BS ISO 17734-2:2013

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

Part 2: Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives

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National foreword

This British Standard is the UK implementation of ISO 17734-2:2013. It supersedes BS ISO 17734-2:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/2, Work place atmospheres.

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INTERNATIONAL STANDARD

ISO 17734-2

Second edition
2013-12-01

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

Part 2: Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives

Détermination des composés organiques azotés dans l'air par chromatographie liquide et spectrométrie de masse —

Partie 2: Amines et aminoisocyanates par les dérivés de la dibutylamine et du chloroformate d'éthyle

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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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

This second edition of ISO 17734-2 cancels and replaces ISO 17734-2:2006, which has been technically revised.

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*

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Introduction

In many applications, when considering isocyanates as a workplace contaminant, there is also a need to investigate the presence of aminoisocyanates and amines. During thermal decomposition of polyurethane (PUR), not only isocyanates, but also amines and aminoisocyanates, are formed.[1][2][3][4][5][6]

The determination of isocyanates in the work environment using DBA as a reagent has been demonstrated to be a robust method (see ISO 17734-1). Using the DBA method and derivatization with ethyl chloroformate in the following work-up procedure makes simultaneous determination of amines, aminoisocyanates, and isocyanates possible.[6][7]

For quantification of amine and aminoisocyanate derivatives, reference compounds are necessary, but are only available for a few diamines. Aminoisocyanates cannot be analysed directly because they react with themselves. In this method, a nitrogen-specific detector has been used for quantification of amine and aminoisocyanate derivatives 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.[6]

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INTERNATIONAL STANDARD ISO 17734-2:2013(E)

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

Part 2: Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives

1 Scope

This part of ISO 17734 gives general guidance for the sampling and analysis of airborne amines and aminoisocyanates in workplace air. It is strongly recommended that the determination of amines and aminoisocyanates is made together with the determination of isocyanates in air, using DBA as a reagent (see ISO 17734-1).

The method can be used for simultaneous determinations of amines, such as 4,4'-methylenediphenyldiamine (4,4'-MDA), 2,4- and 2,6-toluenediamine (2,4- and 2,6-TDA), and 1,6-hexamethylenediamine (1,6-HDA), and compounds containing both isocyanate and amine groups, such as 4,4'-methylenediphenyl aminoisocyanate (4,4'-MAI), 2,4-, 4,2-, and 2,6-toluene aminoisocyanate (2,4-, 4,2-, and 2,6-TAI), and 1,6-hexamethylene aminoisocyanate (1,6-HAI). The method is suitable for collecting amines and aminoisocyanates in both the gas and particle phases. The instrumental detection limit for the amines is about 5 nmol/sample and for the aminoisocyanate, it is about 0,3 nmol/sample. For a 15 l air sample, this corresponds to 0,4 ng·m^{-3} for TDA and 0,03 ng·m^{-3} for TAI.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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, *Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography — Part 1: Pumped sampling method*

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*

3 Principle

The method permits the simultaneous sampling and analysis of amines, aminoisocyanates, and isocyanates. Only amines and aminoisocyanates are discussed in this part of ISO 17734, because isocyanates are considered in ISO 17734-1.

Samples are collected by drawing a known volume of air through a midget impinger flask followed by a filter. The impinger contains 10 ml of 0,01 mol·l^{-1} of di-*n*-butylamine (DBA) in toluene, and the filter is a glass fibre filter with no binder. After sampling, deuterium-labelled amine-ethyl chloroformate (ET) and isocyanate-DBA 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 liquid chromatography (LC) and electrospray (ESP) mass spectrometric (MS) detection, monitoring positive ions. Quantification is made by quantifying selected ions.

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

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

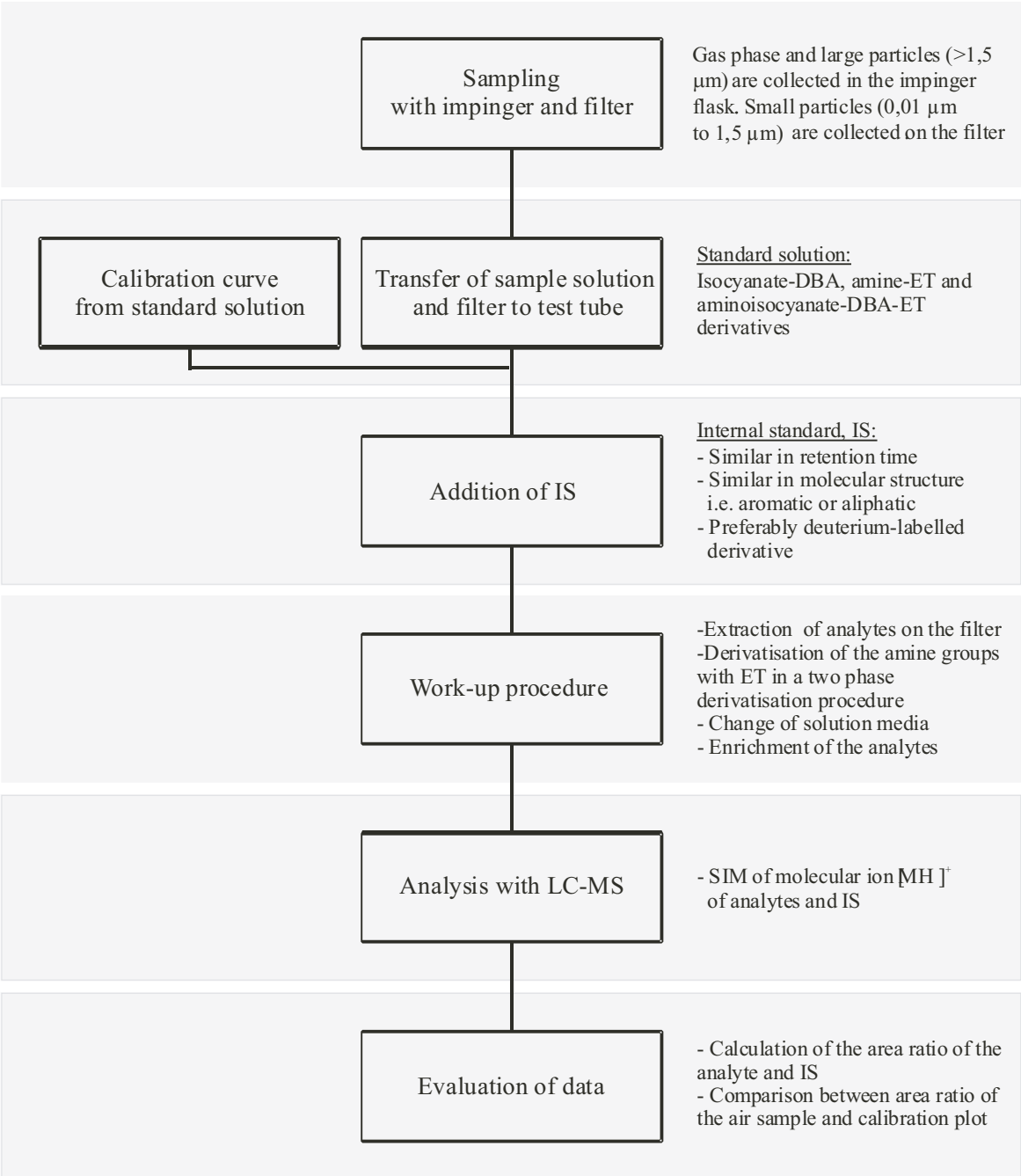

Figure 1 — Principle of the described method

4 Reagents and materials

4.1 DBA reagent.

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

4.2 Ethyl chloroformate reagent.

Analytical grade ethyl chloroformate is commercially available.

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4.3 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.

4.4 Sodium hydroxide, 5 mol·l^{-1}.

Dissolve 200 g of NaOH in water in a beaker, then transfer the solution to a 1 l volumetric flask and make up to the mark.

4.5 Pyridine, analytical grade.

4.6 Solvents.

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

4.7 Formic acid, concentrated formic acid, analytical grade.

4.8 Ethanol, absolute, extra pure 99,5 %.

4.9 HPLC mobile phases.

4.9.1 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/methanol (5/70/25 volume fraction) and 0,05 % formic acid. The mobile phases are degassed prior to use.

4.9.2 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 Standard solutions

5.1 Reference compounds

Reference compounds are necessary for LC-MS determination. For the commercially available amines, the ethyl chloroformate (ET) derivatives are easily prepared by direct derivatization with ET for use as calibration standards. The aminoisocyanate derivatives are prepared by reacting one of the isocyanate groups with DBA and the other group with ethanol. The mixed derivatives formed shall be characterized before use as calibration standards. Isocyanate, aminoisocyanate, and amine derivatives for compounds that are not commercially available can be made from the bulk material or from the thermal decomposition of PUR. Alternatively, standard solutions can be purchased.

5.2 Amine and deuterium-labelled amine derivatives

Calibration standards are made by spiking accurately weighed amounts (ca 0,1 mmol) of amines in 100 ml of toluene. The solution is further diluted to ca 0,01 µmol·ml^{-1}. 5 ml toluene solutions are spiked with volumes of the amine solutions appropriate for the construction of a calibration curve. The work-up procedure is then performed; this is described in 8.2.

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The procedure for the synthesis of derivatives is as follows.

1) Dissolve a 10 mmol aliquot of the amines and the deuterium-labelled amines in 20 ml of toluene. Thereafter, add 150 µl pyridine and 40 ml of 5 mol·l^{-1} NaOH. Then add 1,5 ml of ET dropwise under continuous stirring.

2) After 10 min, separate the toluene phase.

3) Evaporate the reaction mixture to dryness in a rotating evaporator, and dry the residue under vacuum.

5.3 Aminoisocyanate derivatives

5.3.1 Preparation

Two procedures, A and B, are used to enrich different mixed aminoisocyanate derivatives. The isocyanate groups in, for example, 2,4-TDI have different reactivity and two different derivatives can be formed.

In procedure A: Dissolve 0,5 mmol of the isocyanates (HDI, 2,4- and 2,6-TDI, and 4,4'-MDI) in 50 ml isooctane. Add 0,5 mmol of DBA dissolved in isooctane under continuous stirring to the isocyanate solutions. After 30 min, add excess ethanol to the solutions. Allow the mixtures to react for 16 h. Evaporate the solutions to dryness and dissolve in methanol.

In procedure B: Dissolve 0,5 mmol of the isocyanate (2,4-TDI) in 50 ml of isooctane; 0,5 mmol of ethanol dissolved in isooctane is added under continuous stirring to the isocyanate solution. After 16 h, excess DBA dissolved in isooctane is added to the solution. The solution is allowed to react for 1 h. The solution is evaporated under a gentle stream of nitrogen. The residue is dissolved in methanol.

The solutions are characterized as described in 5.3.2.

5.3.2 Characterization

Dilute the solutions in methanol to appropriate concentrations and characterize them on the LC-MS and quantify them on the LC-CLND. This technique is nitrogen specific and any nitrogen-containing compound (e.g. caffeine) can be used as external standard. The technique is used in several applications. [8][9][10]

5.4 Thermal decomposition products of polyurethane (PUR)

5.4.1 Preparation of mixed isocyanate, amine, and aminoisocyanate derivatives

During the thermal decomposition of PUR, isocyanates, aminoisocyanates, and amines are formed that are not commercially available. PUR-based material can be thermally decomposed at appropriate temperatures. Collect emitted degradation products in impinger flasks (filters in series) containing 0,5 mol·l^{-1} DBA and follow this by the work-up procedure described in 7.2. The solution is characterized as described in 5.4.2.

5.4.2 Characterization

Qualitative data are obtained with LC-MS. The obtained structural data together with the LC-CLND data make it possible to calculate the concentrations of different components in the solution. The characterized and diluted sample solution is used as a calibration standard for LC-MS.

5.5 Stability of the amine and aminoisocyanate derivatives

Solutions of amine-ET and ET-DBA-aminoisocyanate derivatives (MDA, 2,4- and 2,6-TDA, HDA, MAI, 2,4-, 4,2-, and 2,6-TAI, and HAI) have been found stable in toluene, acetonitrile, and methanol for 6 mo (stored in a dark fridge).

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