MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

HSE Health & Safety Executive

25/3

Organic isocyanates in air

Laboratory method using sampling either onto 1-(2-methoxyphenyl)piperazine coated glass fibre filters followed by solvent desorption or into impingers and analysis using high performance liquid chromatography

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Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations[1] are designed to ensure that the exposure of people at work to substances which could cause health damage is either prevented, or where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH regulations also require that persons who could be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS. Guidance is given in the Approved Codes of Practices for the Control of Substances Hazardous to Health (the General COSHH ACOP) and the Control of Carcinogenic Substances (the Carcinogens ACOP), which are included in a single publication with the COSHH Regulations.[2]

Definition

2 Unless otherwise stated, reference to 'isocyanates' in this method includes both mono- and multifunctional monomers, oligomers and isocyanate-based prepolymers containing unreacted isocyanate groupings. These species may be present as either vapour or as a mixture of vapour and/or airborne particles (aerosol).

INTRODUCTION

Properties and uses

3 Organic isocyanates exist as liquids or solids at room temperature and are soluble in aromatic hydrocarbons, nitrobenzene, acetone, ethers and esters. They are highly reactive compounds, which react exothermally with water, alcohols and amines. They react violently with sodium hydroxide in the presence of tertiary amines. The most important commercial reaction of isocyanates is that between diisocyanates and difunctional alcohols to produce polyurethanes.[3,4] Monofunctional isocyanates have some uses in organic synthesis.

4 Examples of aromatic isocyanates include toluene diisocyanate (TDI), which is used in the production of flexible elastomers and polyurethane foams, and 4,4'-methylenebis(phenyl isocyanate), which is used to make rigid foams and is employed in the foundry industry as a core binder. Polyurethanes made from aromatic isocyanates tend to yellow on prolonged exposure to light, while those made from aliphatic isocyanates have better resistance to discolouration and are consequently used in the manufacture of transparent elastomers and paint sprays. Examples of aliphatic isocyanates include isophorone diisocyanate (IPDI) and 1,6-hexamethylene diisocyanate (HDI). Organic isocyanates can arise from thermal decomposition of polyurethanes.

Health effects

5 The critical health effect associated with isocyanates is respiratory sensitisation, for which it has not been possible to establish a no-adverse-effect level. In higher doses, isocyanates can cause irritation to the eyes, skin and respiratory system. After periods of exposure, the worker may become responsive to extremely low concentrations. The inhalation of isocyanates has been associated with a range of complaints, including coughing, wheezing, chest discomfort, acute oedema and interstitial pulmonary fibrosis, as well as covert decrement of lung function. The health effects of isocyanates are summarised in HSE Guidance Note EH 16[5] and are fully covered in *Preventing asthma at work*.[6]

First aid

6 Following significant exposure, remove the patient to a clean atmosphere and give artificial respiration if breathing has ceased. Administer oxygen if breathing is laboured, remove contaminated clothing and alert the emergency services. If the eyes have been splashed, wash them with cold running water. Wash splashes on the skin promptly with soap and water. If a person is sent for medical

attention, the appropriate note on treatment in the CIA series *Chemical Exposure Treatment Cards* should accompany them (Label 19 for isocyanates).[7]

7 HSE leaflet MS 8[8] summarises the risks involved in working with isocyanates and what can be done to control them. Prevention and control of exposure, emergency procedures and health surveillance are described more fully in HSE Guidance Note EH 16.[5]

Exposure

8 Isocyanates are widely used as intermediates in a variety of chemical processes and applications. Exposure is likely to occur during spraying (eg 2-pack paint), cutting of the freshly made foam block and during the rising phase of the foam (eg foam manufacture) or during mixing of the unreacted isocyanate.

Exposure limits

9 Regulation 7 of the Control of Substances Hazardous to Health Regulations (Amended) 1997[1] lays down the requirements for using maximum exposure limits (MELs) and occupational exposure standards (OESs) for the purpose of achieving adequate control of worker exposure.

10 Schedule 1 of the Control of Substances Hazardous to Health (COSHH) Regulations[1,2] specifies a maximum exposure limit of 0.02 $mg.m^{-3}$, 8-hour time-weighted average reference period, for isocyanates. A short-term exposure limit, 15 minute reference period, of 0.07 $mg.m^{-3}$ is specified. This limit is expressed as 'weight of NCO groups', not of a specific monomer or other NCO-containing unit. These limits are reproduced in HSE Guidance Note EH 40[9] and the criteria on which they are based are documented in the 1994 supplement of HSE Guidance Note EH 64.[10] These limits are subject to occasional revision and users should check the current value.

Analytical methods

11 This is not a 'reference' method in the strict analytical sense of the word. There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

12 This method has been evaluated for compliance with BS EN 482 *Workplace atmospheres: general requirements for the performance of procedures for the measurement of chemical agents* (BSI, 1994).[11] The results, for various monomers, an oligomer (trimeric HDI) and some prepolymers, are presented below (see paragraph 88). If an alternative method is used it is necessary to demonstrate that it meets these performance requirements.

Principle

13 A measured volume of air is drawn through a glass impinger containing absorbing solution and/or a filter impregnated with the appropriate 1-(2-methoxyphenyl)piperazine (1-2MP) solution. Any organic isocyanates present will react to form non-volatile urea derivatives. The resultant solution is concentrated and analysed by high performance liquid chromatography (HPLC) with ultraviolet (UV) and electrochemical (EC) detection. Isocyanate-derived peaks are identified on the basis of their EC and UV responses and also by diode array detection (DAD) and comparison with derivatised bulk (where available). Quantification is by comparison with the relevant isocyanate monomer standard. Total isocyanate-in-air concentration is calculated from the sum of all the isocyanate-derived peaks.

Scope

14 The method can be used to determine time-weighted average concentrations of organic isocyanates in workplace atmospheres and is suitable for sampling over periods in the range 15 minutes to 8 hours. The method is designed for personal monitoring, but may also be used for fixed location monitoring by suitable modification.

Note 1: *HSE Guidance Note HSG173[12] advises employers on how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health, which are present in workplace air. The objective of air monitoring is usually to determine worker exposure and, therefore, the procedures described in this method are for personal sampling in the breathing zone. The method may be used for background or fixed location sampling. However, it should be recognised that, due to aerodynamic effects, samplers designed for personal sampling do not necessarily exhibit the same collection characteristics when used for other purposes.*

15 The method is suitable for the measurement of airborne organic isocyanates in the concentration range approximately 0.1 to 140 µg $NCO.m^{-3}$ (NCO = free isocyanate groups) for a 15 l sample volume. For a 15 l air sample, the estimated limit of quantification has been found, by experiment, to be ~0.1 µg $NCO.m^{-3}$ (using EC detection, S/N ratio is 3). The qualitative and quantitative detection limits for isocyanate (as stated in the draft ISO method ISO/TC146/SC2/WG4 N215, *Workplace air quality: determination of total isocyanate groups in air using 1-(2 methoxyphenyl)piperazine reagent and liquid chromatography*),[13] which are defined as three times and ten times the standard deviation of six blank determinations, have been found to be typically around 0.001 and 0.004 µg NCO per sample respectively (EC detection). For a 15 l air sample, these figures correspond to qualitative and quantitative detection limits of 0.07 $µg.m^{-3}$ and 26.27 $µg.m^{-3}$ respectively.

SAMPLING EQUIPMENT

Sampler

16 The sampler used depends on the form in which the isocyanate is present. For vapour phase isocyanates, sampling may be carried out using a filter only. In this case, the sample is collected using a sampling head

suitable for personal sampling. Details of suitable sampling heads are given in MDHS 14/2.[14] Of the examples given, the 25 mm IOM head fitted with a stainless steel cassette or similar is the most suitable. If no particles less than 2 µm are expected, then sampling may be carried out with an impinger only.

17 For mixtures of airborne particles and/or vapour, the use of an impinger backed by an impregnated filter is suggested. This combination has been shown to be the most effective sampler for a mixture of vapour and airborne particles. Details of sampling procedures are given below.

Preparation of absorbing solution (50 µg.ml^{-1})

18 Accurately weigh approximately 50 mg of 1-2MP and transfer to a dry 100 ml volumetric flask. Dissolve and make up to the mark with dried toluene (dried with either anhydrous calcium chloride or magnesium sulphate), mixing thoroughly. Dilute 10 ml of this stock solution to 100 ml with dry toluene in a second volumetric flask to give a 260 µM absorbing solution. Prepare fresh absorbing solution weekly.

Midget impinger

19 A number of designs of bubblers and impingers are available, some of which are described in ref 15. A midget impinger consists of a graduated receiver and a tapered inlet tube. The two parts should be matched so that the distance between the inlet tube tip and the receiver bottom is 1-2 mm.

Note 2: *Spill-proof impingers are available commercially*.

Filters

20 25 mm diameter filters are used in the selected sampler. The chosen filter type should have a capture efficiency of not less than 95% and be suitable for collection of stable samples of isocyanate. 1-2MP-impregnated glass-fibre filters have been found to be suitable. Desorption of the filters is carried out in acetonitrile at the laboratory and sampling/transport from site in absorbing solution (see paragraph 53) so the filter used must be compatible with both acetonitrile and toluene. The preparation of impregnated filters is described below.

Preparation of impregnated filters

21 Accurately weigh out approximately 0.25g of 1-(2-methoxyphenyl)piperazine and transfer to a 25 ml volumetric flask. Make up to the mark with dried toluene and shake to mix. This is solution 'A'.

22 In an area free from dust and isocyanates and using blunt tweezers, place a number of 25 mm glass-fibre filters on a clean glass plate so that no filters touch. Using a suitable microlitre syringe, dispense 200 µl of solution 'A' onto the surface of each filter, ensuring that the reagent impregnates the whole filter. Allow the filters to dry in air for several hours. When completely dry, transfer the filters from the glass plate to a screw-cap brown bottle using blunt tweezers. Label the bottle with the preparation and 'use before' date. Store until required in a dark cupboard or refrigerator for up to six months from preparation.

Sampling pumps

23 Sampling pumps, complying with the provisions of BS EN 1232,[16] with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the selected flow rate to within ±5% of the nominal value throughout the sampling period, and which can be worn by persons without impeding normal work activity.

24 Some of the more modern pumps are made largely of plastic. These pumps can be attacked by toluene vapour generated during sampling. If this is found to be the case a charcoal trap or similar can be fitted, before the pump and after any sampling equipment, to trap the vapour (ie impinger then/or filter, trap, pump). If a charcoal trap is to be used then calibration of the sampling pump should be carried out with the trap in place.

Calibration of sampling pumps

25 Measurement of the air volume sampled may be a significant source of error in the final calculation of isocyanate-in-air concentrations. Therefore, in a clean atmosphere, calibrate the sampling pump with an impinger or filter in line, using an appropriate externally calibrated meter. The impinger should contain absorbing solution (or toluene).

Flowmeter

26 Flowmeter, portable, capable of measuring the appropriate flow rate to within ±5%, and calibrated against a primary standard.[14] Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers, provided they have adequate sensitivity.

Ancillary equipment

27 Flexible plastic tubing, of a diameter suitable for making a leak-proof connection from the sampler(s) to the sampling pump. Fluran or similar tubing has been found to be suitable. Belts or harnesses to which the sampling pump may be conveniently fixed unless the pump is sufficiently small to fit into a worker's pocket. Flat tipped tweezers for handling the filters; containers to transport the filters and/or impinger solutions.

LABORATORY APPARATUS

Glassware

28 A selection of laboratory glassware, including: beakers, vials, pasteur pipettes, etc complying with the requirements of BS 1792.[17]

Disposable gloves

29 Disposable gloves, to avoid the possibility of contamination from the hands and to protect them from

contact with harmful substances. Nitrile or PVC gloves are suitable. Details of gloves (including 'protection' times) and other protective equipment suitable for use with isocyanates are given in the Society of Plastics (Polyurethane Division) technical bulletins AX179 and AX178.[18,19]

Balance

30 A balance, calibrated against a primary standard, for the preparation of the internal standard solution and calibration standards. The balance should be capable of weighing to ±0.1 mg over the range 0 to 100 mg.

Micropipettes

31 A set of adjustable positive displacement micropipettes, calibrated against a primary standard, for the preparation of calibration and sample solutions.[20]

Filtration equipment

32 A solvent-resistant plastic filter unit of 13 mm diameter and <2 µm pore size for filtration of LC solvents. Syringeless filters or 0.2 µm syringe filters for filtration of the desorbed samples prior to LC analysis.

Reagents

33 During the analysis, use only reagents of a recognised analytical grade. Use chromatographic quality toluene, free from compounds co-eluting with the analyte of interest, and dried with anhydrous calcium chloride or magnesium chloride. This is because part of the sample work-up procedure involves evaporating off the toluene. Any involatile impurities present will remain and possibly interfere with the analysis.

SAMPLING PROCEDURES

34 For long-term samples, select a sampling period of an appropriate duration, such that the filter does not become overloaded with particulate material (note that an 8-hour time weighted average concentration may be derived from the results of two or more consecutive samples, as described in HSG173.[12]

Preparation of sampling equipment (general)

35 Clean the samplers (filter cassette and/or impingers) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water, wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Preparation of sampling equipment (filters)

36 Load the filters into clean, dry samplers using clean flat-tipped tweezers. Connect each loaded sampling head to a sampling pump using plastic tubing, ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter to the sampling head so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate with an accuracy of ±5%. Switch off the pump and seal the sampler with a protective cover to prevent contamination during transport to the sampling position.

Preparation of sampling equipment (impingers)

37 Immediately before sampling, transfer 10 ml of the absorbing solution into an impinger and assemble it. Place the impinger in a protective holder and connect to the sampling pump with suitable tubing. Ensure that all connections are free from leaks.

Collection of filter samples

38 In an area free from isocyanates, fix the sampler to the worker, on their lapel and as close to their mouth and nose as possible. Place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes the minimum inconvenience, eg to a belt around the waist. When ready to begin sampling, remove the protective cover from the sampler and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, ensure that this is set to zero.

39 Draw a measured volume of air through the sampler at a rate of 2 $l.min^{-1}$. The recommended air volume is within the range 20-900 l. For mixtures of airborne particles and vapour, when an impinger/filter combination should be used, a sampling rate of 1 $l.min^{-1}$ is recommended.

40 Since it is possible for a filter to become clogged, monitor the performance of the sample periodically, a minimum of every two hours (or more frequently if heavy filter loadings are suspected). Measure the flow rate with the calibrated flowmeter and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within ±5% of the nominal value throughout the sampling period .

41 Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside ±5% of the nominal value.

42 At the end of the sampling period, measure the flow rate with an accuracy of ±5% using the calibrated flow-meter, switch off the sampling pump, and record the flow time and the time. Also observe the reading on the elapsed time indicator, where fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within ±5%, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

43 Carefully record the sample identity and all relevant sampling data. Calculate the mean flow rate by averaging the flow rate measurements throughout the sampling period and calculate the volume of air sampled,

in litres, by multiplying the flow rate in litres per minute by the sampling time in minutes.

44 With each batch of ten samples, submit for analysis at least two unused filters from the same lot of filters used for sample collection. Subject these blank filters to the same handling procedure as the samples, but draw no air through them.

Collection of impinger samples

45 The comments made above regarding monitoring flow rate and recording of sample identity also apply to impingers. When used for personal sampling, the impinger should be mounted in the worker's breathing zone, eg on the lapel. The sampled air should not pass through tubing prior to entering the impinger. The impinger should be retained in an approximately vertical position. Also check impingers periodically to ensure that the absorbing solution has not evaporated.

46 Draw a measured volume of air through the impinger. The minimum recommended sample volume is 15 l. For an 8-hour sample, several shorter samples should be taken, at up to 1 $l.min^{-1}$ and summed to produce the 8-hour result. For sampling over shorter periods, which is more usual, the flow rate may be increased proportionately, but should not exceed 1 $l.min^{-1}$. Thus, a 15-minute sample should be taken at 1 $l.min^{-1}$. It may be necessary to top up the impinger with dry toluene during the sampling period because of solvent loss due to evaporation.

47 Prepare sample blanks using impingers identical to those used for sampling. Subject them to the same handling procedure as the sample impingers (except for the actual period of sampling).

Collection of impinger backed by filter samples (mixtures of airborne particles and/or vapour, isocyanate aerosols)

48 Both filters impregnated with derivatising reagent and impingers containing solutions of derivatising reagent have been successfully used to collect airborne isocyanate monomer vapours. Both filters impregnated with derivatising reagent and impingers containing solutions of derivatising reagent have also been used to collect mixtures of airborne particles and/or vapour. However, neither of these systems has been found to be effective alone for these mixtures.[21,22] Mixtures of airborne particles and/or vapours (isocyanate aerosols) are not collected satisfactorily on coated filters because the isocyanate function may react with other compounds, either in the airborne particle or already collected on the filter. Furthermore, impingers appear unsuitable for sampling the range of isocyanate aerosols likely to be encountered in the workplace as particles of less than about 1 µm diameter are inefficiently collected by an impinger. Isocyanate species present in large particles (>10 µm) are not efficiently derivatised when collected on reagent-coated filters and stick to the filter cassette.[22] For this reason it is advisable to desorb the filter immediately after sampling with 1-2MP solution. However, the combination of an impinger followed by a reagent-coated filter should collect both isocyanate aerosols and/or vapours satisfactorily.

49 For the impinger backed by filter combination a sampling rate of 1 $l.min^{-1}$ is suggested. If using an impinger/filter combination, the filter must be placed after the impinger, otherwise the filter will clog, ie impinger-filter-pump.

Sampling efficiency

50 Sampling efficiency (SE) may be less than 1.0 (100%) due to incomplete absorption, particularly if a large air volume is taken or the sampling rate is too high. Normally, sampling efficiencies are in the range 0.95-1.05. Correct for incomplete absorption if the SE falls below 0.95 under the sampling conditions used. Alternatively, use two samplers in series and add together the results of the isocyanate determination for each sampler.

Determination of sampling efficiency

51 If a single impinger is used, the sampling efficiency for each isocyanate compound of interest should be determined over the sample concentration range. This can be done by using a standard vapour atmosphere generator to sample the isocyanates of interest at appropriate concentration, temperature, humidity, time and sampling flow rate. Treat these SE samples in the manner described previously. The SE is the weight (in mg) recovered from the impinger divided by the weight (in mg) applied. If the SE under the conditions used during sampling is less than 0.75 (75%), the result should be discarded.

52 For isocyanate polymers (oligomers and prepolymers), it is impractical to use a standard vapour atmosphere generator, as these preparations exist largely as mixtures of airborne particles and vapours at the concentrations of interest. It is also difficult to prepare accurate, stable standard vapour atmospheres for monomers. Typically, actual concentrations are 20-30% below calculated values, due to adsorption of the monomers onto the surface of the equipment. Therefore, SE is taken to be 1.0 for both monomers and polymers, for most practical purposes.

Transportation

53 For transport to the laboratory, remove each filter from the sampler, place in a 50 mm x 35 mm glass vial containing 1-2MP absorbing solution (2 ml) and cap the vial. If deposition from aerosols is suspected, rinse the inlet of the sampler head with a little dilute 1-2MP solution.

54 For impinger samples, transfer the contents to a glass vial and seal with a PTFE-lined screw-cap. Rinse the impinger and its inlet tube with a small volume of toluene and add the washings to the vial. It is not necessary to note the final volume of the solution or to make it up to its original volume.

ANALYSIS PROCEDURES

55 Wear disposable gloves during analysis to reduce the possibility of contamination and to protect the hands

from harmful solvents/reagents.[18,19] A checklist summarising the steps required for isocyanate analysis is given in Appendix 2.

Cleaning of glassware

56 Before use, clean all glassware to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution and then rinse thoroughly with water.

Pre-reaction of impinger samples before HPLC analysis

57 Acetylation of unreacted 1-2MP reagent improves the chromatographic separation of isocyanate derivatives. After sampling, transfer the contents of the impinger to a screw-cap vial as described above. Allow at least 24 hours to elapse from the time of sampling to ensure complete reaction of the isocyanate polymers. Pipette acetic anhydride (100 µl) into the vial and mix well. Evaporate to dryness, redissolve the residue in acetonitrile or mobile phase (2 ml) and transfer to a glass vial. Analyse using LC as described below.

Pre-reaction of filter samples before HPLC analysis

58 Pipette acetic anhydride (100 µl) into each glass vial containing the 1-2MP solution and filter paper and mix well. Evaporate to dryness and redissolve the residue in acetonitrile or mobile phase (2 ml). Filter this solution into an autosampler vial, using a syringeless filter or 0.2 µm syringe filter. Analyse using LC as described below.

System calibration

Preparation of monomer derivatives

59 Prepare standard solutions of recrystallised isocyanate monomer derivatives. Add the appropriate isocyanate (0.1 g) to 0.6 g of 1-(2-methoxyphenyl) piperazine dissolved in dry toluene (10 ml) and leave to stand for one hour. A white crystalline urea will be precipitated. Collect this on a Whatman No 1 filter paper and wash several times with dry toluene to remove excess reagent.

60 Recrystallise the urea from toluene, by warming to about 60°C and slowly adding methanol to dissolve the urea. Allow to cool and filter the resulting crystals, washing with cold, dry toluene. Dry the solid in air. The urea derivatives are only slightly soluble in toluene but readily soluble in methanol or acetonitrile. MDI and HMDI (Dicyclohexylmethane-4,4'-diisocyanate) and some isocyanate prepolymers are rather insoluble in toluene. The alternative method of preparation given below (paragraph 61) may be more suitable for these compounds.

61 Slowly add a solution of the appropriate isocyanate (0.5 g) in dichloromethane (25 ml) to a solution of 1-(2methoxyphenyl)piperazine (0.7 g) in dichloromethane (50 ml). A white suspension will form. Add this dropwise to a beaker of hexane (500 ml) with stirring. Filter the resultant precipitate and redissolve it in a minimum volume of dichloromethane. Add hexane to re-precipitate the solid, filter this and wash with hexane. Dry the urea derivative in air. The urea derivatives are more soluble in methanol than acetonitrile. Therefore if the urea derivatives will not dissolve in acetonitrile, dissolve them in a minimum of methanol and then make up to the required volume with acetonitrile.

62 Weigh out a known mass of the urea derivative, place in a 100 ml volumetric flask and make up to the mark with acetonitrile or methanol. Take aliquots of this solution and dilute volumetrically in acetonitrile or mobile phase to create a series of standard solutions over the concentration range 0.01-1.0 µg NCO.ml^{-1}. Prepare further standard solutions if the concentration range of the samples exceeds that of the standards.

Note 3: *Concentration of isocyanate groups in standard (µg NCO.ml^{-1}) = (W x M_n x N)/M_u*

where:

W = weight of urea derivative in standard (µg.ml^{-1})
M_n = molecular weight of NCO
N = number of isocyanate groups/molecule
M_u = molecular weight of the urea derivative

63 The analyst should keep a record of response factors for the monomer standards and the LC conditions used, eg mobile phase composition. This will allow changes in the performance of the system to be identified.

Preparation of calibration standards

64 Prepare at least six calibration standards to cover the range 1 µg.ml^{-1} NCO to 0.01 µg.ml^{-1} NCO. Standards are prepared from the relevant monomer derivative, ie for an HDI-based prepolymer use HDI.

High performance liquid chromatography (HPLC)

HPLC mobile phase

65 Dissolve 5 g of anhydrous sodium acetate in distilled water (1 l). Adjust the pH of this solution to 6.0 with glacial acetic acid. Add 550 ml of this solution to acetonitrile (450 ml) and degas this solution by filtering under vacuum or by bubbling a stream of helium through it, to give a 45% acetonitrile/55% sodium acetate buffer. Increasing the acetonitrile concentration of the mobile phase will decrease the retention time of the isocyanate peaks. If the LC back pressure is high then using a less concentrated buffer should improve this. A buffer with a lower sodium acetate concentration will also give a lower UV background at 220 nm and below; this is useful if DAD is being used (ie for library matching as described in paragraph 78).

Instrumentation and conditions

66 An HPLC linked to ultraviolet (UV) and electrochemical (EC) detectors is required. The EC detector should be used in the oxidation mode. A diode

array detector is also advisable for confirmation of identification.

67 Temperature fluctuations must be avoided in order to obtain the sensitivity required in this method. This can be achieved by thermostatting the HPLC column and EC detector. EC performance can be improved by recirculating the mobile phase and by use of a guard cell (set to ~ +50 mV above analytical cell potential) before the injector. A pulse dampener will also decrease the LC system noise (pulse ripple) and so increase signal to noise (S/N) ratio.

68 A variety of chromatographic conditions may be used for the analysis of organic isocyanates in solution. The choice will depend largely on the nature of interfering compounds, which may affect the chromatographic analysis. Typical conditions are as follows**:**

Column dimensions	100 mm length x 4.6 mm ID
Column packing	Hypersil ODS 5 µm (FSA Cartridge System) or similar
Column temperature	20°C
Flow rate	1 $ml.min^{-1}$
UV detector	242 nm and/or diode array detector
EC detector	porous graphite electrode or similar, operating at a potential of + 0.7 V

Retention time data under these conditions:

HDI	6.0
MDI	11.5
TDI	5.0 (2,6-isomer)
	6.7 (2,4-isomer)

69 The retention times of oligomer and prepolymer peaks will vary depending on the source of the sample. The reagent peak may mask the isocyanate monomer peak. To improve the separation, decrease the acetonitrile concentration of the mobile phase and acetylate the sample prior to analysis. For successful analysis of MDI, modify the mobile phase by increasing acetonitrile concentration, eg with the above system 56% acetonitrile will give an MDI retention time of 7.0 minutes. Where high concentrations are found, dilute the sample solutions with acetonitrile to bring the concentration back within the calibration range. Repeat the analysis and record the dilution factor.

Determination of airborne isocyanate from monomers

70 Pre-react the samples, blanks and the samples used to determine sampling efficiency as described above. Analyse by injecting a known fixed volume (10-20 µl) of each standard solution into the liquid chromatograph and using EC detection as described below. A standardised injection technique is required to obtain reproducible peak heights/areas. Prepare a calibration graph of EC response (height or area) versus analyte concentration in the standard solutions.

71 Inject the same fixed volume of the pre-reacted sample solution into the liquid chromatography. Determine the EC response and read the concentration of the analyte in the pre-reacted sample from the calibration graph. Analyse the sample blank and the samples used to determine sampling efficiency in the same way.

Determination of airborne isocyanate from isocyanate polymers (oligomers and pre-polymers)

72 For routine analysis of monomers, only EC detection need be used. If the presence of isocyanate oligomers and prepolymers is suspected, examine all peaks in the HPLC trace and calculate the ratio of the EC to UV response for each peak. Also analyse the corresponding isocyanate monomer derivative standard under the same operating conditions. Normally, the monomer is also present in the oligomer or prepolymer chromatogram.

73 The ratio of the peak responses in the two detectors is calculated as follows:

polymer peak response, EC detector/polymer peak response, UV detector = y

monomer peak response, EC detector/monomer peak response, UV detector = x

74 Peaks which have a $(EC_{POLY}/UV_{POLY})/(EC_{MONO}/UV_{MONO})$ detector response ratio (y/x) of 0.6-1.7 are assigned as being derived from isocyanates. To calculate the total isocyanate concentration in the sample solution, measure the EC response of these peaks relative to the monomer derivative calibration graph, and sum these values.

75 With some higher oligomers and prepolymer preparations, it can take over 40 minutes to elute all the components. In such cases, it is advisable to modify the mobile phase after the initial run. Increasing the acetonitrile content will reduce elution times and improve peak shapes in the latter portion of the chromatogram, allowing accurate integrals to be calculated.

Note 4: *Ideally, the (y/x) ratio would be 1, ie polymeric and monomeric isocyanates would have the same EC to UV response ratio. In practice the UV response for monomers and polymers is different. It has been found empirically that isocyanates give ratios of (y/x) between 0.6 and 1.7.*[23]

Note 5: *The detector response ratio varies with isocyanate type and from day to day, depending on the condition of the EC detector. It is also dependent on the wavelength of the UV detector and the potential at which the EC detector is set. However, in a series of analyses performed on the same day, this ratio should remain approximately constant for a given isocyanate monomer and its derived prepolymers and oligomers.*

Confirmation of identification for isocyanate polymers (oligomers and prepolymers)

76 In addition to the ratio method described above it may be possible to confirm the presence of isocyanate polymers if a bulk sample of the oligomer or prepolymer is available. This can be achieved by comparing retention times in the bulk and sample chromatograms. This approach may not be successful for end-capped or stoved isocyanates.

77 In principle, peaks in the sample chromatogram may not correspond with those in that of the bulk, as some modification of oligomers and prepolymers may take place in the atmosphere, eg by partial reaction with atmospheric polyol compounds. In practice, additional peaks have not been found in the samples routinely analysed at HSL. If partially reacted species exist, the EC response of the polymer 1-2MP derivative should still be proportional to the number of free NCO groups remaining, since this is primarily a function of the attached methoxyphenyl groups, not of the isocyanate matrix.

78 The use of diode array detection (DAD) is also of use for confirmation that a peak is an isocyanate-derived one.[23] DAD detection allows retention time matching of the samples to be carried out against monomer and bulk derivative standards. Peak purity routines can be run to detect co-eluting compounds and library matching carried out to aid identification. It has been found that isocyanate prepolymers and oligomers give DAD spectra that closely match that of the parent monomer. DAD, on a second LC system, also allows the use of gradient elution to decrease run times and improve peak shapes for any late eluting peaks. Running a gradient up to 100% acetonitrile should remove any highly polymerised isocyanates if these compounds are suspected to be present. Gradient elution is not suitable for EC detection as the response factors of the EC are dependent on mobile phase composition.

79 Other techniques may also be used for confirmation of identity. A fluorescence detector has been found to give acceptable results for the quantification of isocyanate monomers (ex 280 nm, em 360 nm). For polymeric isocyanates these conditions are suitable only for confirmation.[23] Liquid chromatography with mass spectroscopic detection has also been used to confirm peak identity.[24] Titration or Fourier transform infra-red spectrometry can be used to determine isocyanate content.[25] If an underivatised bulk sample is available. Other useful sources of information for underivatised bulks are safety data sheets or manufacturer's information.

Calculation of results

80 Calculate the volume, V_s, in litres, of each air sample. Calculate the isocyanate concentration in the sample (in µg NCO/ml), by comparison with standard solutions. Correct for blanks and sampling efficiency as follows:

Total isocyanate-in-air

concentration, µg $NCO.m^{-3}$ = $(m-m_{blank}) \times 1000 \times V_d / SE \times V_s$

where:

m	=	concentration isocyanates in sample, µg $NCO.ml^{-1}$
m_{blank}	=	concentration isocyanates in blank, µg $NCO.ml^{-1}$
SE	=	sampling efficiency
V_s	=	volume of air sampled, litres
V_d	=	desorption volume, ml

Test report

81 Report the isocyanate-in-air concentration(s) to the nearest µg $NCO.m^{-3}$. Appendix 1 gives recommendations for information to be included in the test report.

METHOD PERFORMANCE

82 This method is similar to that described by Bagon, Warwick and Brown,[26] and Bagon[27] has been evaluated, according to CEN criteria,[11,28] for the HDI trimer (oligomeric HDI), Desmodur N 3390[29] and prepolymer preparations derived from TDI (Desmodur L), MDI (Desmodur VL) and HDI (Desmodur N).[26,27] Overall uncertainty data are included below for these compounds. The method has been evaluated previously for phenyl isocyanate, TDI and HDI.[30] The method has also been used successfully for other organic isocyanates.

83 The upper limit of the useful range is set by the quantity of absorbing reagent, which must be maintained in excess. Normally a solution with an absorbing capacity equivalent to 110 µg NCO is used in the impinger. Very high concentrations of isocyanates will not be sampled efficiently. The lower limit of the useful range depends on a number of constraints, including the noise levels on the detectors, adequate sampling efficiency and the ability of the integrator to quantify poorly shaped peaks. The detection limits for the EC detector are given below.

Effectiveness of desorption efficiency

84 Recovery experiments on Desmodur N 3390 spiked filters gave acceptable recoveries after seven and twenty-seven days' storage in a freezer.[29] Spiking levels were equivalent to 2x, 1x and 0.1x the limit value (15 l air sample). An overall recovery for Desmodur N 3390 was calculated as 91 ±10.5%. This is within the CEN criteria for storage.[11,28]

Detection limits

85 The qualitative and quantitative detection limits for isocyanate, defined as three times and ten times the standard deviation of six blank determinations, have been found to be typically around 0.001 and 0.004 µg NCO per sample respectively (EC detection). For a 15 l air sample, these figures correspond to qualitative and quantitative detection limits of 0.07 $\mu g.m^{-3}$ and 0.27 $\mu g.m^{-3}$ respectively.

Overall uncertainty

86 The overall uncertainty for a measuring procedure is defined in BS EN 482[11] as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is quoted as a percentage combining bias and precision using the following equation:

$$\text{Overall uncertainty} = \frac{\left| \bar{x} - x_{ref} \right| + 2s}{x_{ref}} \times 100$$

where:

$\bar{x}$ is the mean value of results of a number n of repeated measurements;
x_{ref} is the true or accepted reference value of concentration;
s is the standard deviation of measurements.

87 Pump bias has been found previously to be 2% and pump precision 5%. These values are added to the precision and variance obtained for the analysis when calculating the overall uncertainties shown below. The performance requirements quoted in BS EN 482[11] for overall uncertainty, where the task is 'measurement for comparison with limit values', are ≤50% for samples in the range 0.1 to 0.5 LV and ≤30% for samples in the range 0.5 to 2.0 LV (LV = limit value). Unless otherwise stated, the LV used was the long-term limit (8 hr) assuming a 15 l sample.

88 The overall uncertainty of the method for Desmodur N 3390[29] (oligomeric HDI) has been determined as 63% for samples in the range 0.1 to 0.5 LV (worst case) and 26% for samples in the range 0.5 to 2.0 LV (worst case). The overall uncertainty of the method for Desmodur N (polymeric HDI) has been determined, using data published previously,[26] as 30% for samples in the range 0.1 to 0.5 LV and 23% for samples in the range 0.5 to 2.0 LV. For these results the short-term LV was used. The overall uncertainty of the method for Desmodur VL (polymeric MDI) has been determined, using data published previously,[26] as 18% for samples in the range 0.1 to 0.5 LV and 21% for samples in the range 0.5 to 2.0 LV. For these results the short-term LV was used. The overall uncertainty of the method for Desmodur L (polymeric TDI) has been determined, using data published previously,[26] as 55% for samples in the range 0.1 to 0.5 LV and 36% for samples in the range 0.5 to 2.0 LV. For these results the short-term LV was used.

89 Thus, depending on the isocyanate type, the method performance either meets, or nearly meets, the CEN criteria.[11] In the latter case, the method may be used under the provisions of the note in clause 0 of the standard,[11] ie is the best available method.

Interferences

90 The sampled atmosphere may contain compounds which give chromatographic peaks under the conditions chosen for LC analysis. In particular, aromatic amines frequently occur in association with isocyanates. The method of identification described above using detector response ratio, DAD detection and if necessary fluorescence or MS detection should enable an accurate identification to be made. If interfering compounds are known or suspected, the identity of the interfering compounds should be communicated to the analyst.

Stability

91 Isocyanate ureas (MP) derivatives have been found to be stable for several years on storage in a freezer. Stock solutions of isocyanate monomer derivatives have been found to be stable for over six months if kept in a freezer. Isocyanate monomers (TDI) on filters and in toluene solution have been found to be stable for up to 90 days (73% and 81% recoveries respectively).[31]

QUALITY CONTROL MEASURES

Quality control

92 Analyse freshly prepared quality control samples as a quality check. An appropriate level of quality control should be employed when using this method. Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.[32]

93 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.

Advice

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield S3 7HQ (telephone 0114 2892000, fax 0114 2892500, email info@hsl.gov.uk).

The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

APPENDIX 1

Recommendations for the test report

It is recommended that the test report should include the following information:

(a) complete identification of the sample, including the date and place of sampling;

(b) reference to this MDHS and a description of any deviation from the procedures described;

(c) the type and diameter of filter used, and the type of sampling head (if filter used);

(d) the type of sampling pump and flowmeter used, the primary standard against which it was calibrated, and the range of flow-rates for which the flowmeter was calibrated;

(e) the duration of the sampling time in minutes and/or the time at the start and at the end of the sampling period;

(f) the volume of air sampled, in litres;

(g) the name of the person who collected the sample;

(h) the time-weighted average isocyanate concentration found in the air sample, in micrograms per cubic metre

(i) the overall uncertainty of the method;

(j) the name of the analyst;

(k) the date of the analysis;

(l) any unusual features noted during the determination.

APPENDIX 2

Checklist for isocyanate analysis

(a) Prepare MP derivative of bulk (if available, not necessary if monomer only present).

(b) Run on EC/UV, sort out LC conditions.

(c) Work **y/x** ratios for peaks, identify 'candidate' isocyanate peaks.

(d) Run on DAD, confirm 'candidate' isocyanate peaks using DAD, library search and peak purity routines. Use a larger injection (100 µl) to increase sensitivity if required.

(e) Calibrate EC system using relevant monomer.

(f) Run samples.

(g) Check samples and NCO identification. Look for partially reacted species. If necessary, run samples on DAD for confirmation of identity.

(h) Report. Keep a record of monomer response factors to check system performance.

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