
**Workplace atmospheres — Determination
of total isocyanate groups in air using
1-(9-anthracenylmethyl)piperazine (MAP)
reagent and liquid chromatography**

*Air des lieux de travail — Dosage des groupements isocyanates totaux
dans l'air par réaction avec la 1-(9-anthracénylméthyl)pipérazine (MAP)
et par chromatographie en phase liquide*



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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 17735 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

This International Standard specifies the use of 1-(9-anthracenylmethyl)piperazine (MAP) to measure monomeric and oligomeric isocyanate species in workplace atmospheres. MAP was designed to improve the reliability of identification of isocyanate species in sample chromatograms and to improve the accuracy of quantification of these species relative to established reagents. The high performance liquid chromatography (HPLC) analysis uses a pH gradient to selectively accelerate the elution of MAP derivatives of oligomeric isocyanates that might be unobservable in an isocratic analysis. The performance of MAP has been compared to other reagents used for total isocyanate analysis (Reference [7]). MAP has been found to react with phenyl isocyanate (used as a model isocyanate) as fast or faster than other reagents commonly used for isocyanate analysis. The UV response of MAP derivatives is comparable to that of 9-(methylaminomethyl)anthracene (MAMA) derivatives and considerably greater than other commonly used reagents [approximately three times greater than 1-(2-methoxyphenyl)piperazine (1-2MP) derivatives of aromatic isocyanates and 14 times greater than 1-2MP derivatives of aliphatic isocyanates]. The compound-to-compound variability of UV response per isocyanate group for MAP derivatives is smaller than the variability of any other commonly used reagent/detector combination (the coefficient of variation is 3,5 % for five model isocyanates). This results in accurate quantification of detectable non-monomeric isocyanate species based on a calibration curve generated from analysing standards of monomeric species. The monomeric species used for calibration is generally the one associated with the product being analysed, but others could be used due to the very small compound-to-compound response variability of the MAP derivatives. The intensity of fluorescence response of MAP derivatives is comparable to that of MAMA derivatives and considerably greater than other reagents (e.g. approximately 30 times more intense than that of tryptamine derivatives). The compound-to-compound variability in fluorescence response has been found to be smaller than that of MAMA derivatives but larger than that of tryptamine derivatives (MAMA = 59 % coefficient of variation, MAP = 33 % coefficient of variation, and tryptamine = 16 % coefficient of variation for 5 model isocyanates). The compound-to-compound fluorescence variability of MAP derivatives is considered too great for accurate quantification of non-monomeric isocyanate species based on calibration with monomer standards. However, the sensitivity of the fluorescence detection makes it especially suitable for quantification of low levels of monomer, and the selectivity is very useful to designate an unidentified HPLC peak as a MAP derivative. MAP derivatives also give a strong response by electrochemical detection. The pH gradient used in the HPLC analysis selectively accelerates the elution of amines (MAP derivatives are amines), and is very strong (it accelerates MDI more than 100-fold). Re-equilibration to initial conditions is almost immediate. Many oligomeric species can be measured in the 30 min MAP analysis that may be unobservable in a much longer isocratic analysis.

MAP has been used in several studies comparing it side-by-side with other methods. Reference [8] found MAP impingers and NIOSH 5521 impingers (comparable to MDHS 25) to give comparable results in spray painting environments. Reference [8] used MAP reagent, but the pH gradient was not employed. Reference [9] compared MAP impingers with several other impinger methods (NIOSH 5521 and NIOSH 5522) and the double filter method. The average MAP oligomer value was substantially higher than the other impinger methods and slightly higher than the double filter method. The pH gradient was used in these MAP analyses.

The MAP method is currently available as NIOSH Method 5525 (Reference [11]). The performance characteristics of the method have been evaluated in Reference [12].

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Workplace atmospheres — Determination of total isocyanate groups in air using 1-(9-anthracenylmethyl)piperazine (MAP) reagent and liquid chromatography

1 Scope

This International Standard gives general guidance for the sampling and analysis of airborne organic isocyanates in workplace air.

This International Standard is appropriate for a wide range of organic compounds containing isocyanate groups, including monofunctional isocyanates (e.g. phenyl isocyanate), diisocyanate monomers (e.g. 1,6-hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI)), prepolymers (e.g. the biuret and isocyanurate of HDI), as well as intermediate products formed during production or thermal breakdown of polyurethane.

In mixed systems of HDI and IPDI products, it is impossible to identify and quantify low levels of IPDI monomer using this International Standard, due to coelution of IPDI monomer with HDI-uretidinedione.

The useful range of the method, expressed in moles of isocyanate group per species per sample, is approximately 1×10^{-10} to 2×10^{-7} .

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*

ISO 16200-1, *Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography — Part 1: Pumped sampling method*

3 Principle

A measured volume of air is drawn through either an impinger containing a solution of 1-(9-anthracenylmethyl)piperazine (MAP), a filter impregnated with MAP, or a sampling train consisting of an impinger followed by an impregnated filter. The choice of sampler depends on the chemical and physical characteristics of the airborne isocyanate (Reference [13]). If an impinger is used, the solution is subjected to solid-phase extraction (SPE) and the eluate is concentrated and analysed by reverse phase high performance liquid chromatography (HPLC) with ultraviolet (UV) absorbance and fluorescence (FL) detection in series. If an impregnated filter is used for sampling, it is extracted with solvent either in the field after completion of sampling or in the laboratory. Waiting to extract the filter until after the sample has been received by the analytical laboratory is acceptable only for analysis of isocyanates collected as vapour. This solution is filtered and analysed by HPLC/UV/FL. Isocyanate-derived peaks are identified based on their UV and FL responses and by comparison with the chromatogram of a derivatised bulk isocyanate product if available. Quantification of compounds for which analytical standards are available (generally monomers) is achieved by comparison