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ANALYSIS OF FORMALDEHYDE BY GAS CHROMATOGRAPHY USING PORAPAK N

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SUMMARY

Gas chromatography, at 120°, on porous polymer beads, Porapak N, can be used to analyse formaldehyde solutions. The rapid elution of formaldehyde, water and methanol with excellent peaks allows the determination of formalin liquors, as well as trace amounts of formaldehyde and methanol in water. A quantitative procedure is described and the results are the same or better than those obtained by classical methods for analysis of technical formalin.

INTRODUCTION

The use of gas chromatography in the analysis of formaldehyde–methanol–water mixtures is of great practical significance. Product testing, chemical engineering considerations of the parameters of a production line and studies of various reactions of formaldehyde with other compounds, all necessitate an accurate analytical method.

Gas chromatographic separation of formaldehyde has been the subject of a number of papers[1–15]. However, only a few of them were aimed at elucidating the analysis of formaldehyde solutions[1–6]. The main common denominator for all the above papers is the statement that polymerization of formaldehyde in the column has to be prevented by raising the column temperature to about 100°. This requirement is a complicating factor with respect to the choice of stationary phase. The recommended packings have been Tide on Fluoropak 80[1], Ethofat 60/25[3], polyethyleneglycol adipate[4], and sucrose octaacetate[2,3]. Recently, MANN AND HAHN[6] recommended the last of these and were against the use of Porapak N. We are not able to reproduce their findings.

Thus this paper deals in detail with the use of the synthetic porous polymer—Porapak N (Waters Associates Inc., Framingham, Mass., U.S.A.), which proved to be suitable for the analysis of the whole range of formaldehyde solutions. The separation of components is very sharp and the peaks of all the components are well suited for analytical purposes. Column performance remained unchanged even after one year of operation and elution times of the components remained constant throughout this period.

EXPERIMENTAL

Apparatus

The work was performed on a Carlo Erba, model C chromatograph (Milano, Italy). The instrument was equipped with a T.C.D. A glass column, 196 cm long, I.D. 0.175 cm was used and packed with Porapak N, batch 547, particle size 100/120 mesh. The carrier gas was pure argon at a flow rate of 5.6 ml/min and an overpressure of about 57 cm Hg. The column temperature was 120°, that of the vaporizer was 200° and the detector was heated to 240°. The samples were introduced with a 1 μl Hamilton micro syringe (Whittier, Calif., U.S.A.). The sample size was 0.1 μl. The identification of peaks was made by injecting pure components and making the test for the aldehyde with 2,4-dinitrophenyl hydrazine acidified with hydrochloric acid. Relative peak areas were measured with a Carlo Erba integrator, model 71, and printed out by a Kienzle printer.

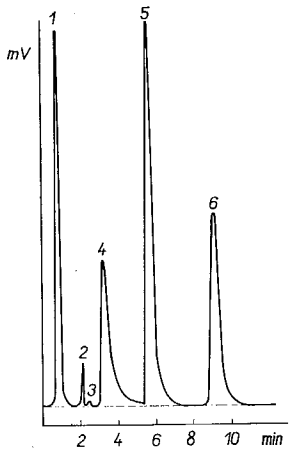
Standard solutions

The solutions for calibration purposes were prepared by weighing binary methanol–water mixtures and adding water or methanol to a high-percentage formaldehyde-in-water solution prepared in our laboratory. Concentrations of components were determined according to ref. 16. The time of analysis was 12 min. The chromatogram resulting from the analysis of a formaldehyde solution is shown in Fig. 1.

The appropriate column temperature can be found from the log V_{Rm} *vs.* T^{-1} plot in Fig. 2.

Analysis of solutions

Chromatograms of the mixture under test. In routine analysis, the standard mixture



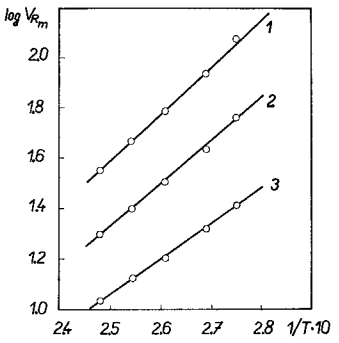
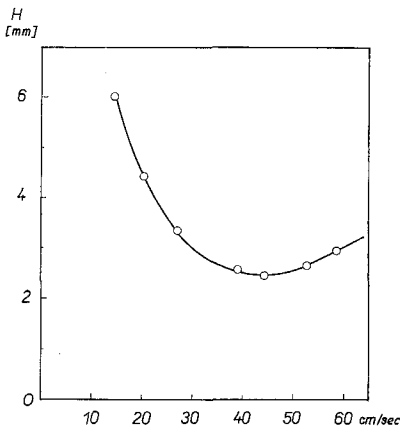


Fig. 1. A chromatogram of formaldehyde solution on Porapak N. 1 = Air; 2,3 = not identified; 4 = formaldehyde; 5 = water; 6 = methanol.

Fig. 2. The plot of log V_{Rm} against T^{-1}. 1 = Methanol; 2 = water; 3 = formaldehyde.



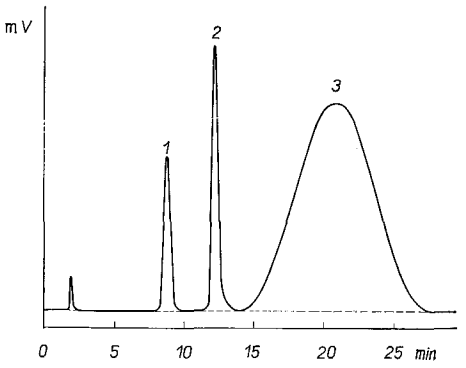


Fig. 3. The dependence of HETP on linear velocity of the carrier gas for water at 122°.

Fig. 4. A chromatogram of formaldehyde solution on a 5 m long column packed with Columnpak T + 10% Ethofat 60/25, at 115°. 1 = Methanol; 2 = water; 3 = formaldehyde.

is analysed first and then at least once again every day, as long as serial runs are made. In serial analyses it is recommended that the column is reactivated overnight at 200° at a reduced carrier gas flow, once every two weeks. Another point to be observed is that the volume of the injected mixture should be constant.

RESULTS AND DISCUSSION

The height equivalent to a theoretical plate for the above column is not particularly small as can be seen from the data for water in Fig. 3.

The column, when operated at optimum conditions, has only 800 theoretical plates per 196 cm. This number, however, will separate, in a satisfactory manner, formaldehyde, water and methanol, in contrast to a 5 m long column packed, according to ref. 4, with Columnpak T and 10% Ethofat 60/25. The latter does not give such a

TABLE I

QUANTITATIVE GAS CHROMATOGRAPHIC AND VOLUMETRIC ANALYSES OF FORMALDEHYDE SOLUTIONS

	Formaldehyde		*Methanol*	
	GC	*Titration*	*GC*	*Titration*
1	0.06	0.08	0.10	0.00
2	0.58	0.59	0.16	0.00
3	1.20	1.30	0.67	0.55
4	3.65	3.60	1.06	0.90
5	12.4	12.3	16.6	16.7
6	16.0	16.1	0.06	0.00
7	34.4	34.4	14.1	14.1
8	35.5	35.6	11.6	11.5
9	36.1	36.2	6.59	7.10
10	46.1	46.1	1.42	0.96

sharp separation and yields a very broad formaldehyde peak, as can be seen by the comparison of Fig. 3 and 4.

Another advantage of the Porapak N packed column is the short time of analysis. We found that the real elution sequence is: formaldehyde, water, and methanol. This is in contradiction with the statement by MANN AND HAHN[6] that "formaldehyde elutes after methanol and water on Porapak N".

The quantitative data summarized in Table I show that gas chromatography gives results which compare well with those obtained by the classical procedure[16] and which are reproducible. Larger deviations are only encountered with a low methanol content, thus showing that the classical method is unsuitable for the determination of methanol in formaldehyde at lower methanol concentrations. The only disadvantage to the analysis on this column is that elution of higher molecular weight components possibly present is very slow in an isothermal run and trace impurities are then very difficult to determine, particularly when present in minute concentrations.

CONCLUSIONS

Gas chromatography in a gas–solid system using Porapak N as adsorbent at 120° will separate formaldehyde, methanol and water. Rapid elution of all the components and their sharp separation permit a quantitative determination of the above compounds. The results are easily reproducible.

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