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DETERMINATION OF FORMALDEHYDE IN AIR BY GAS CHROMATOGRAPHY

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SUMMARY

Formaldehyde in air was analyzed by gas chromatography (GC) using instruments equipped with thermal conductivity, flame-ionization and photoionization detectors. A method of making formaldehyde standards in air, to calibrate the GC system, was tested. The rate of polymerization increase in air, with increase in relative humidity, was also determined. The application of the method to the determination of formaldehyde desorbing from urea–formaldehyde foam and particle board is discussed.

INTRODUCTION

Formaldehyde (HCHO) is widely used in many industrial and domestic processes such as adhesive manufacture, electroplating, fermentation, fireproofing agents, pigment manufacture, for cotton durable press, preservatives for wool, synthetic resins, mirrors, in the production of urea–formaldehyde foam, an anticoagulant for natural rubber and in agriculture for the control of insects in fresh vegetables. Formaldehyde in air polymerizes easily[1] to a linear polymer, $HO(CH_2O)_nH$, but low levels of formaldehyde could remain for some time. Because it may be a hazard to human health, a level of 2 ppm has been set by AGGIH[2] as the TLV–TWA for an 8-h exposure. To determine such low levels with accuracy and reliability, very sensitive methods are required.

Methods currently available rely on large volumes, complex apparatus and chemical reactions. The NIOSH[3,4] method requires a sample size of 6–25 l, a procedure involving several steps and elaborate apparatus. Methods using detector tubes require sample sizes of 300–1600 ml for analysis in the 35–0.5 ppm range. A recent gas chromatographic–mass spectrometric (GC–MS) method[5] determines formaldehyde at the parts per billion level by trapping a formaldehyde–air mixture. In this method cooling at −72°C is used for conditioning the trap and a temperature of 240°C is required to release formaldehyde from the trap. Elaborate apparatus is also necessary. As GC can provide direct methods for the determination of vapors, equipment and procedures for the on-site determination of formaldehyde in a variety of environments were investigated and methods of analysis developed.

EXPERIMENTAL

For the direct determination of formaldehyde in air at parts per million levels, GC was selected. For these GC determinations, three instruments with three different detectors were used, but it was first necessary to develop methods for making precise standards of formaldehyde in air.

These standards were generated from formaldehyde decomposed by heat on a stainless-steel plate placed on a hot-plate. The stainless-steel plate was heated to 160°C and an inverted beaker placed on it so that small amounts of paraformaldehyde could be introduced and formaldehyde generated to produce a saturated atmosphere. The size of the beaker was 10–100 ml, depending on the amount of formaldehyde needed. The formaldehyde–air mixture was drawn from this space with a syringe and injected directly into a gas chromatograph or into flasks of various sizes for subsequent analysis. As formaldehyde is explosive in the range 7–73% by volume in air, precautions were taken to produce only small amounts of vapor on the hot-plate and to provide adequate protection against flying glass in the event that an explosion occurred. Another method for producing the vapors at a low concentration involved introducing 16–100 mg of paraformaldehyde powder into 12.7-l flasks and applying heat to the powder to release formaldehyde. The first gas chromatograph used for this part of the investigation was a Bendix Model 2300 with a flame-ionization detector (FID) and a nickel column (2 m × 3 mm I.D.) packed with Tenax GC (35–60 mesh). At 40°C and a nitrogen flow-rate of 20 ml/min the retention time of formaldehyde was 3.15 min. A sensitivity setting of $5 \cdot 10^{-12}$ was used. By using the FID the effect of time and concentration on formaldehyde vapor was tested by drawing formaldehyde–air samples of 1–5 ml from various flasks at time intervals ranging from 1 min to 60 days and then analyzed. Another factor affecting polymerization is the relative humidity (RH), and this was also tested using GC with an FID. Levels of 30–70 and 75% RH were obtained by keeping the flasks in a room with a controlled RH. The 10% RH air or nitrogen atmospheres were obtained by flushing the flasks for 1 h with the respective gases from compressed gas cylinders and the RH was determined by GC. Samples up to 5 ml were injected directly into the GC system. For larger samples the trapping method previously described by Dumas[6] was used. For the trapping of formaldehyde a tube (20 cm × 3 mm I.D.) filled with Chromosorb 101 (60–80 mesh) was found to be effective. The trap was maintained at 25°C. Using this method, 10-ml samples of formaldehyde–air mixture were analyzed by injection into a trap at 25°C and placing the trap in the GC system, where formaldehyde was released at 60°C.

A second gas chromatograph, a Bendix Model 2200 with a thermal conductivity detector (TCD), was also used with the same column to determine the air in the formaldehyde–air mixture. The conditions used with this chromatograph were the same as used previously except that helium was used as the carrier gas and the retention time of formaldehyde was 2.7 min. The results were calculated with a Hewlett-Packard Model 3380A integrator.

A third gas chromatograph with very high sensitivity and portable so that it could be used for on-site analysis was also tested. This was the Photovac Model 10A10 instrument, equipped with a photoionization detector and a 1.2 m × 3 mm I.D. PTFE column packed with Carbopack BHT. A column temperature of 25°C and a carrier gas flow-rate of 12 ml/min in air (less than 0.1 ppm of hydrocarbon impurities) was used. Under these conditions the retention time of formaldehyde was 3.6 min. Either a 100-mV recorder or a Hewlett-Packard 3380A integrator was used to register the signal.

The desorption of formaldehyde from materials containing derivatives of this compound were tested using the above methods. Desorbing vapors from urea–formaldehyde foam were determined from 2 l (20 g) of foam placed in a 6-l desiccator and from 160 g of particle board placed in a 600-ml flask. Kitagawa and Dräger glass detector tubes were used to determine the formaldehyde content of the standards used for calibration. In a published GC method[5], various concentrations of formaldehyde in water were used as standards. To test such standards, a 37% formaldehyde solution stabilized with methanol was used to prepare dilute mixtures with water at concentrations down to 0.03%. These mixtures were tested by titration[7] to verify the actual concentration of formaldehyde.

RESULTS AND DISCUSSION

The possibility of preparing standards with low levels of formaldehyde in water was tested and the results in Table I show the actual formaldehyde contents determined by titration. The results for up to 100-fold dilution were close to the calculated amounts. For dilutions greater than 100-fold, the determined amounts were higher, being as high as 0.048% at 1000-fold dilution when the calculated amount was 0.03%. This interference makes the use of these dilute mixtures unreliable as standards.

TABLE I

FORMALDEHYDE CONCENTRATION IN SOLUTION DETERMINED BY TITRATION

Formaldehyde in solution (%)	
Calculated	*Determined*
37*	36.1
0.72**	0.77
0.37**	0.38
0.072**	0.082
0.037**	0.048
0.037**	0.042
0.037**	0.045
0.0185**	0.024

* 37% Formaldehyde solution stabilized with 13% of methanol.

** Dilutions with distilled water.

The instability of formaldehyde vapor makes it difficult to prepare an exact standard; however, at low levels, in air at levels of 120 ppm or less, the changes in concentration after 48 h is not detectable and this allows a formaldehyde–air mixture to be used as a standard for GC calibration.

Because paraformaldehyde decomposes at temperatures above 160°C to re-

TABLE II

DETERMINATION OF FORMALDEHYDE AT VARIOUS TIME INTERVALS AND RELATIVE HIMIDITIES USING DIFFERENT DETECTORS

Detector	*Flask volume*	*Sampling time*	*PF (mg)*	*Formaldehyde applied*	*Sample size*	*Formaldehyde integrator counts*	*Air integrator counts*	*Formaldehyde (ng/ml)* [a]	*RH (%)*	*HCHO (ppm)*
TCD	100 ml	1 min	100	100 μl	100 μl	42,000	82,686	–	–	–
TCD	100 ml	5 min	100	100 μl	100 μl	1300	134,000	–	–	–
TCD	100 ml	1 min	–	100 μl**	100 μl	–	133,500	–	–	–
FID	12.7 l	60 days	–	100 ml	1 ml	600	–	150***	33	–
FID	12.7 l	1 day	16*	–	5 ml	1400	–	70	70	50
FID	12.7 l	3 days	16*	–	5 ml	1100	–	55	70	–
FID	12.7 l	1 day	100*	–	5 ml	4500	–	225	75	162
FID	12.7 l	3 days	100*	–	5 ml	3600	–	180	75	–
FID	150 ml	60 days	–	5 ml	5 ml	2790	–	140	10	–
FID	150 ml	60 days	–	5 ml	5 ml	2200	–	110	30	–
FID	150 ml	60 days	–	5 ml	5 ml	1530	–	76	70	54
FID	100 ml	1 min	10	–	50 μl	12,000	–	3 μg/50 μl	–	–
Kitagawa	12.7 l	3 days	–	100 ml	100 ml	–	–	–	75	120

* Paraformaldehyde (PF) decomposed by heat into the 12.7-l flask, generating formaldehyde.

** Air only.

*** This amount was calculated based on Kitagawa reading of 120 ppm.

[a] The amounts of formaldehyde were calculated based on the Kitagawa reading of the standard formaldehyde–air mixture.

lease formaldehyde, this procedure proved a convenient means of producing a mixture of formaldehyde in air. Table II shows the effect of various conditions on formaldehyde concentration in air. On drawing 100 μl of formaldehyde–air mixture into a syringe, after the first minute integrator counts of 82,686 for air and 42,000 for formaldehyde were obtained. On holding for 5 min the 100 μl of formaldehyde–air mixture in the syringe before injection, the counts were 134,000 for air and much lower (1300) for formaldehyde. The same amount of 100 μl of air alone showed 134,000 counts. This demonstrates that saturated formaldehyde in air could not be obtained because of its instability. By generating high levels of formaldehyde on the shot surface from paraformaldehyde and injecting 100 ml from the trapped vapor under the beaker into a 12.7-l flask, a standard was obtained. On sampling this standard after 6 days, 600 counts were obtained when 1 ml was injected into the gas chromatograph. On testing this flask with the Kitagawa glass detector tubes 120 ppm of formaldehyde was found, which corresponds to 150 ng/ml. Therefore, 1 ml containing 150 ng gave 600 counts on the integrator. Using this relationship, counts were converted into amounts of formaldehyde. The results for two 12.7-l flasks, containing 16 mg of paraformaldehyde in one and 100 mg in another, are shown in Table II. The paraformaldehyde was decomposed by heat, producing formaldehyde. The formaldehyde level in the flask with 16 mg of paraformaldehyde added at 70% RH, was 70 ng/ml after 1 day, and 55 ng/ml after 3 days. For the flask with 100 mg of paraformaldehyde added, at 75% RH the values were 225 ng/ml and 13.5 ng/ml after 1 and 3 days, respectively. This shows a higher loss at the higher concentration of formaldehyde.

The formaldehyde results for the 150-ml flasks at 10, 30 and 70% RH after 60 days showed that the remaining amounts of formaldehyde were becoming closer together, 140, 110 and 80 ng/ml. This indicates that at a low concentration and after a long time the rate of polymerization is very low, and the effect of RH is reduced.

The results in Fig. 1 show the effect of relative humidity and of formaldehyde concentration on the rate of polymerization as a function of time. The conversion was higher at the higher RH. This increases the rate of polymerization, especially in the first few minutes when the formaldehyde concentration is higher. For the 500 μg/150 ml (3333 ng/ml) of formaldehyde flask applied in a 10% RH atmosphere, after 15 min the concentration had fallen to 3000 ng/ml, where as at 70% RH it was much lower,

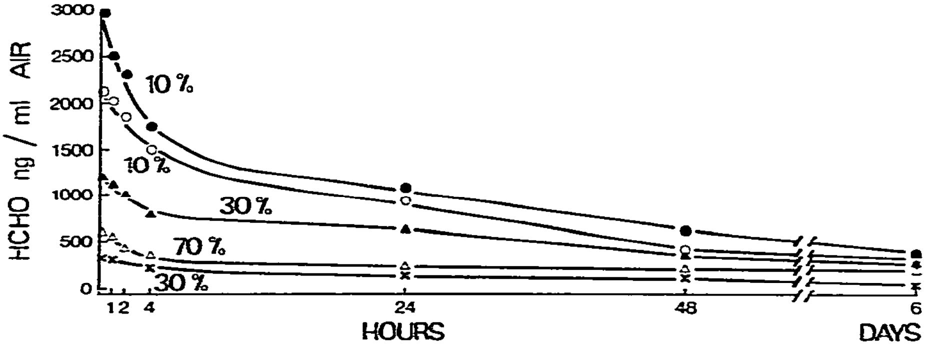

Fig. 1. Formaldehyde concentration as a function of time. ●▲,△, 500 μg of formaldehyde applied in a 150-ml flask with air; ○, 500 μg of formaldehyde applied in a 150-ml flask with nitrogen; ×, 100 μg of formaldehyde applied in a 150-ml flask with air.

600 ng/ml. After 6 days the amounts of formaldehyde were much lower and closer together for all relative humidities with the same initial formaldehyde concentration. Comparing the polymerization at 30% RH, for initial applied amounts of formal-

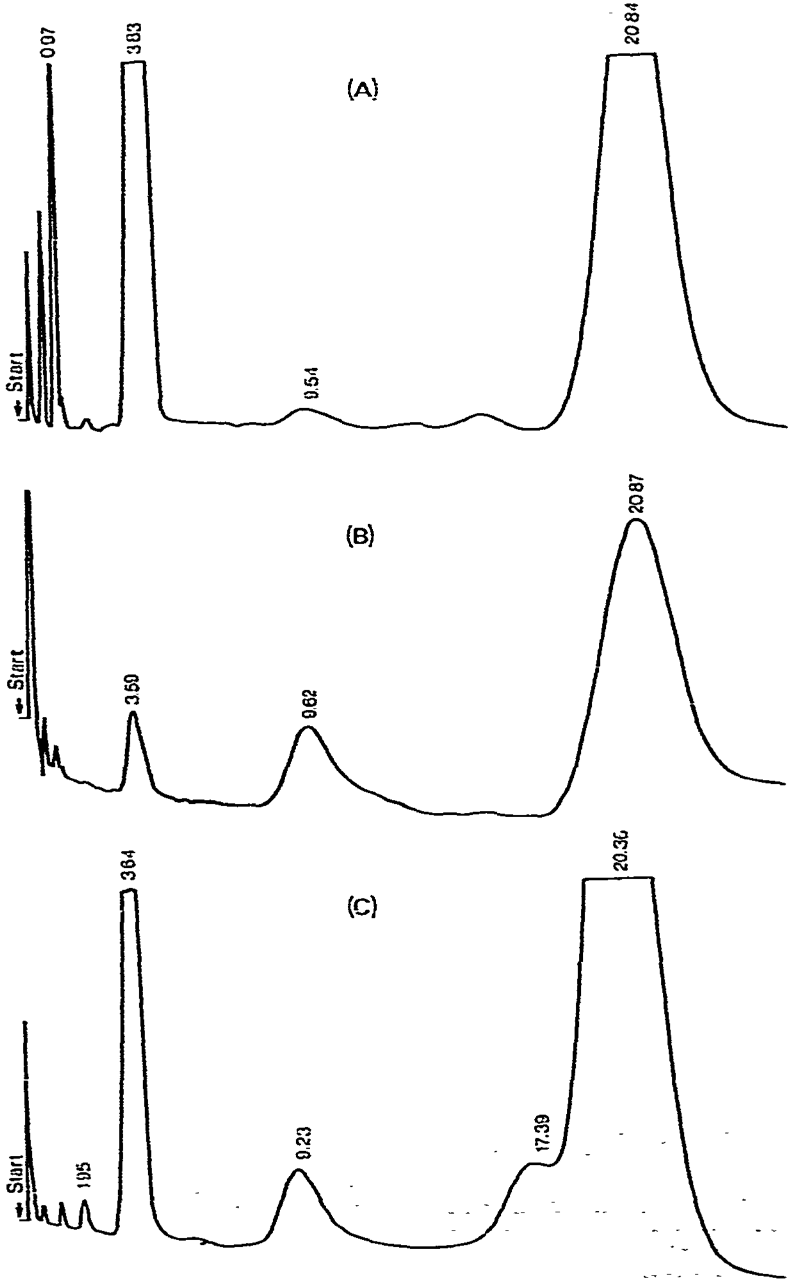

Fig. 2. Determination of formaldehyde using gas chromatograph with a photoionization detector. (A) 100-μl sample from particle board stored in a 600-ml flask; (B) 500-μl sample from formaldehyde standard in a 12.7-l flask; (C) 100-μl sample from urea–formaldehyde foam stored in a 6-l desiccator.

dehyde of 500 and 100 μg in the 150-ml flasks, after 6 days both were closer together in formaldehyde concentration. This indicates a continuous decrease in polymerization rate. Also, the polymerization rate was shown to be a function of concentration, time and relative humidity.

The desorption of formaldehyde from urea–formaldehyde foam was also tested, by placing samples in a 6-l desiccator for 6 months. Samples of 100 μl were drawn by a syringe and injected into the Photovac gas chromatograph for analysis. Fig. 2C shows the results for a 100-μl air sample from a 6-l desiccator containing 2 l (20 g) of urea–formaldehyde foam left for 6 months. The formaldehyde peak was at 3.64 min and there were also three other significant peaks, at 9.23, 17.39 and 20.36 min, which at present have been identified. The formaldehyde concentration for this sample was 120 ppm. When no interfering components with retention times close to 3.64 min are present in the air, a 1-ml sample could be injected into the gas chromatograph and smaller amounts of formaldehyde could be determined. The sample in Fig. 2B, generated from paraformaldehyde in the 12.6-l flask, produced the same two peaks at retention times of 3.59 and 20.87 min, which indicates that the peak at 20.36 min is due to formaldehyde and not to other components. In Fig. 2A, the same two peaks were also present for desorbed vapors from 160 g of particle board stored for 6 months in a 600-ml flask.

When formaldehyde–air standards of 55 ppm were analyzed using the FID, a 1-ml sample size produced a response of 286 counts on the integrator, but with the photoionization detector only 0.03 ml was required for a response of 285 counts. The photoionization detector has a higher sensitivity than the FID, but further studies, using the concentration method previously described by Dumas[6], which allows the analysis of larger samples, should be conducted to increase the sensitivity further.

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