6.2 Solution 2: 1,5 mol l⁻¹ DBA.

Mix 60 ml methanol and 25 ml DBA in a 100 ml volumetric flask. Then while stirring, slowly add 8,32 ml of acetic acid to the flask. Finally, add methanol to the flask, and make up to the mark.

4.7 HPLC mobile phases.

4.7.1 LC-MS.

The weak mobile phase (mobile phase A) consists of water/acetonitrile (95/5 volume fraction) and 0,05 % formic acid. The strong mobile phase (mobile phase B) consists of water/acetonitrile (5/95 volume fraction) and 0,05 % formic acid. The mobile phases are degassed prior to use.

4.7.2 LC-CLND.

The weak mobile phase (mobile phase C) consists of water/methanol (95/5 volume fraction) and 0,05 % formic acid. The strong mobile phase (mobile phase D) consists of water/methanol (5/95 volume fraction) and 0,05 % formic acid. The mobile phases are degassed prior to use.

5 Preparation of standard solutions

5.1 Reference compounds

Reference compounds are necessary for LC-MS determination of isocyanate derivatives. For the commercially available isocyanates, the DBA derivatives are easily prepared by direct derivatization with DBA. DBA derivatives for the isocyanates not commercially available can be made from the bulk material or from the thermal decomposition of PUR or urea-based resins used at the work place. Alternatively, standard solutions can be purchased.

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5.2 Di-*n*-butylamine (DBA) derivatives of isocyanates

5.2.1 Preparation of isocyanate-DBA derivatives of commercially available isocyanates

Many frequently used isocyanates are commercially available from companies supplying laboratory chemicals such as HDI, 2,4- and 2,6-TDI, 4,4'-MDI, 4,4'-HMDI, 1,5-NDI, IPDI, PHI, MIC, EIC, PIC and BIC. The purity of the isocyanates varies, and some contain isomers.

Calibration standards are made by spiking accurately weighed amounts or volumes (ca 0,1 mmol) of isocyanates in 100 ml of isooctane. A 1-ml volume is added to 100 ml of toluene containing 0,01 mol·l⁻¹ of DBA (ca 0,01 μmol·ml⁻¹ of the DBA derivative).

Synthesis of derivatives:

- Dilute 6 mmol of isocyanate in 2 ml of isooctane, and dissolve 60 mmol of DBA in 20 ml of isooctane.
- Add the isocyanate solution to the DBA solution dropwise under continuous stirring.
- Evaporate the reaction mixture to dryness in a rotating evaporator, and dry the residue under vacuum to remove excess DBA.

It is also possible to prepare the isocyanate-DBA derivatives by collecting thermal degradation products of corresponding carbamate esters in an impinger flask containing DBA solution (as in 5.2.3.3).

5.2.2 Preparation of ICA and MIC-DBA

When urea is thermally degraded, isocyanic acid (ICA) is formed.

Heat an amount of urea (20 mg) to about 300 °C in a glass tube. Collect the degradation products in an impinger flask containing DBA in toluene (0,5 mol·l⁻¹). Wash the toluene solution containing the ICA-DBA derivatives with water, whereupon the organic phase is evaporated in a vacuum centrifuge and the residue is dissolved in methanol. Characterize the solution as described in 5.2.4.

The same procedure can be applied for preparation of MIC-DBA derivatives, by collecting thermal degradation products of 1,3-dimethyl urea.

5.2.3 Preparation of deuterium-labelled isocyanate-DBA derivatives

5.2.3.1 Internal standards

For accurate LC-MS quantifications, it is important to use proper internal standards, not only to compensate for variations during the work-up procedure, but also to compensate for fluctuation in the MS instrument response. Ideally, each analyte should have its own deuterium-labelled analogue. For isocyanate-DBA determinations, it is possible to use DBA derivatives of deuterium-labelled isocyanates or d₉- and d₁₈-DBA derivatives of the isocyanates as internal standards.

The quality of the quantification is influenced by the number of deuterium substitutions in the internal standard (less deuterium in the molecule resulting in higher precision). Having the deuterium on the isocyanate, and not on the DBA, has advantages when performing structural identification using MS and MS/MS. It is then possible to distinguish between labelled and non-labelled fragments that originate from the isocyanate itself. Therefore, the ideal internal standards are the DBA derivatives of the deuterium-labelled isocyanates. However, they are labour intensive to prepare, and they are only available for a few isocyanates.

The deuterium-labelled d₉- and d₁₈-DBA derivatives are easy to prepare, and any technical isocyanate or thermal degradation product can be derivatized and used as internal standard.