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Note

Determination of formaldehyde, acetaldehyde and associated components in solution and in vapours by gas chromatography

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Formaldehyde is widely used in many manufacturing processes but is very unstable in air; it polymerizes rapidly and combines with moisture in air to produce the hydrate, and for this reason indirect methods are usually used for analysis. By one method[1] HCHO is reacted, oxidized and determined colorimetrically. In another method[2] it is converted into $CH_2(SC_2H_5)_2$ and then analysed by flame photometric gas–liquid chromatography (GLC). Both of these methods are time-consuming and difficult to use, especially where the HCHO needs to be collected in traps for subsequent analysis.

Acetaldehyde has recently been used as a fumigant for the control of insects on fresh vegetables[3], and simple trapping methods from air and gas chromatographic (GC) analysis are needed to measure gas concentrations during treatments. One method[4] has been developed for trap-collecting CH_3CHO, but this requires liquid oxygen for cooling and is not practical for field use. A modified GC method of analysis and simple practical trapping methods for field use at ambient temperature were also investigated using various column packings.

MATERIALS AND METHODS

A Bendix 2300 gas chromatograph equipped with a flame ionization detector and a nickel column (2 m × 3 mm I.D.) filled with Chromosorb 101 (80–100 mesh) was used for analysis of the compounds. The column temperature was 100°C and the flow-rate of the nitrogen carrier gas was 50 ml/min. When a solution of 37% HCHO in water stabilized with 13% methanol was injected under these conditions two main peaks were found, one at 1.3 min and one at 5.8 min. The same two components were also present when vapour from above the HCHO in water was analysed.

To collect the first component, a 10-ml air sample was drawn in a gas-tight syringe and injected through a septum into a 10 cm × 3 mm I.D. stainless steel tube filled with Tenax GC (35–60 mesh). This tubing had Swagelok fittings at each end with a Swagelok nut and septum at one end for injection of the samples. For the second component at 5.8 min, a 100-ml syringe was used to draw the sample which then was injected into nickel tubing (10 cm × 3 mm I.D.) filled with Chromosorb 101 (80–100 mesh). These operations were performed at 25°C. When the trap temperature

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was lowered, larger amounts could be injected. The tubing with the sample was then inserted into the modified chromatograph as described by Dumas[5], and the results were calculated using a Hewlett-Packard model 3380A integrator.

In the analysis of acetaldehyde, only one peak was found when either the solution or saturated vapour in air was injected. The retention time for the compound was 8.4 min. Using the above Tenax GC collecting tube, up to 50 ml of acetaldehyde–air mixture could be trapped and analysed.

To reduce the possibility of decomposition in the chromatograph at high temperatures, a shorter nickel column (50 cm × 3 mm I.D.) filled with Chromosorb 101 (80–100 mesh) was used and the column temperature was lowered to 40°C. The carrier gas and its flow-rate were the same. Under these conditions the retention time for the first component was 1.2 min and the second was 11 min when the formaldehyde solution was injected. In the case of acetaldehyde the retention time was 1.6 min. The retention time of methanol was also determined because it is used in the formaldehyde solution as a stabilizer. Under the above conditions the methanol retention time was 1.2 min. Using the 2-m nickel column at 40°C and 50 ml/min nitrogen flow-rate, the retention times for vapour and formaldehyde solution were 6.4 min for the first component and 56 min for the second. The acetaldehyde retention time was 8.4 min and for methanol 5.2 min. For the injection of gas samples smaller than 5 μl a Hamilton syringe for liquids was used as previously described by Dumas[6].

For better separation, Chromosorb 107 (60–80 mesh) was used with the 2-m nickel column at 120°C and 50 ml/min nitrogen flow-rate. The retention times for the two components in the formaldehyde vapour were 5.8 and 17 min. Those for methanol and acetaldehyde were 5.7 and 5.6 min, respectively. The reaction product of methanol and formaldehyde, methylal $CH_2(OCH_3)_2$, was also tested on the Chromosorb 101 column at 100°C. For this compound the retention time was5.8min for vapour or solution and on Chromosorb 107 at 120°C it was 17 min.

The influence of the nitrogen flow-rate was tested by using Porapak N in the 2-m nickel column. At 120°C and 50 ml/min the retention time for CH_3OH was 2.2 min and for $CH_2(OCH_3)_2$ 8 min. At 140°C and 15 ml/min the retention time for HCHO was 2.7 min, for CH_3OH 6.4 min and for $CH_2(OCH_3)_2$ 23 min.

RESULTS AND DISCUSSION

When the aqueous solution was injected two components in large amounts were found, one giving a large peak at 1.3 min and the other a small peak at 5.8 min.

The saturated vapour taken from above the 37% formaldehyde solution gave a small peak at the retention time of 1.3 min and a large one at 5.8 min in the ratio of 1:8 (at 100°C in the 2-m column packed with Chromosorb 101). By comparing retention times and peak heights using a 0.37% solution of formaldehyde in water and 0.13% methanol in water, similar results were obtained. This indicates that the component detected at 1.3 min in the formaldehyde solution is methanol. It is used as a stabilizer in the formaldehyde solution and makes up 13% of the solution.The second component of the 37% formaldehyde solution had the same retention time as a methylal standard when injected into two separate columns with different packings. The temperature, in the range 40–120°C, did not affect the components analysed as shown in Table I.

TABLE I

RETENTION TIMES (t_R) AND FULL SCALE RESPONSES AT 1×10^{-10} A SENSITIVITY

Compound	*Chromosorb 101 column*						*Chromosorb 107 column, 2-m length, 120°C*		*Porapak N column, 2-m length, 120°C*	
	2-m length				*50-cm length, 40°C*					
	40°C		*100°C*							
	t_R	μl	t_R	μl	t_R	μl	t_R	μl	t_R	μl
Formaldehyde 37% in water	6.2	0.5 (4*)	1.3	0.3 (32*)	1.2	0.3 (16*)	5.8	0.4 (8*)	2.3	0.6 (32*)
			5.8	0.3	11	0.6	17	0.4	8.1	0.6
Formaldehyde 37% water solution vapour	6.4	600	1.3	250	—	—	5.8	800	2.3	500
	56	300	5.8	30	11.2	80	17	150	8.1	70
Formaldehyde 0.37% in water	5.3	6	1.3	1.2	1.2	1.7	5.7	3.3	—	—
Acetaldehyde 1% in water	8.4	0.5	1.6	0.3 (2*)	1.6	0.3 (2*)	5.6	0.6	—	—
Acetaldehyde vapour	8.3	3	1.6	0.6	1.6	0.6	5.6	1.6	—	—
Methanol 0.13% in water	5.4	4.4	1.3	1	1.2	1.5	5.7	3	2.16	2
Methanol vapour	5.2	4.0	1.3	10	1.2	20	5.8	40	2.2	20
Methylal solution			5.8	0.1 (64*)			17	0.1 (8*)	7.8	0.3 (32*)
Methylal vapour			5.8	0.15			17	5	8	1.5

* These numbers represent recorder attenuations.

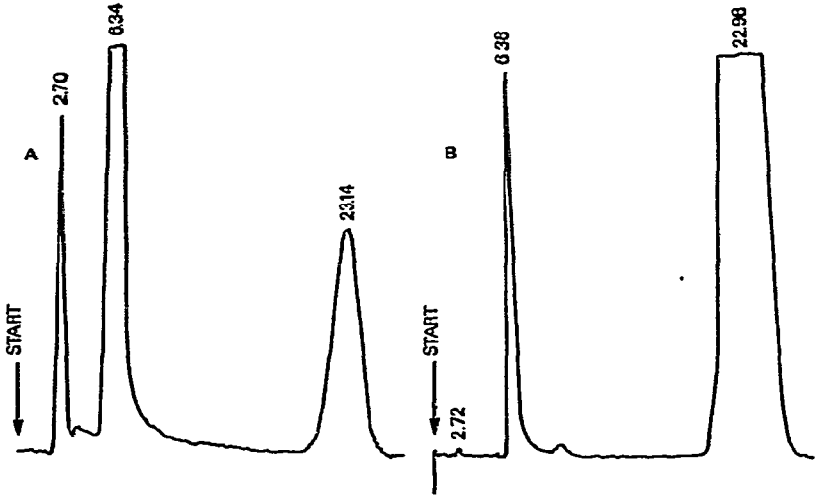

Fig. 1. GC responses for HCHO, CH_3OH and $CH_2(OCH_3)_2$ at 1×10^{-11} A sensitivity on a Porapak N column at 140°C. A, For a 0.3-μl sample from a 37% HCHO solution. B, For a 200-μl sample from saturated vapour above a 37% HCHO solution. Retention times are given in minutes.

When acetaldehyde was injected, the retention times at 100 and 120°C were close to that of methanol, but at 40°C were considerably longer and clearly separated. The acetaldehyde had a much shorter retention time than the main (second) component in the saturated vapour of the formaldehyde solution. This observation further indicates that the second peak for the formaldehyde solution is neither formaldehyde nor acetaldehyde but is methylal $CH_2(OCH_3)_2$, which has a higher boiling point than both HCHO and CH_3CHO.

Pure formaldehyde standards necessary for quantitative determination are very difficult to produce. To find the retention time for formaldehyde, paraformaldehyde was decomposed by heat in a flask filled with nitrogen. A sample drawn with a syringe and injected into chromatograph gave a peak with a retention time of 2.8 min with Porapak N at 140°C and 15 ml/min nitrogen flow-rate. Assuming saturation of HCHO in the flask, a full scale peak was obtained from the 100-μl sample analysed, which corresponds to *ca.* 100 μg of HCHO. Injection of 200 μl of saturated vapour from the 37% HCHO solution produced a very small response for HCHO at a retention time of 2.8 min. Fig. 1A and B show the relative amounts of HCHO, CH_3OH and $CH_2(OCH_3)_2$ in the 37% HCHO solution stabilized with 13% methanol, and in the saturated vapour above the solution. The amount in solution of HCHO is 4.26%; only a very small amount is present in the vapour.

A foam insulating material which uses formaldehyde as a reaction material was tested for the presence of residual formaldehyde at various intervals after the reaction was complete. Freshly produced 2 l foam was placed in a 6-l desiccator, and from the space above, consecutive samples were taken for several days and analysed by the GC method described here. Only one component was found and this had the same retention time as methanol using all the above columns and conditions. No formaldehyde was detected in a 100-ml sample trapped on Tenax at dry ice temperature at a sensitivity of 1×10^{-11} A.

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