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## Note

# Determination of formaldehyde and acetaldehyde (as cyanohydrins) in water by gas chromatography

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Aqueous solutions of aldehydes are usually analysed by using colorimetric methods[1,2]. However these procedures cannot be applied to colored or unclear solutions without a preliminary treatment. Additionally, these methods are hardly selective, except for the determination of formaldehyde with chromotropic acid[3]. Gas chromatographic procedures have been reported, but the sensitivity of the flame-ionization detector is not sufficiently high with formaldehyde and acetaldehyde because of the unfavourable C/O ratio.

The method suggested in this paper is based on the following reactions:

$$\mathrm{RCHO} + \mathrm{CN^-} \rightarrow \mathrm{RCH(O^-)CN} \xrightarrow{\mathrm{H^+}} \mathrm{RCH(OH)CN} \qquad (\mathrm{R} = \mathrm{H}, \mathrm{CH_3}) \qquad (1)$$

The cyanohydrins formed are analysed by gas–solid chromatography and selectively detected with a nitrogen–phosphorus detector.

## EXPERIMENTAL

### *Reagents*

Sodium cyanide, 40% formaldehyde, acetaldehyde and 85% orthophosphoric acid were pure products supplied by Carlo Erba (Milan, Italy).

### *Apparatus*

The gas chromatograph was a Perkin-Elmer Model Sigma 3B equipped with a nitrogen–phosphorus detector.

### *Chromatographic conditions*

The column was made of borosilicate glass (70 × 0.3 cm I.D.) packed with Porapak Q-S, 80–100 mesh (Waters Assoc., Milford, MA, U.S.A.). Nitrogen was used as the carrier gas at a flow-rate of 40 ml/min; the flow-rates of hydrogen and air were 4 and 100 ml/min, respectively. The injector and detector temperatures were

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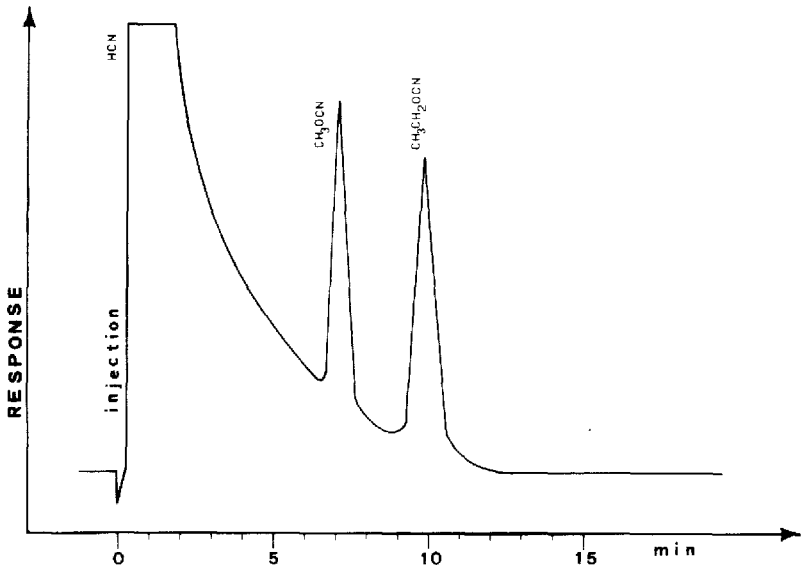


Fig. 1. Gas chromatogram obtained from an aqueous solution containing 1 ppm each of formaldehyde (A) and acetaldehyde (B) and 40 ppm of cyanide.

140 and 170°C, respectively, and the oven temperature was 160°C. Under these conditions, the retention times of hydrogen cyanide–formaldehyde and hydrogen cyanide–acetaldehyde were 7 and 10 min, respectively. The use of a glass column and injector is recommended.

*Determination of formaldehyde and/or acetaldehyde*

A 9.0-ml volume of a sample containing a neutral or weakly alkaline solution of formaldehyde (0.2–10 ppm) or acetaldehyde (0.5–10 ppm) was introduced into a 10-ml volumetric flask, then 0.5 ml of an 800-ppm cyanide solution and, after shaking, 0.5 ml of 85% phosphoric acid were added. Distilled water was added to volume. A 1-$\mu$l sample was then taken with a microsyringe and injected into the gas chromatograph.

The unknown concentrations of formaldehyde and acetaldehyde were deduced from the peak heights by means of a calibration graph.

*Calibration graphs*

Calibration graphs were constructed by plotting the heights of the peaks against the concentration of samples containing accurately known amounts of formaldehyde and/or acetaldehyde, treated as described above.

## RESULTS AND DISCUSSION

Concentrations of formaldehyde and acetaldehyde in the ranges 0.2–10 and 0.5–10 ppm, respectively, were studied. Obviously reaction (1) must proceed quantitatively in order to produce accurate results.

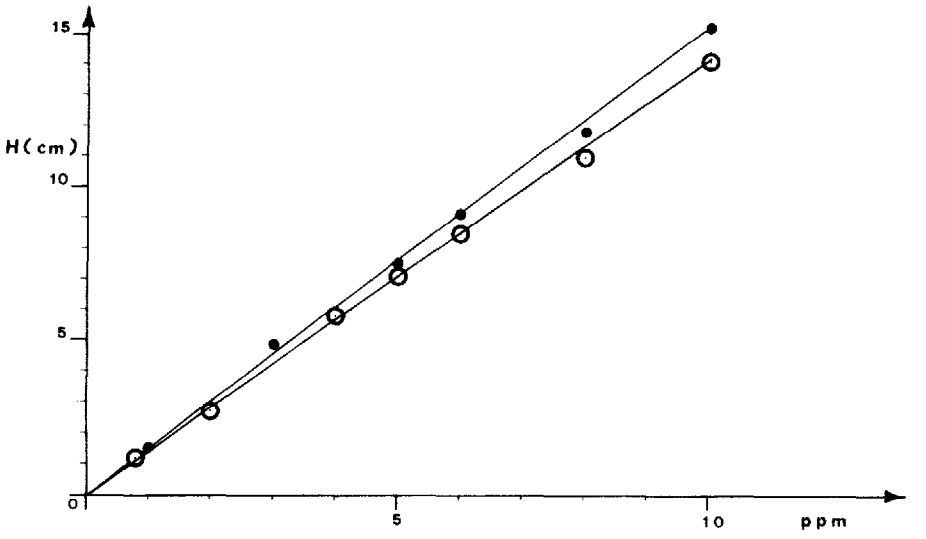


Fig. 2. Calibration graph obtained from solutions of formaldehyde (●) and acetaldehyde (○) containing cyanide.

It was found that the optimal conditions were a concentration of 40 ppm of cyanide and a pH lower than 3. Reaction (1) then proceeded instantaneously and completely.

Fig. 1 shows that the cyanohydrins obtained give symmetrical peaks, so that peak heights can be used instead of peak areas in the calculations.

Fig. 2 shows that the calibration graphs are straight lines for concentrations of formaldehyde and acetaldehyde not exceeding 10 ppm.

The results of a series of measurements are reported in Table I.

The proposed method seems to be specific for formaldehyde and acetaldehyde, as higher carbonylic compounds either do not react with $CN^-$ or the products of the reaction do not interfere in the gas chromatographic determination.

TABLE I

RESULTS OF DETERMINATION OF FORMALDEHYDE AND ACETALDEHYDE

| *Aldehyde* | *Amount of aldehyde (ppm)* | *No. of measurements* | *Average peak height (cm)* | *Standard deviation (cm)* | *Relative standard deviation (%)* |
|---|---|---|---|---|---|
| Formaldehyde | 10 | 4 | 14.2 | 0.260 | 1.42 |
| | 6 | 4 | 8.5 | 0.250 | 2.94 |
| | 0.8 | 4 | 1.2 | 0.075 | 1.42 |
| Acetaldehyde | 10 | 4 | 15.3 | 0.075 | 1.09 |
| | 6 | 4 | 9.2 | 0.100 | 1.08 |
| | 1 | 4 | 1.5 | 0.100 | 1.08 |

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