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Workplace air quality — Determination of isocyanate in air using a double-filter sampling device and analysis by high pressure liquid chromatography

Qualité de l'air des lieux de travail — Dosage des isocyanates dans l'air au moyen d'un dispositif d'échantillonnage à filtre double et par analyse par chromatographie liquide à haute performance

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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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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.

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 17736 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

Isocyanates are commercially available chemicals used in the polyurethane industry. They are known to cause health problems, such as asthma, contact dermatitis and hypersensitivity pneumonitis, in workers even at very low levels in occupational environments.

Since isocyanates are highly reactive compounds and exposure limits are very low, the sampling and the analysis of these substances are critical.

This method is based on the standard method developed by the Institut de Recherche en Santé et en Sécurité du Travail [Occupational Health and Safety Research Institute] (IRSST) of Quebec. It has been in use for more than 18 years as the standard government method in that province of Canada. Since 1996, it has been introduced into the marketplace in the USA, Brazil, and the UK. After a year's study (Reference [10]), the method was adopted in 1998-11 by the US Air Force as an acceptable alternative to NIOSH Method 5521 for monomeric isocyanates (now withdrawn).

The method is now routinely used in the Canadian provinces of Alberta, British Columbia, and Ontario, and in the US state of Washington, which has validated the method for TDI. Thirteen laboratories have been schooled in this analytical method, three in Canada, eight in the USA and Mexico, one in Brazil, and one in the UK. This method has been in use in several countries for many years and 13 laboratories participate in round robin testing on a regular basis in order to maintain their proficiency.

The double-filter method has been validated for different applications of isocyanates such as spray-painting (Reference [11]) and foam manufacturing. It has also been compared with other established methods and demonstrated equivalent results (Reference [10]).

Double-filter methods are also available in ASTM D6561[7] and ASTM D6562[8] for HDI, and ASTM D5932[9] for TDI.

ISO draws attention to the fact that it is claimed that compliance with this document may involve the use of a patent concerning the double-filter sampling device for isocyanates.

Workplace air quality — Determination of isocyanate in air using a double-filter sampling device and analysis by high pressure liquid chromatography

1 Scope

This International Standard gives general guidelines for the sampling and analysis of airborne isocyanates in workplace air. This International Standard is appropriate for organic compounds containing free isocyanate functional groups and is specific for the quantification of monomers, polymers and prepolymers, vapours and aerosols. Differential air sampling is performed with a segregating device which can show the physical state of the isocyanates analysed as found in the field. This capacity, however, may show limitations for given situations, e.g. when aerosols collected on the first filter contain free monomer that migrates to the second filter and is then quantified as vapour phase isocyanate. The determination of aromatic monomers includes toluene diisocyanate (TDI) and 4,4'-diisocyanato-diphenylmethane (MDI). Aliphatic monomers include isophorone diisocyanate (IPDI), 4,4'-methylene bis-(cyclohexyl isocyanate) (HMDI) and 1,6-hexamethylene diisocyanate (HDI). Isocyanate oligomers and prepolymers can also be determined using this method.

The double-filter method is designed to determine short-term (15 min) exposure concentrations of organic isocyanates in a workplace environment by personal monitoring or by fixed location monitoring. However, if the exposure is expected to be in vapour form only, then sampling time can be extended to 8 h. Since the filter is derivatized in the field immediately after sampling, loss of isocyanate aerosol because of its reaction with other chemicals is negligible except for very fast-reacting isocyanate systems such as foam spraying of MDI in polyurethane applications. The method is suitable for the measurement of airborne organic isocyanates in the NCO equivalent concentration range of 0,01 µg/sample to 2,1 µg/sample, corresponding to approximately 0,67 µg/m^3 to 140 µg/m^3 for a 15 l sample volume. This range brackets about eight times the current established threshold limit value (TLV) of 5 ppb for monomers set by many national authorities.

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 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*

EN 1232*, Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods*

3 Principle

A measured volume of air is drawn through a double-filter sampling device in which the first filter made of polytetrafluoroethylene (PTFE) collects the aerosols and then the isocyanate vapour is absorbed on a glass fibre (GF) filter impregnated with 9-(methylaminomethyl)anthracene (MAMA). The isocyanate present as an aerosol is collected on the PTFE filter and derivatized immediately after sampling, in a 5 ml solution of 1-(2-methoxyphenyl)piperazine (MP), 0,1 mg/ml in toluene.

Both isocyanate monomer and oligomer urea derivatives solutions are separated using reversed phase high performance liquid chromatography (HPLC). Vapour monomers are analysed by HPLC using an ultraviolet (UV) and fluorescence (FL) detector. Fluorescence detection is used when concentrations are less than 25 % of the TLV. Monomeric and oligomeric aerosols are analysed by HPLC with a UV detector for quantification and a diode array detector (DAD) for identification. Quantification of the monomeric aerosols is made by comparison with the relevant isocyanate monomer standard. The total isocyanate-in-air concentration is calculated from the sum of all the isocyanate-derived peaks calculated as NCO function. In some cases, a bulk sample is used for calibration and results are reported as mass of base per volume.

The quantitative detection limits for isocyanate, defined as $10s$, where s is the standard deviation obtained from 10 measurements carried out on a standard solution whose concentration is close to the expected detection limit, has been estimated to be approximately 0,026 µg/sample, 0,029 µg/sample, and 0,036 µg/sample for vapour phase HDI, TDI, and MDI, respectively. The quantitative detection limit for aerosol phase HDI, TDI, and MDI is 0,031 µg/sample.

NOTE The calculation of oligomeric isocyanates by this method is expressed as the total NCO function equivalent, utilizing the response factor of the corresponding monomer for the oligomer calculation.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity.

4.1 Water, HPLC grade or equivalent.

4.2 1-(2-Methoxyphenyl)piperazine (MP) [CAS No. 35386-24-4], >98 % mass fraction.

4.3 9-(Methylaminomethyl)anthracene (MAMA) [CAS No. 73356-19-1], >99 % mass fraction.

4.4 Acetic acid, glacial [CAS No. 64-19-7], HPLC grade.

4.5 Acetic anhydride [CAS No. 108-24-7], certified ACS.

4.6 Triethylamine [CAS No. 121-44-8], >98 % mass fraction assay by GC.

4.7 Phosphoric acid [CAS No. 7664-38-2], certified ACS.

4.8 Reagent solvents, commonly toluene [CAS No. 108-88-3], dimethylformamide [CAS No. 68-12-2], and acetonitrile [CAS No. 75-05-8], should be HPLC grade. They shall be free from compounds co-eluting with the substance(s) of interest. To avoid any interference from the solvent, perform quality controls on each different lot of solvent.

4.9 Buffer solution and HPLC mobile phase.

4.9.1 Triethylamine buffer — vapour analysis. In a 1 l volumetric flask, dilute 30 ml triethylamine (4.6) in water, and make up to the mark with water. Adjust the pH of this solution to 3 using phosphoric acid (4.7). Filter the solution under vacuum with a 0,22 µm filter.

4.9.2 Sodium acetate buffer — aerosol analysis. Weigh approximately 12,5 g of sodium acetate in 1 l HPLC grade water (4.1). Adjust the pH of this solution to 6 with glacial acetic acid (4.4). Filter the resulting solution under vacuum with a 0,22 µm filter.

4.9.3 Mobile phase — vapour analysis. A solvent mixture of acetonitrile (4.8) and triethylamine buffer (4.9.1). The appropriate proportion of each solvent depends on the isocyanate analysed, see Table 1.

4.9.4 Mobile phase — aerosol analysis. A solvent mixture of acetonitrile (4.8) and sodium acetate buffer (4.9.2). The appropriate proportion of each solvent depends on the isocyanate analysed, see Table 2.

4.10 Reagent solutions.

4.10.1 Desorption solution — vapour analysis. A solvent mixture of 67 % volume fraction of dimethylformamide (4.8) and 33 % volume fraction mobile phase.

4.10.2 Derivatization solution — aerosol analysis. Weigh 10 mg MP (4.2) and transfer it to a 100 ml volumetric flask. Dissolve and make up to the mark with toluene (4.8). The final concentration of this MP solution is equivalent to 0,1 mg/ml.

5 Apparatus

5.1 Sampling system. A three-piece, closed face, 37 mm cassette is used. The sampling train consists of a 37 mm PTFE filter of porosity 5 µm followed by a binder free 37 mm glass fibre (GF) filter impregnated with MAMA (4.3) and supported by a cellulose back-up pad (see Figure 1).

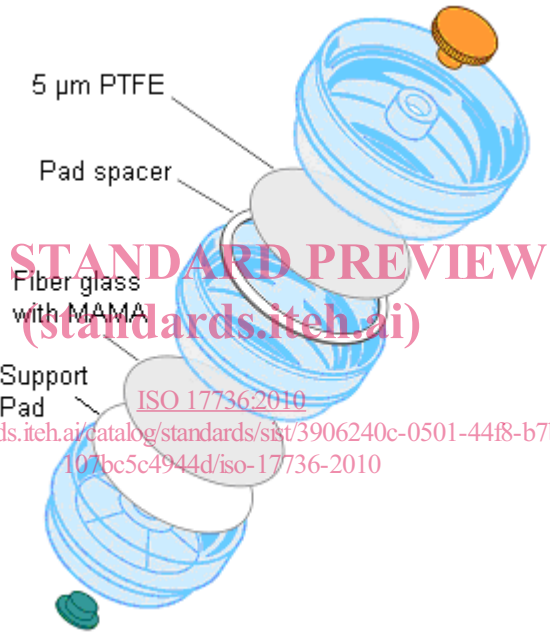

Figure 1 — Three-piece cassette 37 mm

This sampling train is commercially available as ISO-CHEK®[1)].

5.2 Sampling pump. The pump shall fulfil the requirements of EN 1232 or equivalent.

The pump should also be in accordance with local safety regulations.

5.3 Tubing, of plastic, rubber or other suitable material, about 900 mm long, of appropriate diameter to ensure a leakproof fit to both pump (5.2) and double-filter sampling cassette (5.1). Clips shall be provided to hold the cassette and connecting tubing to the worker's lapel within 300 mm of their breathing zone.

5.4 Flow meter, portable, capable of measuring the appropriate flow rate to within ±5 %, and calibrated against a primary standard.

1) ISO-CHEK is the trade name of a product supplied by SKC. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.5 Glass jar, consisting of a 30 ml glass container equipped with a PTFE lined screw cap, capable of receiving 37 mm filters.

5.6 Liquid chromatographic system. An HPLC linked to UV and FL detectors is required. The FL detector should be used for the quantification of monomeric vapours when they are present at less than 0,180 µg/sample of isocyanate. A diode array detector (DAD) is also suitable for confirmation of identification.

5.7 Autosampler, commercially available, with a sampling loop within the range 10 µl to 100 µl.

5.8 HPLC column, of stainless steel, C-18 type, capable of separating the urea derivatives of interest.

6 Air sampling

6.1 Calibration of sampling system

Calibrate the sampling system (5.1) with a representative sampling device assembly in line, using an appropriate external calibrated meter. One end of the calibrated flow meter (5.4) should be at atmospheric pressure to ensure proper operation.

6.2 Preparation of sampling equipment

A glass jar (5.5) containing 5 ml MP derivatization solution (4.10.2) should be prepared in the laboratory before sampling. Prepare one jar for each sample to be used.

6.3 Preparation of MAMA-impregnated filter

Approximately 100 GF filters are put in a beaker containing 25 mg MAMA (4.3) dissolved in 250 ml toluene (4.8) for a period of 30 min. Remove the filters from the beaker with tweezers and transfer them to dry on a sheet of aluminium foil placed in a compartment away from light for 12 h. The volume of solution absorbed by one filter is evaluated to be 500 µl, equivalent to a mass of approximately 50 µg of MAMA on each filter. This quantity corresponds to approximately 0,11 µmol and is 36 times the amount that would be required during sampling before the reagent is exhausted (reacts) at a concentration of 5 ppb sampled at 1 l/min for 15 min.

6.4 Collection of samples

The recommended sampling volume for the double-filter sampling system (5.1) is 15 l (1 l/min for a period of 15 min). This sampling volume is used for short-term exposure and for mixtures of airborne particles and vapour. The sampling time can be extended to 8 h if all the expected exposure is in a vapour form.

In accordance with EN 1232, adjust the pump (5.2) flow rate to approximately 1 l/min. To compensate for any pressure drop due to the cassette, make sure the flow rate is adjusted with a sampling device in place. Turn off the pump and use a new sampler. Record the sample identity and all relevant sampling data.

NOTE Keep a sampling device as a calibrator for further pump calibration.

Fix the sampler to the worker's lapel and position the sample as close to the breathing zone as possible. Place the sampling pump in a convenient pocket (ensure the pump exhaust is not restricted) or fix to a belt around the waist. Turn on the pump and write down the time of the beginning sampling period. At the end of the sampling period, check and make a note of the sample flow rate before removing the cassette. The flow rate of the pump should be within the ±5 % variation of the nominal value; if greater, discard the sample.

Calculate the mean flow rate, in litres per minute, by averaging the flow rate measurements throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the mean flow rate by the sampling time, in minutes.

As soon as the sampling period is over, using tweezers, immediately remove the PTFE filter from the sampling device and place the filter in a glass jar (5.5) containing 5 ml MP derivatization solution (4.10.2).

Take care to avoid contact with the GF filter when removing the PTFE filter from the sampling device. Identify the jar with the corresponding sampler's identification number. Losses of isocyanate aerosol because of their reaction with other chemicals are negligible except for very fast-reacting isocyanate systems such as foam spraying of MDI polyurethane applications (Reference [12]).

6.5 Blanks

Field blanks should be prepared by using cassettes identical to those used for sampling and subjecting them to the same handling procedures as the samples except for the actual period of sampling. Label these as field blanks. Provide a blank for every 10 samples or when changing sampler batch.

7 Procedure

7.1 Safety precautions

Wear safety glasses and appropriate disposable gloves during analysis to protect the eyes and hands from harmful solvents and reagents, and to reduce the possibility of contamination.

WARNING — This International Standard does not purport to address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate health and safety practices and to ensure compliance with any national regulatory conditions.

7.2 Calibration standard

7.2.1 Preparation of monomer derivatives

Slowly add the appropriate diisocyanate to a MAMA solution in a ratio 1 mmol diisocyanate +2 mmol MAMA or 1 mmol monoisocyanate +1 mmol MAMA; a slight excess of MAMA may be used. The choice of solvent may vary from one isocyanate to another; usually dichloromethane is suitable, but some reactions have shown better performance using diethyl ether. Most reactions are exothermic and so an ice bath may be used to cool down the resulting mixture.

Collection of the white crystalline urea precipitate is performed using a paper filter [e.g. Whatman No. 42[2)]]. The resulting precipitate is washed with toluene (4.8) to remove the excess of MAMA. The urea derivatives are slightly soluble in toluene. If needed, purification of the precipitate may be performed by dissolving in warm methanol and then, using an ice bath to cool down the solution to re-precipitate the solid, filter and dry the purified urea derivative. The purity of the derivative is determined by the melting point and HPLC analysis.

7.2.2 Preparation of standard solutions from the isocyanate monomer-urea derivatives (MAMA)

Weigh out precisely about 25 mg of the urea derivative in a 100 ml volumetric flask and make up to the mark with dimethylformamide (4.8). Take aliquots of this solution and dilute volumetrically with the desorption solution to create a series of working standard solutions over an NCO concentration range of 0,01 µg/ml to 2,1 µg/ml. Prepare further standard solutions, if the concentration range of the samples exceeds that of the standards.

The isocyanate concentration in the standard, $\rho_{NCO,std}$, in micrograms per millilitre, is given by Equation (1):

$$\rho_{NCO,std} = \frac{\rho_{ud,std} \, M_{NCO} \, N}{M_{ud}} \quad (1)$$

2) Whatman No. 42 is the trade name of a product supplied by Whatman. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

where

$\rho_{ud,std}$ is the concentration, in micrograms per millilitre, of urea derivative in the standard;

M_{NCO} is the relative molecular mass of NCO;

N is the number of isocyanate groups (functions) per molecule;

M_{ud} is the relative molecular mass of the urea derivative.

7.2.3 Stability of isocyanate-ureas in solutions

Stock solutions of isocyanate monomer-urea derivatives have been found to be stable over a period of 1 year if kept in a refrigerator. Isocyanate monomer-urea working solutions have been found to be stable for up to 90 days.

7.2.4 Preparation of standard solution for the aerosol isocyanates analysis

For each isocyanate to be analysed, produce a stock solution from the monomeric isocyanate by dissolving in a known volume of toluene (4.8) in order to obtain a concentration of approximately 10 mg/l. Working standards are made by further diluting with toluene to generate a working range from 0,1 µg/ml to 1,0 µg/ml.

When kept in a refrigerator, the stock solutions have been found to be stable for several months. However, working standard solution should be made weekly.

8 Sample processing

8.1 Vapour analysis

The samples, quality controls, and blanks should receive the same treatment.

Remove the GF filter from the cassette and place it in a 30 ml glass jar (5.5). Add 2 ml desorption solution (see 4.10.1) to the jar. Close the jar and shake for 30 min on a reciprocating shaker. Filter the solution into an autosampler (5.7) vial, using a 0,22 µm syringe filter. Analyse using the HPLC vapour conditions specified in 9.2.

8.2 Aerosol analysis

The samples, quality controls and blanks should receive the same treatment.

Transfer the solution from the sampling jar (see 6.2) to an evaporator vial. Rinse the sampling jar and the filter three times with 1 ml toluene (4.8).

For the standard solution, place 5 ml MP derivatization solution (4.10.2) in an evaporator vial. Add 1 ml working standard solution (7.2.4) to the vial and mix gently to produce the monomer-urea.

The samples, blanks and standard are then processed as follows.

Place all the vials in a 50 °C pre-heated vacuum evaporator and evaporate to dryness. Allow the vials to cool to ambient temperature. Dissolve the residue in 1 ml acetic anhydride (4.5) 0,5 % volume fraction in acetonitrile (4.8). Filter the solution into an autosampler (5.7) vial, using a 0,22 µm syringe filter. Analyse using the HPLC conditions for NCO oligomers specified in 9.3.