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AN INVESTIGATION INTO THE DIFFERENCES IN COMPOSITION OF FORMALDEHYDE ATMOSPHERES GENERATED FROM DIFFERENT SOURCE MATERIALS AND THE CONSEQUENCES FOR DIFFUSIVE SAMPLING

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Abstract—The results of an investigation into the differences in formaldehyde atmospheres generated from different source materials are presented. It was initiated after discrepancies were found between the results obtained from pumped and diffusive sampling methods when using formalin as the source material for formaldehyde atmosphere generation. The compositions of formaldehyde vapours produced from various source materials have been determined using infrared (IR) spectroscopy and chemical analysis. These showed that those atmospheres generated from paraformaldehyde yield almost entirely formaldehyde monomer, whereas those generated from formalin yield a mixture of formaldehyde monomer and methoxymethanol. This has the effect of varying the effective molecular weight of the formaldehyde species in the atmosphere, thereby changing the effective sampling rate of diffusive sampling devices. Results in this study suggest that there is a possibility that diffusive samplers will give erroneous results if they are used in field environments where the formaldehyde atmosphere differs in composition from that used in the laboratory calibration. This emphasizes the need to be certain of the nature and composition of any pollutant vapour in order that the sampling device can be appropriately calibrated. Crown copyright © 1996 Published by Elsevier Science Ltd.

INTRODUCTION

Diffusive sampling has been recognized as an efficient alternative to pumped sampling in occupational hygiene (Berlin *et al.*, 1987). Several diffusive samplers for formaldehyde have been developed and validated. In 1990, a liquid badge, now no longer available, was validated by the U.K. Health and Safety Executive (Ellwood *et al.*, 1990). This badge, manufactured by SKC Inc., U.S.A., consisted of a liquid-filled chamber, bound at the front by a permeable membrane which allowed passage of the gas or vapour being collected whilst retaining the liquid in the chamber. A diffusive sampler for formaldehyde consisting of a 37-mm, 2,4-dinitrophenyl hydrazine (DNPH)-coated glass fibre filter mounted in a cassette constructed from a standard 37-mm filter holder has been validated and used for both occupational and indoor air applications (Levin *et al.*, 1986, 1989). Another diffusive sampler especially designed for the sampling of reactive compounds using a reagent-coated filter has been developed by the Swedish National Institute of Occupational Health. For formaldehyde, a filter coated in 2,4-dinitrophenyl hydrazine (DNPH) is used (Levin *et al.*, 1988; Lindahl *et al.*, 1989; Noble *et al.*, 1993; Levin and Lindahl, 1994). The sampler is intended for one-time use and is commercially available from GMD Inc.,

U.S.A., as the GMD-570. The investigation reported here was initiated following an inter-laboratory round robin exercise using this diffusive sampler. During the exercise, in which formaldehyde was generated from formalin solution, it was found that results from the GMD-570 diffusive samplers were only about 65% of those obtained from reference methods using pumped sampling techniques. An investigation into the reasons for this discrepancy was therefore carried out. In order to investigate possible reasons for this discrepancy, a number of formaldehyde atmospheres were generated from different source materials, and their chemical composition determined using a combination of Fourier transform infra-red (FT-IR) spectroscopy and chemical analysis.

EXPERIMENTAL AND RESULTS

Sampling of formaldehyde generated from formalin solution

To determine whether the discrepancies noted in the initial exercise were reproducible, a laboratory trial was carried out on three formaldehyde atmospheres generated from syringe injection of formalin (Ellwood *et al.*, 1990). For each of the three atmospheres a batch of six GMD-570 diffusive samplers were exposed in the glass test chamber, while at the same time formaldehyde levels inside chamber were monitored using three impingers (Ellwood *et al.*, 1990) and six pumped 13 mm DNPH-coated filters (Levin *et al.*, 1986). The pumped impinger samples were analysed by a colorimetric method based on 2-hydrazinobenzothiazole (HBT) (Ellwood *et al.*, 1990). The pumped and diffusive DNPH-coated filters were desorbed with acetonitrile and analysed using reversed-phase high-performance liquid chromatography (HPLC) (Levin *et al.*, 1986, 1988). The data from these experiments are summarized in Table 1, and indicate the results from the diffusive samplers to be around 65% of those obtained using the two pumped sampling techniques.

The effective sampling rate of the GMD sampler had been evaluated in an atmosphere generated from heated paraformaldehyde (Levin *et al.*, 1986, 1988) whereas the sampling exercise used an atmosphere generated from formalin solution (Pengelly *et al.*, 1989). The most likely source of the discrepancies observed is therefore that the chemical compositions of the formaldehyde atmospheres generated from paraformaldehyde and formalin are not the same.

Formaldehyde, in a purely aqueous solution is present largely in the form of the methylene glycol (Hendrickson *et al.*, 1970; Ogata and Kawasaki, 1970). However, this has a tendency to polymerize to poly(oxymethylene) glycol $[\text{HO}(\text{CH}_2\text{O})_n\text{H}]$ or paraformaldehyde (Utterback *et al.*, 1985), so methanol is added as a stabilizer.

Table 1. Summary of sampling exercise with formaldehyde generated from formalin (mg m^{-3})

Experiment No.	Pumped filter samples (RSD)	Pumped impinger samples (RSD)	Diffusive badge samples (RSD)
1	0.93 (1%)	0.89 (3%)	0.63 (14%)
2	0.94 (1%)	1.06 (4%)	0.60 (6%)
3	3.63 (1%)	3.73 (4%)	2.35 (2%)

Methanol prevents the formation of polymers, but reacts with formaldehyde to form methoxymethanol and/or dimethoxymethane (also known as methylal). Since commercial formalin solutions typically contain around 10% methanol, it is probable that a high percentage of the formaldehyde present is in one of these two methylated forms. The presence of such a mixture of methylated and unmethylated formaldehyde in formalin solution raises the question of the chemical composition of formaldehyde atmospheres derived from formalin. This is important as the effective sampling rate of a diffusive sampler is directly proportional to the inverse square root of its molecular weight (Laidler and Meiser, 1982). This relationship results in diffusive sampler performance being significantly affected by large variations in molecular weight, such as would be caused by a change in analyte vapour from formaldehyde monomer to methylene glycol or methoxymethanol.

Infra-red analysis of formaldehyde atmospheres

In order to investigate the discrepancies further, formaldehyde atmospheres were generated using the four techniques detailed below and analysed by connecting to a Spectra-Tech 10 m Variable Pathlength Infra-red (IR) Gas Cell (with an approximate internal volume of 4 l.). The gas cell, with the pathlength set at 2.12 m, was placed in a Nicolet 7199 FT-IR and a 32 scan IR spectrum produced over a frequency range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . Each spectrum was referenced against a dry air stream.

Infra-red vapour phase spectra for methanol, dimethoxymethane, water and carbon dioxide were also produced, as some or all of these components were likely to be present as interference in the various atmospheres produced.

Formaldehyde from paraformaldehyde. Around 2 g of paraformaldehyde in a glass container was semi-immersed in a thermostated water bath at a temperature of 70°C. The container was connected to a stream of dry air which was allowed to pass over the paraformaldehyde powder and into the IR gas cell at around 12 l. min^{-1} . Infra-red analysis of the vapour produced by this method showed it to consist almost entirely of formaldehyde monomer, with its characteristic bands at around 1750 cm^{-1} (C=O) and 2800 cm^{-1} (C—H) (see Fig. 1).

Formaldehyde from formalin (syringe injection). Using a glass-PTFE injector heated to around 85°C, formalin (ca 37% formaldehyde + 10% added methanol) was injected at a rate of 5 $\mu\text{l min}^{-1}$ into a dry air stream flowing into the gas cell at around 10 l. min^{-1} . Infra-red analysis of the vapour produced showed it to contain a number of components, including methanol and water vapour from the formalin solution, as well as formaldehyde monomer. If the bands due to these three components were removed, the remaining component was revealed as having absorbance bands at 900–1100 cm^{-1} (C—O), 2900 cm^{-1} (C—H) and 3600 cm^{-1} (O—H). The spectrum showed similarities to dimethoxymethane, but differed in the relative intensities of the C—O bands and the presence of the O—H band (see Fig. 2). From the IR spectrum it was deduced that the probable identity of this fourth component was methoxymethanol.

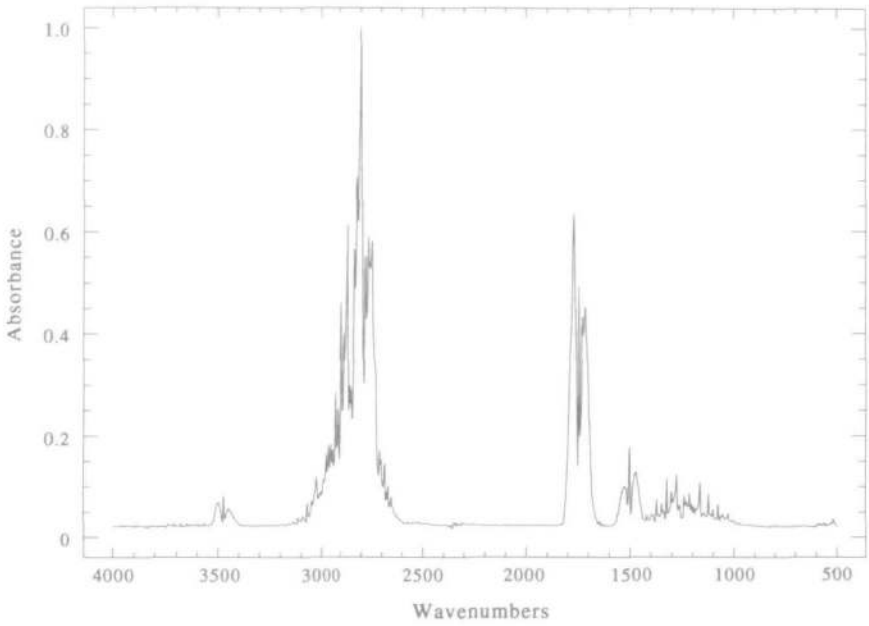


Fig. 1. Infra-red spectrum of an atmosphere generated from temperature controlled paraformaldehyde.

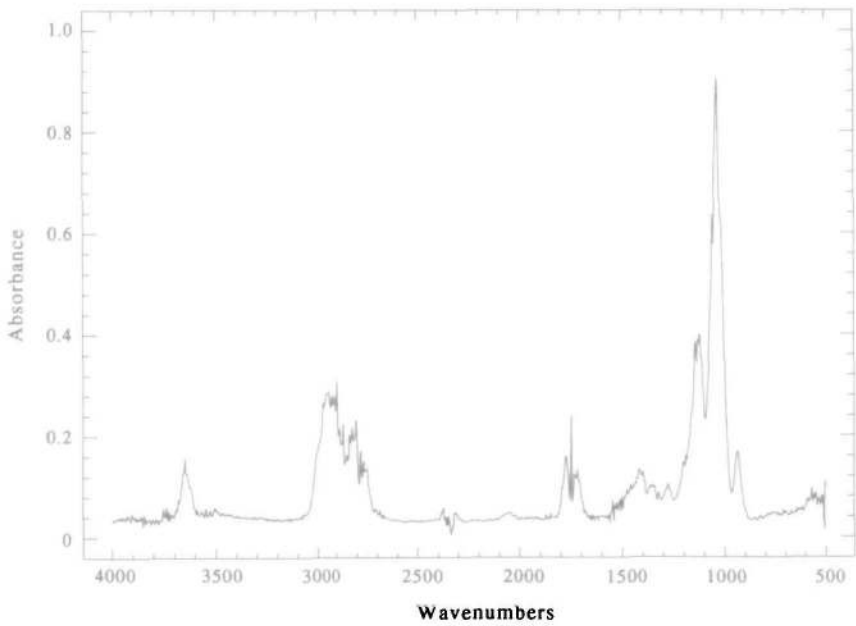


Fig. 2. Infra-red spectrum of an atmosphere generated from syringe injected formalin (with bands due to water and methanol removed).

Formaldehyde from formalin (thermostated bulk liquid). Twenty millilitres of formalin (ca 37% formaldehyde) was placed in a glass container semi-immersed in a thermostated water bath at a temperature of 30°C. The container was then connected to a stream of dry air which was allowed to pass over the formalin solution and into the IR gas cell at around 5 l. min⁻¹. Infra-red analysis of the vapour produced by this method indicated the presence once again of methanol, water vapour and formaldehyde monomer. If the bands due to these components were removed, the remaining spectrum was similar to that obtained from syringe injection of formalin. Examination of the bands between 850 and 1250 cm⁻¹, however, suggested that the remaining component may also contain small amounts of dimethoxymethane in addition to the methoxymethanol proposed above (see Fig. 3).

Formaldehyde from non-methanolic aqueous formaldehyde solution. Around 20 ml of non-methanolic aqueous formaldehyde solution (ca 9% formaldehyde) in a glass container was semi-immersed in a thermostated water bath at a temperature of 25°C. This non-methanolic formaldehyde solution was prepared by mixing 10 g paraformaldehyde with 100 ml of distilled water. The mixture was heated, with stirring, to boiling point and allowed to simmer for about 15 min. After cooling, the mixture was filtered to remove any remaining paraformaldehyde, and the formaldehyde content determined by iodine-thiosulphate assay (Pengelly and Groves, 1991). A stream of dry air was passed over the solution and into the IR gas cell at around 5 l. min⁻¹. Infra-red analysis of the vapour produced in this way

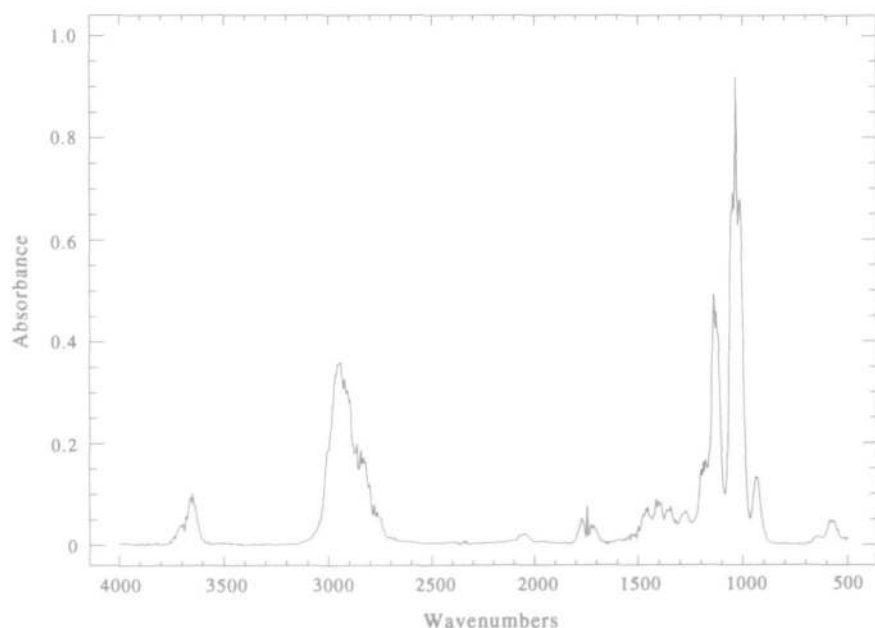


Fig. 3. Infra-red spectrum of an atmosphere generated from temperature controlled formalin (with bands due to water and methanol removed).

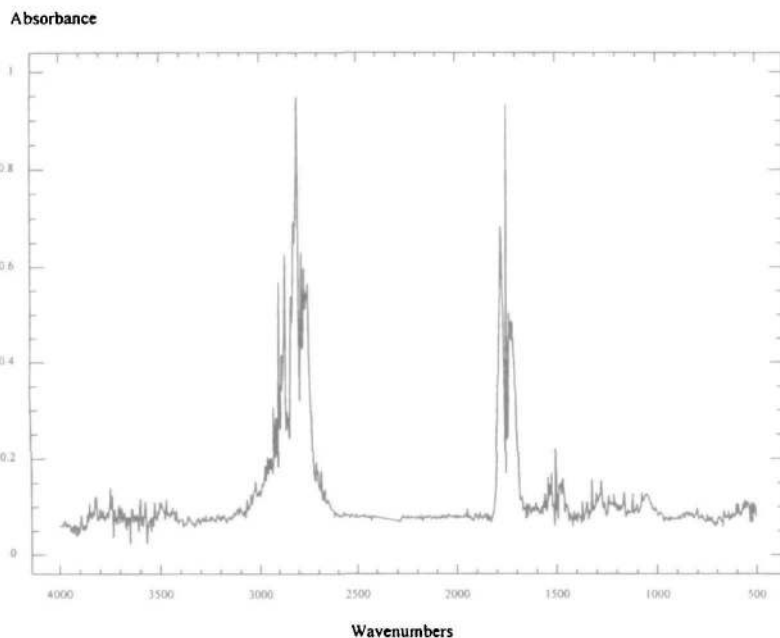


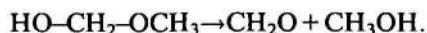
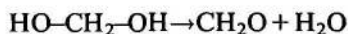
Fig. 4. Atmosphere generated from temperature controlled non-methanolic formaldehyde solution (with bands due to water removed).

showed it to contain a mixture of water vapour and formaldehyde monomer (see Fig. 4).

Effect of formaldehyde species on the performance of the pumped sampling methods

Analysis of the IR spectra obtained from the four test atmospheres described above leads to the conclusion that formaldehyde atmospheres prepared from different source materials have different compositions. Vapours generated from paraformaldehyde or non-methanolic formaldehyde solutions contain primarily formaldehyde monomer, whereas vapours from formalin contain a mixture of components, primarily formaldehyde and methoxymethanol—with the relative proportions dependent on the source material used.

Pumped impinger sampling of these vapours into water results in the majority of any formaldehyde monomer present being converted into methylene glycol, whilst the methoxymethanol remains initially unaltered (Hendrickson *et al.*, 1970; Ogata and Kawasaki, 1970). However, as shown below, both methylene glycol and methoxymethanol are unstable and decompose readily back to formaldehyde (Utterback *et al.*, 1985), which is then able to react with the colorimetric reagents



Since both methoxymethanol and methylene glycol decompose in this way there is good reason to suppose that both will give a similar colour intensity for an analysis where the primary reactant is formaldehyde. The results of the colorimetric analyses

should therefore be largely unaffected by changes in the relative quantities of formaldehyde monomer and methoxymethanol present in a formaldehyde atmosphere. This proposal was tested by producing formaldehyde solutions of a similar total concentration, but with varying ratios of formaldehyde monomer and methoxymethanol. These solutions were analysed colorimetrically, and the results confirmed that the method did not distinguish between the two forms of formaldehyde (Pengelly and Groves, 1991).

This result can be used to consider the case of the pumped filter sampling method, which involves sampling formaldehyde vapour onto reagent impregnated glass fibre filter, followed by HPLC analysis. The results of the sampling exercise in Table 1 showed good agreement between the pumped impinger and pumped filter sampling methods when sampling an atmosphere derived from formalin (syringe injected), which is now known to contain more than one component. This suggests that the DNPH method is also producing a total formaldehyde concentration by reacting with both formaldehyde and methoxymethanol present in the sampled atmosphere. The fact that the DNPH method shows the presence of only one component species during HPLC analysis lends further support to the supposition that the methoxymethanol decomposes to formaldehyde during analysis.

These observations suggest that variations in the composition of formaldehyde atmospheres have little or no effect on the chemistry of either the pumped impinger or pumped filter sampling methods. Therefore, any differences seen between the pumped and diffusive sampling methods are probably due solely to the change in the effective sampling rate caused to the diffusive system by the presence of differing airborne species.

Effect of formaldehyde species on the effective sampling rate of diffusive samplers

Using a combination of IR and chemical analysis, the composition of the four formaldehyde atmospheres generated above was determined. Once the composition of the vapour is known, its molecular weight can be calculated and a correction factor for the effective sampling rate of the diffusive sampler determined (relative to that obtained in an atmosphere generated from paraformaldehyde).

Vapours generated from both paraformaldehyde and non-methanolic formaldehyde solution were found to be effectively 100% formaldehyde giving a molecular weight of 30.0. This figure is used as the basis for calculation of correction factors in the other two atmospheres.

Vapour generated from syringe injection of formalin was found to have a composition of 38% formaldehyde and 62% methoxymethanol giving a mean molecular weight of 49.8 resulting in a correction factor of $\sqrt{(30.0/49.8)} = 0.776$ to be applied to the effective sampling rate of the diffusive sampler.

Vapour generated from thermostated bulk formalin had a composition of 21% formaldehyde and 79% methoxymethanol, giving a mean molecular weight of 55.3 resulting in a correction factor of $\sqrt{(30.0/55.3)} = 0.737$ to be applied to the effective sampling rate of the diffusive sampler.

Comparison of pumped impinger and diffusive badge sampling methods

To obtain good quality IR spectra, all the formaldehyde atmospheres investigated thus far have been at concentrations which are extremely high in

Table 2. Summary of results from laboratory comparison of diffusive and pumped sampling of formaldehyde atmospheres

Atmosphere no.	Source material	Formaldehyde concentration (mg m^{-3})		Calculated badge correction factor	Corrected badge concentration (mg m^{-3})
		Impinger*	Badge†		
1	Thermostated	0.945	0.874	1.000	0.874 (-7.5%)
2	Paraformaldehyde	2.923	3.066	1.000	3.066 (+4.9%)
3	Syringe injected	1.159	0.914	0.776	1.178 (+1.6%)
4	Formalin	4.652	3.803	0.776	4.901 (+5.4%)
5	Thermostated	0.976	0.714	0.737	0.968 (-0.8%)
6	Formalin	2.707	1.913	0.737	2.596 (-4.1%)
7	Thermostated	0.769	0.763	1.000	0.763 (-0.8%)
8	Non-methanolic aqueous formaldehyde solutions	2.544	2.922	1.000	2.922 (+14.9%)

*Mean result from three samplers; †mean result from six samplers.

The figures in parentheses in the final column indicate the percentage error between the corrected diffusive badge results and the pumped impinger results.

relation to normal occupational exposure levels, with concentrations ranging from seven to 600 times the Maximum Exposure Limit (MEL) for formaldehyde of 2 ppm. In order to test whether the correction factors can be applied to lower concentrations, eight formaldehyde atmospheres were set up at typical occupational exposure levels and sampled with pumped impingers and diffusive badges. The atmospheres comprised the four generation techniques used previously at two nominal formaldehyde concentration of 1 and 3 mg m⁻³. Three pumped impinger and six diffusive badges were used to sample each atmosphere over sampling periods of around 1 h at a temperature of 27°C and a relative humidity of 48%.

The results of the eight sets of analyses are shown in Table 2. These indicate that, after correction using the factors calculated previously, diffusive and pumped sampling results are within 8% of each other for all but one of the eight atmospheres. The conclusion from these experiments is therefore that the atmospheric compositions observed in the high concentration formaldehyde test atmospheres prepared previously are also valid at occupational exposure levels.

Formaldehyde atmospheres in the workplace or home environment

If it is the case that formaldehyde atmospheres generated in the laboratory from different source materials have different compositions, then it is probable that this is also the case for formaldehyde containing atmospheres in the factory or home environments. Processes in the factory or home using non-methanolic formaldehyde solutions, paraformaldehyde or non-solution formaldehyde sources will probably produce vapours containing only formaldehyde monomer, while those using methanolic formaldehyde solutions may produce vapours containing a mixture of methoxymethanol and formaldehyde monomer.

The consequence of this is that there is a possibility that diffusive samplers will give erroneous results if they are used in field environments where the formaldehyde atmosphere differs in composition from that used in the laboratory calibration. Table 3 shows the predicted deviations from the true concentration, which may be either high or low depending on the exact circumstances. In the case of a diffusive sampler calibrated in atmospheres generated from formalin it is likely that any deviation in results is likely to be upwards, while for a diffusive sampler calibrated in atmospheres generated from paraformaldehyde, the opposite is true, with any deviation from the true concentration likely to be downwards.

Two diffusive samplers, the SKC liquid badge and the GMD filter badge, have undergone evaluation in the laboratory and in field tests. In the laboratory, the SKC badge was evaluated in an atmosphere generated from formalin, and the GMD

Table 3. Predicted effect on diffusive samplers of differing formaldehyde vapour compositions

		Main components present in laboratory calibration atmosphere	
		Formaldehyde	Methoxymethanol + formaldehyde
Main components present in factory or home atmospheres	Formaldehyde	Results correct	Results high
	Methoxymethanol + formaldehyde	Results low	Results correct

Table 4. Summary of field trial results with SKC liquid badge sampler (calibrated in formaldehyde-methoxymethanol atmosphere)

Location no.	Formaldehyde source material	Pumped samplers (mg m ⁻³)	Diffusive samplers (mg m ⁻³)	Difference in pumped/diffusive results (mg m ⁻³) (%)	
1	Solution	6.590	6.670	+0.080	+1.2
1	Solution	0.610	0.550	-0.060	-9.8
1	Solution	0.330	0.440	+0.110	+33.3
1	Solution	5.650	6.010	+0.360	+6.4
2	Spray	2.650	3.160	+0.510	+19.2
2	Spray	1.700	1.870	+0.170	+10.0
2	Spray	5.070	5.480	+0.410	+8.1

Location 1 = Plant producing formaldehyde impregnated glass fibre tissue

Location 2 = Plant impregnating animal skins with formaldehyde.

Table 5. Summary of field trial results with GMD badge sampler (calibrated in formaldehyde atmosphere)

Location no.	Formaldehyde source material	Pumped samplers (mg m ⁻³)	Diffusive samplers (mg m ⁻³)	Difference in pumped/diffusive results (mg m ⁻³) (%)	
1	Particle board	0.014	0.018	+0.004	+28.6
1	Particle board	0.027	0.027	0.000	0.0
2	Particle board, textiles, paint, insulation, etc.	0.021	0.022	+0.001	+4.8
2	Particle board, textiles, paint, insulation, etc.	0.031	0.026	-0.005	-16.1
3	Glue	0.155	0.141	-0.014	-9.0
3	Glue	1.100	1.040	-0.060	-5.4
4	Formalin	0.150	0.150	0.000	0.0
4	Formalin	0.480	0.430	-0.050	-10.4
5	Textiles	0.042	0.039	-0.003	-7.1
5	Textiles	0.018	0.018	0.000	0.0

Location 1 = office with particle board walls.

Location 2 = home environments (from Brown *et al.*, 1992).

Location 3 = plant producing wood laminates using recorcinol-phenol-formaldehyde glue.

Location 4 = plant producing formalin from methanol.

Location 5 = textile industry using formaldehyde impregnated fabric.

badge in an atmosphere generated from paraformaldehyde. Both evaluations included a number of field trials, some of which have been reported previously (Levin *et al.*, 1988; Lindahl *et al.*, 1989; Ellwood *et al.*, 1990; Levin and Lindahl, 1994). The field tests performed are summarized in Tables 4 (SKC badge) and 5 (GMD badge). In all these experiments the diffusive samplers were used in static sampling, although in the case of the SKC badge a fan was used to produce a face velocity of 0.3 m s⁻¹ (Ellwood *et al.*, 1990). Six diffusive and six pumped samplers were used in each experiment.

The SKC badge results summarized in Table 4 show that, with one exception, there is a tendency for the badge to read higher than the pumped reference method. This deviation is in general agreement with the behaviour predicted in Table 3, and suggests that these factory atmospheres contain a higher proportion of formaldehyde

than the formalin sourced laboratory atmospheres in which the badges were calibrated. This is despite the fact that all the factory samples were all taken in atmospheres generated from formalin-based solutions. The reason for this difference is probably the fact that methoxymethanol decomposes with time to produce formaldehyde and methanol (Utterback *et al.*, 1985), thus increasing the proportion of formaldehyde in the vapour. In the case of the laboratory atmospheres, the time between generation of the vapour and sampling is usually less than 1 min, so the amount of decomposition is almost certainly far less than is the case in factory atmospheres where the time between vapour generation and sampling is generally much longer.

According to the predictions in Table 3, the GMD badge calibrated in a paraformaldehyde-derived atmosphere should tend to read low in the presence of methoxymethanol or other formaldehyde oligomers. The data in Table 5 show that in five of the 10 experiments the diffusive samplers read lower than the pumped samplers, in three the readings are the same and in the remaining two the readings are higher. In most cases however, the difference between the badge results and the pumped samplers is not greater than 10% which is within the overall uncertainty of the method (Nicholls, 1992). Although the GMD badge has been shown to be unaffected by face velocities as low as 0.05 m s^{-1} (Levin *et al.*, 1988), diffusive sampler theory predicts that each type of sampler will have a minimum face velocity below which the effective sampling rate of the sampler will begin to be affected (Tompkins and Goldsmith, 1977). It is possible, therefore, that some of the low readings in Table 3 may be the result of face velocities below the minimum value for this particular sampler.

In a personal sampling exercise performed in the dissection room of a hospital, in which formalin was the source material, the diffusive samplers gave results about 4% lower than the pumped samplers (Lindahl *et al.*, 1989). This is significantly less than the 22–26% predicted from analysis of the formalin sourced atmospheres in the laboratory, and may again be a result of the decomposition of the methoxymethanol.

CONCLUSIONS AND RECOMMENDATIONS

The main conclusion of this investigation is that the exact composition of any given laboratory generated formaldehyde atmosphere is dependent on the source material from which it originated. Paraformaldehyde and non-methanolic formaldehyde solutions tend to generate atmospheres which contain only formaldehyde, while atmospheres generated from methanolic formaldehyde solutions contain a mixture of formaldehyde and methoxymethanol.

When only formaldehyde monomer is present in the vapour, this presents no problem for diffusive sampling because the diffusive sampler can easily be calibrated under similar conditions. However, if both formaldehyde and methoxymethanol are present in the vapour, this can lead to problems for diffusive sampling because the proportions of the two components may vary from atmosphere to atmosphere. This is important because the two components having differing molecular weights, and so the effective molecular weight of any formaldehyde atmosphere depends on their relative proportions in the vapour.

This variation in molecular weight leads to a variation in the diffusion coefficient of the vapour and ultimately to possibly significant variations in the effective sampling rate of the diffusive sampler. In order to obtain an accurate estimate of the effective sampling rate of the diffusive sampler therefore, it is necessary to know the proportions of formaldehyde and methoxymethanol present.

In home or workplace sampling, however, the variations in composition may not be as marked as in the laboratory. While the laboratory atmospheres prepared appear to show reasonably predictable compositions, at both high and low concentrations, the field trial results suggest that formaldehyde atmospheres generated in the home or workplace show some variations from the expected composition. In particular, results from the field trials of the SKC liquid badge appear to suggest that workplace atmospheres generated from formalin contain a higher than expected proportion of formaldehyde monomer. There is also the added complication that in many home or workplace atmospheres other source materials and/or interfering chemicals may be being used.

It is possible that source-dependent mixtures may be produced with other pollutants, particularly other aldehydes. For those pollutant vapours which can be generated from a variety of possible sources therefore, it may be necessary to determine the exact nature and composition of the vapour generated from each source, possibly using an IR technique such as described in this investigation. Such analysis should ensure that in those cases where a single component vapour is required, such as the generation of standard atmospheres for calibration purposes, the correct source material is used.

If it is apparent from the IR analyses that the composition of a given pollutant vapour is source-dependent, then it needs to be borne in mind that, as in this case with formaldehyde, pumped and diffusive sampling methods may not give the same results under some circumstances. Conversely, any disagreement between pumped and diffusive sampler results could be taken as an indication that the pollutant composition in the atmosphere being sampled differs from that which was used to calibrate the diffusive device. It is therefore recommended that side-by-side field comparisons of pumped and diffusive sampling methods should always be carried out, particularly for those vapour monitoring situations where the sort of discrepancies experienced with the formaldehyde samplers are likely to exist.

In the event that pumped and diffusive sampling methods do show significant disagreement, this need not prevent the use of diffusive sampling. If it can be shown by further comparison that the ratio of the results obtained by the two sampling methods remains constant (that is, the composition of the vapour being sampled is constant), then the results of the pumped sampling method can be used to recalculate the effective sampling rate of the diffusive sampler for that particular sampling environment. A system of periodic pumped and diffusive comparisons could then be used to monitor the situation and make sure the vapour composition remained constant.

This investigation has emphasized the need, when evaluating a diffusive sampler, to be certain of the nature and composition of the pollutant vapour being sampled. Provided this need is satisfied, diffusive sampling will continue to offer significant operational advantages over the equivalent pumped sampling techniques.

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