TECHNICAL REPORT

ISO/TR 17737

First edition
2007-04-01

Workplace air — Guidelines for selecting analytical methods for sampling and analysing isocyanates in air

Atmosphères des lieux de travail — Lignes directrices pour la sélection des méthodes analytiques d'échantillonnage et d'analyses des isocyanates dans l'air

Reference number
ISO/TR 17737:2007(E)

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

Published in Switzerland

Contents

Page

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.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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/TR 17737 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

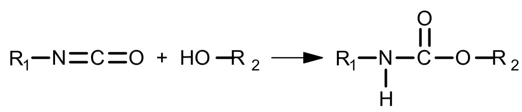
Workplace air — Guidelines for selecting analytical methods for sampling and analysing isocyanates in air

1 Scope

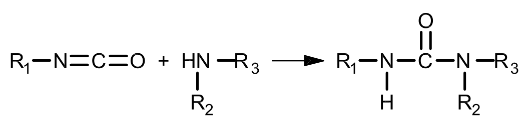
The topic of measuring airborne isocyanates is complicated. Finding the most appropriate sampling strategy and method to use to assess the air concentration of a particular isocyanate product can be daunting. The guidelines in this Technical Report are intended to provide industrial hygienists, employers and workers with a broad overview of isocyanates, their uses in industry, methods of measurement and guidance on choosing the appropriate sampling strategy. While not all issues can be addressed here in detail, this Technical Report discusses areas of concern to alert the industrial hygienist, employer and worker involved with the use of isocyanates to the importance of sampling and the key issues involved in choosing a sampling strategy for their workplace, and directs them to seek further information on the topic(s) of concern.

2 Isocyanates

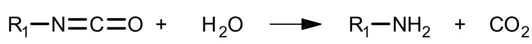
Isocyanates are compounds which contain one or more –N=C=O functional groups attached to an aromatic or an aliphatic molecule. Compounds containing nucleophilic groups with active hydrogen react readily with isocyanates, as in the reaction with primary and secondary amines to form urea compounds and the reaction with alcohols and phenols to form urethane compounds.



a) Reaction with an alcohol to form a urethane



b) Reaction with an amine to form a urea



c) Reaction with water to form the corresponding amine

Figure 1 — Reactions of isocyanates

Exposures to isocyanates may result in respiratory disorders and dermal sensitization and are one of the main causes of occupational asthma. As a result, isocyanates are among the compounds with the lowest occupational exposure limits (OELs), the maximum exposure level recommended to avoid unreasonable risk of disease or injury. Their presence in different exposure situations must be monitored.

3 Where are isocyanates found in industry?

Isocyanates with a functionality (number of NCO groups) of two or more are used in the production of polyurethanes (PUR). The most common isocyanates used in the production of flexible and rigid PUR foams are the aromatic methylenediphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). The two major aliphatic isocyanates, which are used predominantly in coatings and elastomers, are hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI).

Within industry, technical grade isocyanate products are mainly used. In most cases, these products consist of different monomeric isomers and oligoisocyanates that have different functionalities, and are often referred to as polyisocyanates of the diisocyanate monomer. The most frequently used TDI products consist of two isomers, 2,4- and 2,6-TDI. Technical MDI products, often referred to as polymeric MDI (pMDI), are mixtures of monomeric MDI isomers and higher molecular mass polyisocyanates. Technical HDI products used in applications such as spray-painting typically contain less than 1 % of the HDI monomer, with the major components HDI isocyanurate and/or HDI biuret and oligomers thereof. Another route to polyisocyanate production is the reaction of di- or polyfunctional alcohols with an excess of isocyanate molecules, which results in prepolymer mixtures of isocyanates. In addition to improved chemical handling properties, prepolymers also reduce the risk of exposure to vapours from the isocyanate by reducing the amount of monomer present in the product.

Table 1 — Examples of activities/industries where isocyanates are used and/or generated

Activity/industry	"Cold" handling	"Hot" handling
Automotive industry, ships, aircraft and trains	Painting, filling, sealing, windscreen assembly, bonding, manufacturing of composites, roof-liner pressing, acoustic panel processing, truck bed lining	Cutting, welding, grinding, windscreen removal, removal of underseal
Building	Sealing, bonding, painting, caulking, floor and wall coverings, insulation and roofing	Handling of mineral wool, mat welding, copper pipe welding, paint removal, pipe insulation
Clothing and leisure industry	Manufacture of PUR-textile, shoes and sports grounds and equipment	Flame lamination
Electrical and electronics	Packaging, gluing, casting	Soldering circuit boards, connecting optical fibres and varnished wires, cable insulation, heating Bakelite
Paint industry	Manufacturing, automotive and industrial painting	Removal of paints and varnishes with heat
Foundry	Manufacturing of cold-box cores	Manufacturing with hot-box technique, casting cores and shell sand
Graphic trades	Manufacturing of printing inks, lamination	Curing, lamination
Foodstuffs	Food packaging	Repair of conveyors, heat sealing of packaging materials
Plastics industry	Manufacture of foam, automotive fittings	Hot wire cutting
Tunnelling and mining	Sealing, rock consolidation	Self-ignition may occur
Wood and furniture	Manufacture of composite wood panels, use of adhesives, varnishing, upholstery padding, painting	Pressing, cutting and routing, removal of paints and varnishes with hot air gun
Engineering	Gluing, manufacture of elastomers, painting, insulation, fixatives	Repairs and removal of polyurethane materials with heat
White goods industry	Manufacture of refrigerators and freezers (PUR insulation), painting	Mineral wool insulation – Quality assurance (QA) checks, repairs
Medical care	Bandaging, casting, filling, equipment	
Fire extinguishing		Mineral wool, polyurethane in furniture and interior fittings

4 Airborne isocyanates

Airborne isocyanates in workplace atmospheres can occur both in the gas and particle phase. The distribution depends on the physical properties of the isocyanate and on the nature of the work tasks that introduce isocyanates into the air. Monomeric TDI and HDI have vapour pressures (at room temperature) that are sufficient to contribute to air levels of gas-phase isocyanates above the OELs; whereas MDI, adducts of HDI, and prepolymers have vapour pressures that are much lower and, consequently, the gas phase levels will be lower than the OELs (at room temperature). If aerosolization occurs, the air concentrations can be higher than the OEL even if the vapour pressures are low. Airborne particles containing isocyanates can also contain polyols and other ingredients of the formulation that can react with the isocyanates (reacting aerosol).

Polyurethanes start to thermally degrade at temperatures above 150 °C to 200 °C, possibly resulting in the emission of monomeric diisocyanates, monoisocyanates, aminoisocyanates, and amines both in gas and particle phases. Like polyurethanes, urea based resins can also release isocyanates when heated and material safety data sheets may not contain sufficient information regarding compounds that can be formed during thermal decomposition.

5 Alternatives for sampling

5.1 General

Great care must be taken to ensure that representative samples are collected. The analyst and/or industrial hygienist must consider the physical state of the isocyanate(s) likely to be present in the atmosphere being sampled. For example, the isocyanate(s) may be present as a vapour and/or aerosol, or the isocyanate may be coated on another medium, e.g. wood dust. All the above must be considered when selecting a method for monitoring workplace exposures.

The mechanisms for sampling compounds in the gas and particle phase differ. Gas phase compounds are typically collected by diffusion of molecules to a solid or liquid surface within the sampler. Collection of airborne particles is typically achieved by filtration or by impaction.

5.2 Impregnated filters

Filter sampling with a filter impregnated with a derivatizing reagent is commonly used for the collection of isocyanates. Both gas and particle-borne isocyanates can be efficiently collected. However, in some circumstances when collecting particles, incomplete derivatization with the reagent may occur due to the presence of other reactive species in the particle. In these instances, field extraction immediately after sampling improves the derivatization and minimises problems with interfering reactions. If the physical/chemical composition of the air being sampled is unknown, samples should be collected using an impinger containing a derivatizing agent with filter backup (see 5.3). Reagent-impregnated filters are recommended for gas-phase isocyanates.

5.3 Impinger (and filter)

Sampling with a typical industrial hygiene midget impinger containing a derivatizing agent with a reagent-coated filter [except for di-*n*-butylamine (DBA)] in series enables the collection of gas- and particle-phase isocyanates. Isocyanate-containing particles < 2 µm are poorly collected by impingers; however, they are efficiently collected by the filter. (Examples of particles < 2 µm are condensation aerosol formed from cooling of isocyanate vapour, combustion/thermal degradation aerosol and, to some degree, paint-spray.)

In situations where the physical/chemical nature of the atmosphere is unknown, use of the impinger/filter combination is the most appropriate approach to ensure that the widest range of isocyanate species is efficiently collected and derivatized. If the nature of the aerosol is known and a negligible fraction of particles < 2 µm are present, sampling can be performed (simplified) without a filter in series. Collected particles are dissolved and derivatized.

Impinger sampling is cumbersome and there is a risk of breakage and spillage. In addition, impinger solvents are often volatile (such as toluene), limiting sampling time and generating solvent vapour in the vicinity of sampler. Impinger/filter is the recommended sampler when sampling a reacting aerosol.

5.4 Sorbent tubes

Historically, a small glass cylindrical tube packed with an inert support, e.g. glass powder or glass wool that has been impregnated with a derivatizing agent, is used. This technique is primarily for vapour-phase isocyanates. Impregnated sorbent tubes require a reagent-coated filter at the front or at the back for collection of both gas and particle-borne isocyanates. For efficient derivatization, the tube needs to be extracted immediately after sampling.

5.5 Denuder filter

A denuder sampler consists of a cylindrical tube, and as air flows through the tube, the gaseous molecules diffuse from the air stream to the walls, where they either are adsorbed or react with a reagent coating. The majority of the particulate phase in the air stream passes through the denuder unaffected and is collected on a reagent-coated filter. If the tube is coated with a suitable derivatizing reagent and subsequently analysed, the sampler can be used to separate vapour and particle phase species; however, the limitations previously explained under impregnated filters (5.2) in the presence of reacting aerosols also apply to this technique.

5.6 Diffusive sampling

A reagent-impregnated filter or other absorbing material is placed behind a membrane or diffuser. Gas-phase isocyanates diffuse at a certain rate towards the reagent. The simple design makes it desirable for personal sampling, but diffusive samplers are suitable for monitoring isocyanate vapours only. Some diffusive sampling badges enable measurement in the field immediately after sampling. Other diffusive samplers require laboratory analysis analogous to filter and impinger samples.

6 Direct reading instruments

Several direct reading paper tape instruments are available where air is sampled continuously on a reagent-impregnated paper tape. The developed colour is optically read or stored in memory for future retrieval. Instantaneous and long-term exposure profiles can be derived using paper tape instruments; however, measurement uncertainty may be large. Generally, direct reading instruments are calibrated for the monomer and are only suitable for quantifying isocyanates in the vapour phase but they are not specific and will not differentiate the monomers if a mixture is present. The range of these instruments may vary and require a separate calibration for each isocyanate; however, all have adequate sensitivity, i.e. to measure below the OEL, and are convenient to use.

The paper tape technology has been adapted in a variety of techniques for a quick “yes/no” answer in many critical situations. Some examples are listed below.

— The **portable active spot colorimetric sampler** is a spot sampling device that can be used for measuring vapour and, qualitatively, condensation aerosol levels of isocyanate compounds such as MDI, TDI, or HDI down to 1×10^{-12} [i.e. 1 part per billion (ppb)]. In operation, a test card with the reactive paper tape is placed in a holder while a pre-calibrated pump pulls a measured air sample through it (5 min). The intensity of the resulting colour stain is directly proportional to the concentration of isocyanate vapour present. The developed stain is visually matched against a concentration comparator/calculator, providing a readout of concentration in parts per billion.

— **Diffusive badges** are commercially available for both short- and long-term personal monitoring of some isocyanates. The stain developed on the diffusive badges can be read using visual colour comparators or an optical densitometer for better accuracy and reliability. The considerations mentioned for the paper tape instruments also apply to badges.

Ion mobility spectrophotometers (IMS) are also used for the online analysis of workplace air; however, they are only suitable for quantifying isocyanates in the vapour phase.

7 Short description of four proposed and/or adopted methods for airborne isocyanates

7.1 DBA method

ISO 17734-1, *Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry — Part 1: Isocyanates using dibutylamine derivatives*

ISO 17734-2, *Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry — Part 2: Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives*

The sampler consists of an impinger containing a toluene solution of DBA with a glass-fibre filter placed in series after the impinger. Solvent-free sampling is performed using a sampler consisting of a tube with an inner wall coated with a filter, coupled in series with a filter. The filters are impregnated with equimolar amounts of DBA and acetic acid, which reduces evaporation of the volatile DBA.