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

Part 2:

**Amines and aminoisocyanates using
dibutylamine and ethyl chloroformate
derivatives**

ISO 17734-2:2006

*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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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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 17734-2 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

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 (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 can not 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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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 (ISO 17734-1).

The method can be used for simultaneous determinations of amines, 4,4'-methylenediphenyldiamine (4,4'-MDA), 2,4- and 2,6-toluenediamine (2,4-, 2,6-TDA) and 1,6-hexamethylenediamine (1,6-HDA), and compounds containing both isocyanate and amine groups, 4,4'-methylenediphenyl aminoisocyanate (4,4'-MAI), 2,4-, 4,2- and 2,6-toluene aminoisocyanate (2,4, 4,2, 2,6-TAI), 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 50 fmol and for the aminoisocyanate, it is about 3 fmol. 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 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

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

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

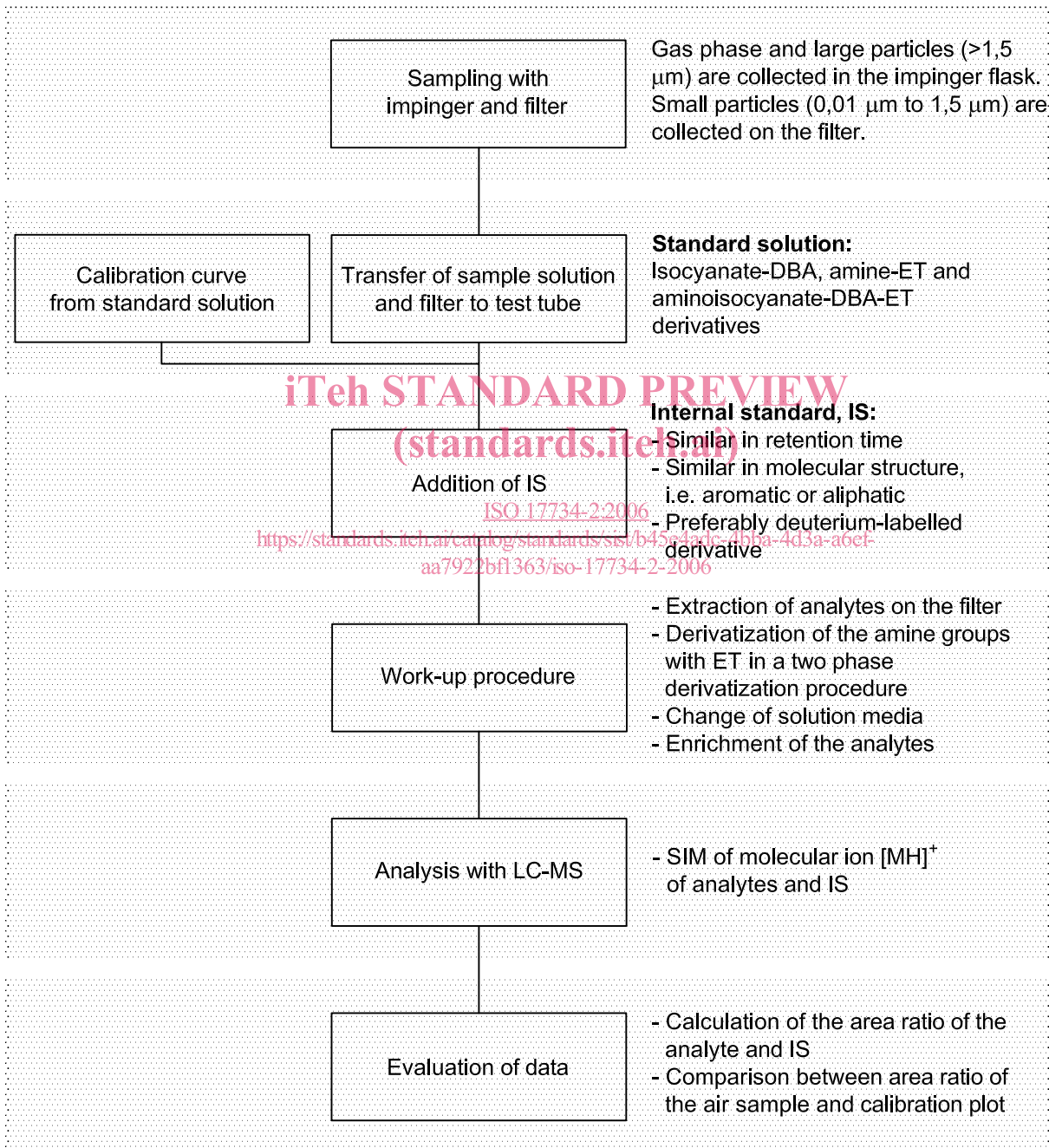


Figure 1 — Principle of the described method

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.

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, 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 %

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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 ET derivatives are easily prepared by direct derivatization with ethyl chloroformate (ET) for the 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 must be characterized before using as calibration standards. Isocyanate, aminoisocyanate and amine derivatives for compounds that not are commercially available can be made from the bulk material or from the thermal decomposition of PUR. Alternatively, standard solutions can be purchased.

5.2 Preparation of 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 $\mu\text{mol ml}^{-1}$. 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.

Synthesis of derivatives:

- 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 ethyl chloroformate dropwise under continuous stirring.
- After 10 min, separate the toluene phase.
- Evaporate the reaction mixture to dryness in a rotating evaporator, and dry the residue under vacuum.

5.3 Aminoisocyanate derivatives

5.3.1 Preparation

Dissolve 0,5 mmol of the isocyanates 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.

To produce both the isomers for the 2,4-TAI, prepare another solution by first allowing the isocyanate solution to react with 0,5 mmol of ethanol during 16 h. Then add excess DBA to the solution. Evaporate the solution to dryness and dissolve in methanol. The solution is characterized as described in 5.3.2.

5.3.2 Characterization

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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, e.g. 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·DBA·l⁻¹ and follow this by the work up procedure described in 7.2. The solution is characterized as described in 5.3.2.

5.4.2 Characterization

Qualitative data are obtained with LC-MS. Obtained structural data together with the LC-CLND data makes it possible to calculate the concentrations of different components in the solution. The characterized 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 six months.

6 Apparatus

6.1 Sampler.

Sample the air with an impinger flask followed by a filter.

6.1.1 Filter.

Use a 13-mm glass fibre filter (binder free) with a pore size of 0,3 µm.

6.1.2 Filter holder.

Use a 13-mm polypropylene filter holder with luer-lock connections.

6.1.3 Midget impingers.

A midget impinger consists of a tapered inlet tube. Match the two parts so that the distance between the inlet and the receiver bottom is 1 mm to 2 mm. A luer-lock fitting is attached to the outlet of the impinger.

6.1.4 Sampling pump.

Use a sampling pump with a calibrated flow rate of 1 l·min⁻¹.

6.1.5 Tubing.

Use rubber tubing of suitable length and of appropriate diameter to ensure a leak-proof fit to both the pump and the sampler outlet.

6.1.6 Vapour trap.

Use a vapour trap with an internal diameter of 17 mm and a length of 140 mm, filled with charcoal (with a medium particle size < 3 mm), between the sampler and the sampling pump.

6.2 Flow meter.

Use a portable flow meter capable of measuring the appropriate flow rate with acceptable accuracy.

6.3 Liquid chromatographic system.

In this method, a micro-LC system is used in order to improve the sensitivity, to minimize the maintenance on the MS and to minimize the consumption of the mobile phase. The micro-LC system is described in the following paragraphs. If desired, this system can be replaced by a conventional LC-system.

6.3.1 Autosampler.

6.3.1.1 LC-MS.

On-column focusing is performed by partially filled loops (typically 10 µl total volume) of 2 µl loop injections between 4+4 µl of 50/30/20 water/acetonitrile/methanol. Any commercially available autosampler capable of making partially filled loop injections and making sample injections of acceptable accuracy and precision can be used.

6.3.1.2 LC-CLND.

On-column focusing is performed by partially filled loops (typically 10 µl total volume) of 2 µl loop injections between 4+4 µl of 50/50 methanol/water. Any commercially available autosampler capable of making partially filled loop injections and making sample injections of acceptable accuracy and precision can be used.

6.3.2 Pumping system (LC-MS and LC-CLND).

An HPLC-pump capable of gradient elution with a flow rate of 100 $\mu\text{L min}^{-1}$ is required.

6.3.3 Analytical column (LC-MS and LC-CLND).

An HPLC-column capable of separating the different analytes is required.

EXAMPLE An example of a suitable column is a PepMap[®] C₁₈¹⁾ (50 × 1,0 mm with 3 μm particles).

6.3.4 Tubing.

Use short (< 40 cm) tubing with a small internal diameter (typically ID < 0,1 mm).

6.3.5 Detectors.

6.3.5.1 LC-MS.

Any modern MS equipped with a robust and stable electrospray interface will have the necessary performance. The MS detection is performed with atmospheric pressure ionization, monitoring positive ions. For quantification, selected ions are monitored. Full spectra are obtained using continuum scans (typically 50-1 500 amu) for identification of unknown analytes. If wanted, a UV-detector can be used in series, prior to the MS. The UV-detector needs to be equipped with a micro flow cell (typically 300 nl) to minimize peak band broadening.

6.3.5.2 LC-CLND.

Use a detector which is specific for bound nitrogen.

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7 Air sampling

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7.1 Pre-sampling laboratory preparation

7.1.1 Cleaning of sampling equipment

Impingers should be taken apart and soaked in alkaline cleaning solution for a minimum of 2 h. The upper part must be rinsed with an alkaline cleaning solution, pure water and finally deionized water. If the nozzle is clogged, place it in an ultrasonic bath, and then continue with the cleaning procedure. The lower part should be cleaned in a laboratory dishwasher. Both parts should be dried in an oven.

The filter cassettes and the gaskets should be immersed in ethanol in a glass beaker, sonicated for at least 15 min, rinsed with deionized water and dried in an oven.

7.1.2 Preparation of reagent solution and extraction solution tubes

Prepare test tubes containing 10 ml of 0,01 mol·l⁻¹ DBA as the reagent solution for the impingers. If the gas phase and the particulate phase are to be collected separately, prepare test tubes containing 10 ml of 0,01 mol l⁻¹ DBA as extraction solution tubes for the filters.

1) PepMap[®] is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 17734 and does not constitute an endorsement by ISO of this product.