



Health and Safety Executive
Occupational Medicine and
Hygiene Laboratory

MDHS 78

Methods for the
Determination of
Hazardous Substances

May 1994

Formaldehyde in air

Laboratory method using a diffusive sampler,
solvent desorption and high performance liquid
chromatography

INTRODUCTION

Properties and uses

1 Formaldehyde, synonyms methanal, oxomethane, oxymethylene, and methylene oxide, CH_2O , is a colourless gas, with a pungent suffocating odour, of boiling point -19.5°C and vapour density 1.067 (air = 1.000). The compound is very soluble in water (up to 55%) and also dissolves in some organic solvents, eg ethanol and diethyl ether. It is less stable in aqueous solution than in the gas phase, slowly polymerising to paraformaldehyde, $-(\text{CH}_2\text{O})_n-$, and other products. Formaldehyde is very reactive and combines readily with many substances. It is supplied commercially as a solution in water containing approximately 37% of the compound, and known as formalin. This usually contains 10-15% methanol to inhibit polymerisation. Formaldehyde is an important industrial chemical in the manufacture of resins to make adhesives and consumer products. It is also present in coal, particularly that used for smoking ham and fish, in wood smoke and in the atmosphere, especially over large cities.

Toxicity and first aid

2 For a review on the toxicity of formaldehyde, see the appropriate HSE toxicity review.¹ For information on first aid, see the NIOSH/OSHA Occupational Health Guidelines² and the CIA Chemical Exposure Treatment Cards.³

Analytical methods

3 This is not a 'reference' method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte.⁴ In the case of formaldehyde, these methods include a colorimetric method (ref 4, MDHS 19), a filter/impinger method,⁵ sorbent tube methods,⁶⁻⁸ a pumped filter method⁹ and a bubbler/polarography method.¹⁰ With the exception of a few cases, where an exposure limit is linked to a specific method (eg for rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have the accuracy and reliability appropriate to the application.

Requirements of the COSHH Regulations

4 The Control of Substances Hazardous to Health (COSHH) Regulations¹¹ require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and

training. The COSHH Regulations also include a requirement to assess the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. Employers must, therefore, ensure that the requirements of the COSHH Regulations are fully satisfied before allowing employees to undertake any procedure described in this method.

DIFFUSIVE SAMPLING

5 Diffusive samplers, unless specifically designed otherwise, collect only vapour, not particulates. In many situations, especially with aldehydes, much of the 'vapour' may be part of an aerosol, either occluded onto dust or as paraformaldehyde. In these circumstances, total formaldehyde should be determined by using a pumped sampler incorporating a 2,4-dinitrophenylhydrazine coated filter⁹ or equivalent. If the extent of formaldehyde aerosol is unknown, a preliminary field comparison using pumped and diffusive methods should be undertaken.

PRINCIPLE

6 The diffusive sampler is exposed to air for a measured time period. The rate of sampling has been determined by prior calibration in a standard atmosphere (paragraphs 13 and 33). The formaldehyde vapour migrates into the sampler by diffusion and is collected on a strip of silica gel tape, which has been coated with 2,4-dinitrophenylhydrazine and phosphoric acid. A stable hydrazone species is formed, which can be desorbed by either methanol or acetonitrile, and the solution analysed with a high performance liquid chromatograph, equipped with a uv detector.

QUALITY CONTROL

7 An appropriate level of quality control should be employed when using this method. Guidance is given in MDHS 71.¹² If a standard operating procedure is used, analysis of an internal quality control sample can be used as a quality check on the basis of a working standard deviation of 6.7% (warning at ± 2 sd; action at ± 3 sd).

SCOPE

8 The method described is for the determination of the time-weighted-average concentrations of formaldehyde vapour in workplace atmospheres. The method is suitable for sampling over periods in the range

15 min to 8 h. The method is designed for personal monitoring and may be used for fixed location monitoring at wind velocities of down to 0.02 m/s.

9 The method is suitable for the measurement of airborne formaldehyde vapour in the concentration range 0.1 to 4.0 mg/m³ (about 0.08 to 3.2 ppm, v/v) for exposure times between 15 min and 8 h. The method is not suitable for determination of formaldehyde present in an aerosol, although a pumped filter method⁹ can be employed.

10 The upper limit of the useful range is set by the sorptive capacity of the 2,4-dinitrophenylhydrazine coated filter tape and the linear range of the liquid chromatograph detector.

11 The lower limit of the useful range depends on a number of factors, including the noise level on the detector (paragraph 23) and adequate desorption efficiency (paragraph 13). Potential interferences should be eliminated by the chromatographic step in the method.

12 The method has been examined, following a diffusive sampler evaluation protocol,¹³ using a GMD 570 Series Formaldehyde Dosimeter Badge. The results of this evaluation¹⁴ are presented in paragraphs 13 to 18.

13 Over the range specified in paragraph 9 the standard uptake rate, or calibration factor, for the GMD Formaldehyde Badge is approximately 25.2 ± 1.7 cm³ min⁻¹ (30.9 ng ppm⁻¹ min⁻¹) (1.9 µg ppm⁻¹ h⁻¹) at 25°C. This value assumes that a correction has been made for desorption efficiency. It has been obtained by exposure of the GMD Badge to standard atmospheres of formaldehyde, generated from paraformaldehyde, with subsequent desorption of the filter by acetonitrile.¹⁵ Methanol may also be used as the desorbing solvent, but the resulting solutions are unstable, and it is, therefore, advisable to analyse them within 8 h of desorption. Both acetonitrile and methanol are >95% efficient at desorbing the hydrazone coated filter.¹⁶ Where formalin is present as a source of formaldehyde, the uptake rate may differ.¹⁷ Therefore, if possible, side-by-side comparisons between the GMD Badge and parallel pumped sampling methods should be carried out in potential sampling situations. Disagreement between the two sets of results gives good evidence for the existence of a mixture of components within the pollutant vapour.

14 The standard uptake rate is independent of exposure dose between 0.26 and 24.0 mg m⁻³ x hours (0.2 and 19.2 ppm x hours).

15 From laboratory experiments, the within-laboratory precision of replicate measurements is 6.7%, expressed as a coefficient of variation, ie a repeatability (ISO 5725) of 19.0%. In a field trial, bias was approximately 12% in the range 0.01 to 4.0 mg m⁻³ formaldehyde.

16 The uptake rate of the sampler is not significantly affected by ambient air movement, and can be used in situations with wind velocities down to 0.02 m s⁻¹. The manufacturer recommends that the badges are kept in a freezer before use, and are refrigerated and analysed within 2 weeks of sampling. Back-diffusion is effectively eliminated with this sampler because the formaldehyde is derivatised to a stable species on contact with the coated filter.

17 Humidity has no effect on sampler uptake rates up to 80% rh at 25°C and 24.0 mg m⁻³ x hours (19.2 ppm x hours).

18 Field tests of the GMD 570 Series Formaldehyde Badge have been conducted in a variety of industrial and residential locations. In most cases, a pumped sampler, incorporating a 2,4-dinitrophenylhydrazine coated filter, has been used as the independent sampling method, but comparisons with an Interscan instrument and an impinger have also been carried out. In tests by several different authors, formaldehyde measurements overall ranged from 0.01 to 4.0 mg m⁻³.

19 Any compound that co-elutes with the formaldehyde-hydrazone at the operating conditions chosen by the analyst is a potential interferent; changing the chromatographic conditions, eg by employing gradient elution or changing the HPLC column, may solve the problem. However, interference was not found to be a problem for the authors reviewed, as it was effectively eliminated by the derivatisation and chromatographic separation steps in the method.

20 When interfering compounds are known to be present in the air, or are suspected of being present, the identity, or suspected identity, of the compounds should be transmitted with the sample. If possible, potential interferences should be checked before routine monitoring is carried out. The presence of large amounts of carbonyl compounds may cause consumption of the derivatising reagent, leading to a reduction in the uptake rate of the badge for formaldehyde.

REAGENTS

21 During the analysis, use only reagents of recognised analytical reagent grade. The acetonitrile, methanol and water should be of HPLC Grade quality.

Diffusive samplers

22 The GMD Formaldehyde Badge is not the only commercially available 2,4-dinitrophenylhydrazine based diffusive sampler. Details of those known to be currently available in the UK are given in Appendix A. A diffusive sampler for formaldehyde can be constructed by the user, following the procedure laid down in ref 9. The use of the GMD sampler in evaluating the method should not be taken as indicating a preference for this particular device. Other devices may be more or less suitable, depending on the application, but are likely to have slightly different performance characteristics to those described here.

Liquid chromatograph

23 A high performance liquid chromatograph linked to a uv detector is suitable. The detector output should be monitored at a wavelength of 365 nm.

24 A reversed phase HPLC column should be used for the analysis of the formaldehyde hydrazone. A suitable choice might be, for example, an octadecylsilane column such as a Waters Radial-PAK A (100 x 5 mm id, 10 µm particles), used in conjunction with a mobile phase consisting of a methanol/water mixture (eg 70% methanol,

30% water). The exact composition of the mobile phase required will depend on a number of factors, including the length and particle size of the column, and the presence of interfering compounds. Either a gradient or isocratic elution programme may be employed.

PROCEDURE (for GMD 570 Series Formaldehyde Dosimeter Badge)

Collection of samples

25 Immediately before sampling, remove the diffusive sampler from its protective bag. When used for personal monitoring, the sampler should be mounted in the worker’s breathing zone, for example on his or her lapel. Ensure that, when mounted, the sampler is freely open to the atmosphere, ie that it is not obscured by clothing or other objects. At the end of a measured time period of exposure, the sampler is removed and the closure window is shut. The sampler is then replaced in its protective bag for transport. The protective bag contains a coated filter in a metal screen. This is to minimise contamination, and should not be analysed.

Sample blanks

26 Each GMD Formaldehyde Badge incorporates a portion of coated filter tape which is not exposed during sampling and, therefore, acts as a sample blank. However, at very high sample loadings, migration of the stain from the exposed to the unexposed portion may occur. In these circumstances, ie if visible hydrazone stain extends beyond the interface between the portions of tape, use the whole tape as a sample and an unexposed badge as a sample blank.

Desorption

27 Desorption should be carried out in a clean atmosphere in a fume hood. The sliding cover and screen are removed from the sampler, and the coated tape lifted out with forceps. The blank and exposed sections of the tape are separated, and each is placed into a 4 mL glass vial. Desorption is achieved by pipetting 3.0 mL of acetonitrile to each vial, followed by agitation for one minute.

Preparation of standard solutions

28 Formaldehyde hydrazone for use in standard solutions should be prepared according to the method detailed in ref 15. The resulting yellow crystalline solid should be recrystallised twice from hot ethanol.

29 A standard solution of formaldehyde hydrazone in acetonitrile should be prepared. Further standard solutions to cover the range of interest should be prepared by serial dilution of the first solution. The concentration range of interest should exceed the concentration range of the desorbed samples (paragraph 30). Prepare fresh standard solutions with each batch of samples.

30 It may be necessary to prepare a few standards covering a wide range of concentrations (say 0.5 µg mL⁻¹

to 100 µg mL⁻¹) in order to determine the approximate concentration range of the desorbed samples and hence the concentration range of interest. Further standards can then be prepared as necessary.

Analysis

31 Inject the liquid chromatograph with a known fixed volume of each standard solution (paragraph 29), eg 10 µL. A standardised injection technique should be used such that reproducible peak heights or areas are obtained. Prepare a calibration graph of peak response against analyte concentration. The precision quoted in paragraph 14 has been obtained using an autosampler.

32 Inject into the liquid chromatograph the same fixed volume of the solution from the desorbed sample. Read from the calibration graph the concentration of the analyte in the desorbed sample. Analyse the sample blank in the same way.

Calibration

33 The standard uptake rate for the GMD Badge is given in paragraph 13. For another sampling device it may be necessary to follow the protocol¹³ to determine the relevant uptake rate and its range of applicability.

CALCULATIONS

34 Calculate the weight, in µg, of formaldehyde in the sample by comparison with standard solutions. Correct for sample blanks as follows:

$$\text{Concentration of formaldehyde in air (mg m}^{-3}\text{)} = \frac{(m - m_{\text{blank}}) \times 0.143 \times 1000}{U' \times t}$$

where
 m = mass (µg) of formaldehyde hydrazone in exposed portion of badge

m_{blank} = mass (µg) of formaldehyde hydrazone in blank portion of badge

U' = uptake rate (cm³ min⁻¹), calibrated as 25.2 cm³ min⁻¹

t = exposure time (min)

$$0.143 = \frac{M_w \text{ formaldehyde}}{M_w \text{ formaldehyde hydrazone}}$$

35 Alternatively, the concentration of formaldehyde in the sampled air may be expressed in ppm:

$$\text{Concentration of formaldehyde in air (ppm)} = \frac{(m - m_{\text{blank}}) \times 0.143 \times 1000}{U \times t}$$

where

U = uptake rate (ng ppm⁻¹ min⁻¹)

36 Uptake rates in $\text{cm}^3 \text{min}^{-1}$ and $\text{ng ppm}^{-1} \text{min}^{-1}$ are related by:

$$U' = U \times \frac{24.5}{M_w} \times \frac{T}{298} \times \frac{101}{P}$$

($\text{cm}^3 \text{min}^{-1}$) (ng $\text{ppm}^{-1} \text{min}^{-1}$)

where

24.5 = molar volume (litres) at 298 K and 101 kPa

M_w = molecular weight of formaldehyde (30)

T = temperature of sampled air in Kelvin

P = pressure of sampled air in kPa

When expressed in units of $\text{ng ppm}^{-1} \text{min}^{-1}$, U is almost independent of temperature and only slightly dependent on pressure.

REPORT

37 Report the analyte-in-air concentration(s) to the nearest 0.1 ppm (0.13 mg m^{-3}).

ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, Broad Lane, Sheffield S3 7HQ (telephone 0742-892000).

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.

REFERENCES

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APPENDIX A

Suppliers of 2,4-dinitrophenylhydrazine based diffusive samplers that may be suitable for this method, and that are available in the UK.

GMD
570 Formaldehyde Dosimeter
Detectawl, 2 Cochran Close, Crownhill, Milton Keynes, MK8 0AJ. Tel: (0809) 568076/568077

Airbadge
Formaldehyde Airvial
Airbadge Limited, Unit 2F, Brighthouse Business Village, Riverside Park Road, Middlesbrough TS2 1RT. Tel: (0642) 250879

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