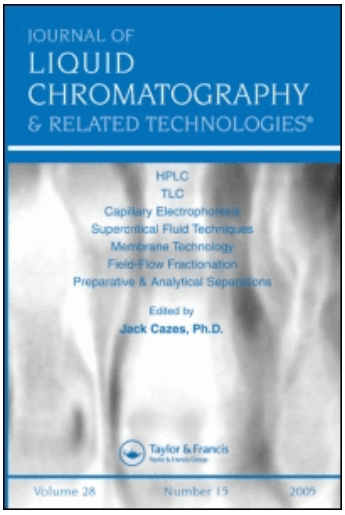

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HPLC DETERMINATION OF TRACE LEVELS OF ALIPHATIC ALDEHYDES C_1 - C_4 IN RIVER AND TAP WATER USING ON-LINE PRECONCENTRATION

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ABSTRACT

A simple method has been developed for the separation and quantification of trace amounts of C_1 - C_4 aldehydes in river and tap water. This method utilized the separation of the aldehydes as their 2,4-dinitrophenylhydrazones derivatives by high performance liquid chromatography using on line preconcentration and gradient solvent elution. The reaction of the derivatization was studied on a microscale in water solution at different pH. It was found that aldehydes in spiked sample (at 1 ppb level) are decomposed and unknown compounds are formed. The limits of the detection at a wavelength of 355 nm and a signal/noise ratio of 5 range from 50 ppt for formaldehyde to 200 ppt for butyraldehyde. The mean relative standard deviations for all aldehydes were 10% at 1 ppb level.

INTRODUCTION

Water from polluted rivers is used to feed buffer reservoirs as a first step in the production of drinking water. As the quality of river water is not constant, continuous monitoring is necessary. Aldehydes are important

pollutants of river water, being products of many industrial processes. Aldehydes are known contributors to irritants of the skin, eyes and nasopharyngeal membranes and formaldehyde has been identified as a suspected carcinogen (1,2).

Some HPLC methods for the determination of aliphatic aldehydes after the derivatization have been reported. The commonly used method for aliphatic aldehydes are 2,4- dinitrophenylhydrazine (DNPH) method. In this method, individual aldehydes react with an acidic solution of DNPH to form hydrazone derivatives. The derivatives of aldehydes are diluted in a solvent suitable for gas chromatography (3) or high performance liquid chromatographic analysis (4,5).

HPLC has proved suitable for the separation of certain carbonyl compounds by adsorption chromatography (6 - 8). The use of HPLC has been also published with reversed phase columns (9-12). The application of off-line preconcentration of 2,4-dinitrophenylhydrazones of aldehydes has been described by Kuber at al. (13).

The aim of this paper is to develop a method for the determination of aliphatic aldehydes (C_1- C_4) in which the derivatization reaction is performed directly in a water sample. The quantitative conversion of aldehydes to their corresponding 2,4-dinitrophenylhydrazones on a microscale at room temperature is also studied. To improve the limit of the detection on-line preconcentration has been developed.

EXPERIMENTAL

The LC system for the determination of 2,4-dinitrophenylhydrazones consisted of two Waters pumps (Model 510) and a 150 x 3.2 mm I.D. column packed with 5 μm particles Separon SGX C18 (Tessek, Prague). The preconcentration pump was a Waters pump (Model 501) used at a

flow rate of 1.0 ml/min. Preconcentration was carried out using a 30 x 3.2 mm I.D. precolumn which was packed with Separon C18 (5 μm) (Tessek, Prague). A Waters spectrophotometric detector (Model 484) was used. The analysis was optimized for the determination of 4 dinitrophenylhydrazones (C_1- C_4). Several of these compounds are important for in-time monitoring because they are produced by many technological processes in significant quantities.

The precolumn was washed with 10 ml river or tap water (after derivatization) and subsequent chromatographic separation with gradient elution was done. The mobile phase for the linear gradient was prepared by mixing two solutions : A-: acetonitrile - water 1 : 1

B-: acetonitrile

100% A to 66.7% B over 30 minutes, then to 100% B over 15 minutes.

Prior to use, the water samples were filtered over a 0.45 μm membrane filter. LC gradient - grade acetonitrile was used for the solutions. Water deionized with synthetic resins may contain formaldehyde. All experiments were done at ambient temperature.

RESULTS AND DISCUSSION

Taking advantage of the specific reaction between aldehydes and DNPH we have selected HPLC studies of aldehydes (C_1- C_4) in the tap or river water, to analyze trace levels of aldehydes as 2,4-dinitrophenylhydrazones. A study of the effect of the acid catalyst (hydrochloric acid) concentration on the reaction kinetics was undertaken. Known amount (100 ppb) of propylaldehyde was injected into DNPH solution containing variable amounts of hydrochloric acid catalyst. The reaction mixture was analyzed by reversed phase HPLC at various times after the reaction was initiated . The results indicate that the

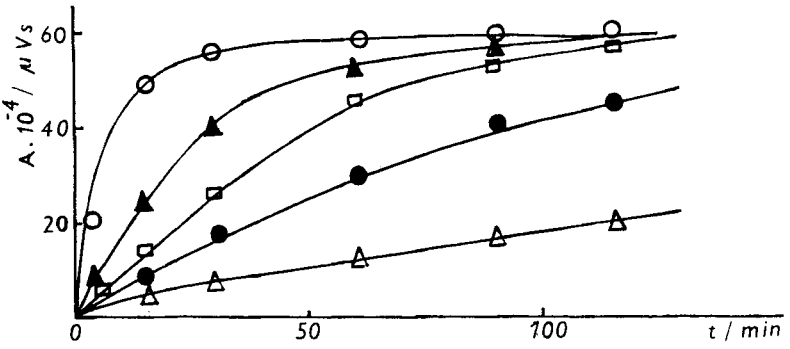

Fig.1. Dependence of reaction yield of 2,4-dinitrophenylhydrazone of propylaldehyde on time at different pH
△ - pH=7; ● - pH=4; □ - pH=3; ▲ - pH=2; ○ - pH=1.

reaction proceeds slowly and the best results can be achieved at pH = 1 (Fig. 1).

The reaction between aliphatic aldehydes and DNPH was studied on a microscale at room temperature in water solution at pH = 1. Aldehydes (10 ppb) were added to an excess of DNPH reagent (30 x). The chemical reaction between DNPH and aliphatic aldehydes procceds slowly and the yield depends on the reaction time. Fig. 2 shows that the high yield was achieved during 30 min. for all aldehydes.

A reversed phase C18 packing material for the enrichment column was chosen to conform with the stationary phase used in the analytical column. A high capacity is required for the precolumn, whereas selectivity and efficiency are important for the analytical column. The relationship of sample volume to the adsorbent amount is determined by the substance with the lowest retention. The type and amount of packing material in the precolumn determines the maximum sample volume that can be passed trough the column without sample components breaking through. The break through volume of the phenylhydrazone of formaldehyde was determined

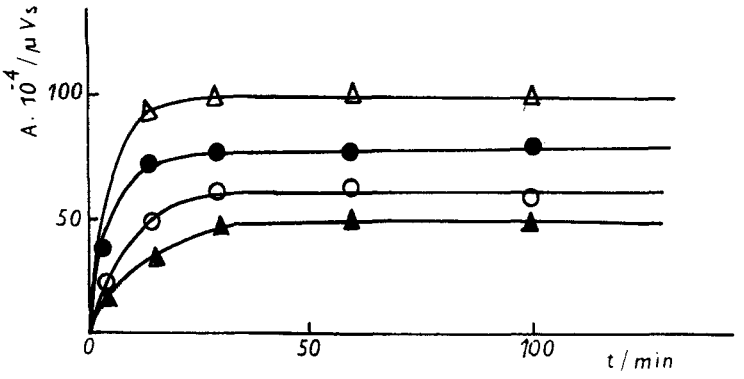

Fig.2. Dependence of reaction yield of 2,4-dinitrophenylhydrazones of C_1- C_4 aldehydes on time.
△ - C_1; ● - C_2; ○ - C_3; ▲ - C_4.

in water at a spiking level 1 ppb by using UV detector at 355 nm. Fig. 3 shows that under the conditions used 2,4-dinitrophenylhydrazone of formaldehyde is quantitatively adsorbed on the 5 μm d_p Separon C18 packing with sample volumes of up to 30 ml. Therefore, when using these conditions quantitative sorption of other derivatives of aldehydes with similar and higher retention can by expected. However, a volume of only 10 ml was used. Compared with a 30 ml sample volume sufficient capacity for sorbent washing is guaranteed.

Filtration of the water sample is a prerequisite for trouble - free operation. Without filtration, the inlet sieve of the enrichment column becomes blocked after a few runs. The pH of the water sample should be between 6 and 7 for the enrichment step and for this reason the tap or river water must be neutralized after the derivatization of aldehydes.

In Figs. 4 and 5 two chromatograms are reproduced to demonstrate blank contribution. Fig.6 shows the chromato-

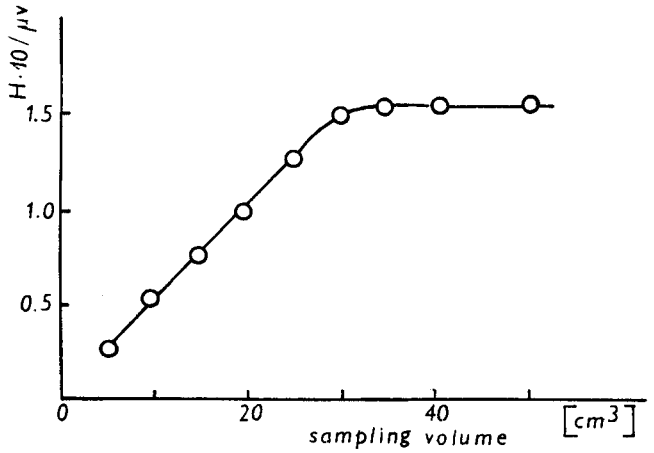

Fig.3. Determination of the break through volume of 2,4-dinitrophenylhydrazone of formaldehyde (1 ppb)
Column Separon C18 (30 x 3.2 mm I.D.)
Flow rate 1.0 ml/min, H - height of the peak

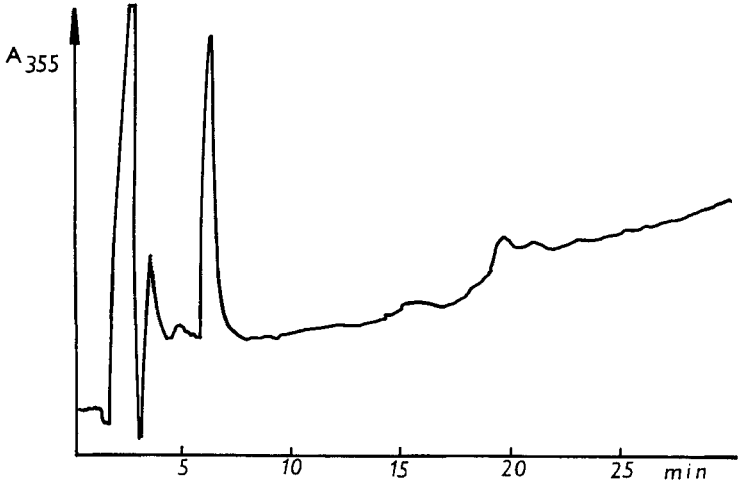

Fig.4.Chromatogram of a blank redistilled water after on-line preconcentration (sampling volume 10 ml, pH = 7)
Chromatographic column Separon SGX C18,
flow rate 0.5 ml/min, mobile phase - see experimental part, UV detection 355 nm.

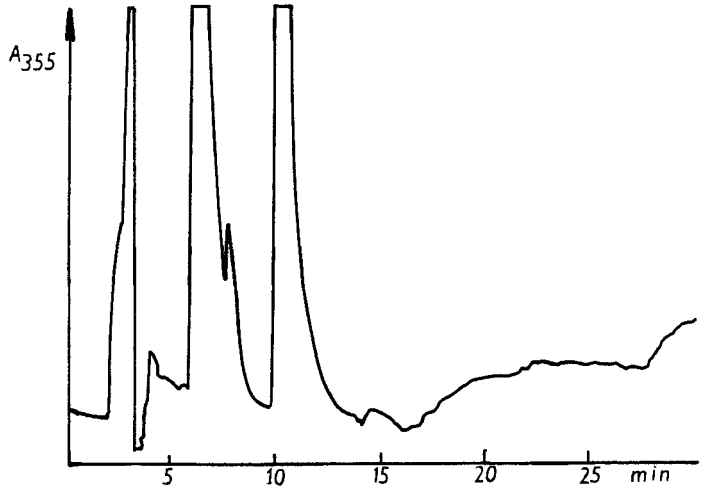

Fig.5.Chromatogram of a blank redistilled water with derivatization reagent after on-line preconcentration (sampling volume 10 ml, pH = 7)
For the chromatographic conditions see Fig. 4.

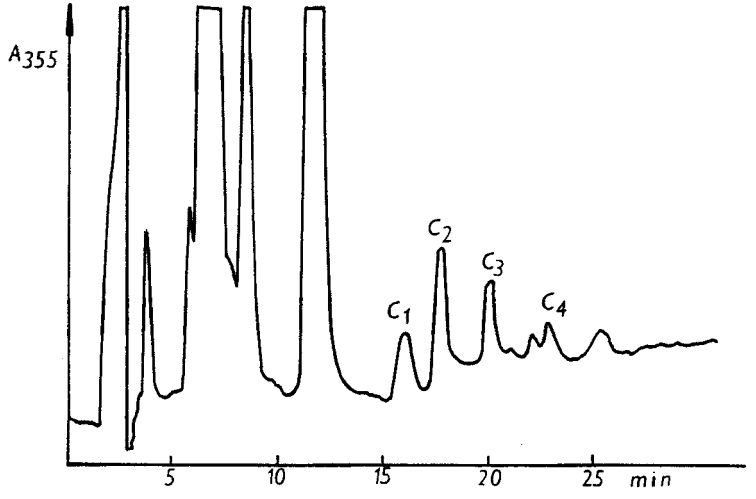

Fig.6.Chromatogram of the spiked redistilled water (1 ppb of aldehydes) after on-line preconcentration (sampling volume 10 ml, pH = 7).
For the chromatographic conditions see Fig. 4.

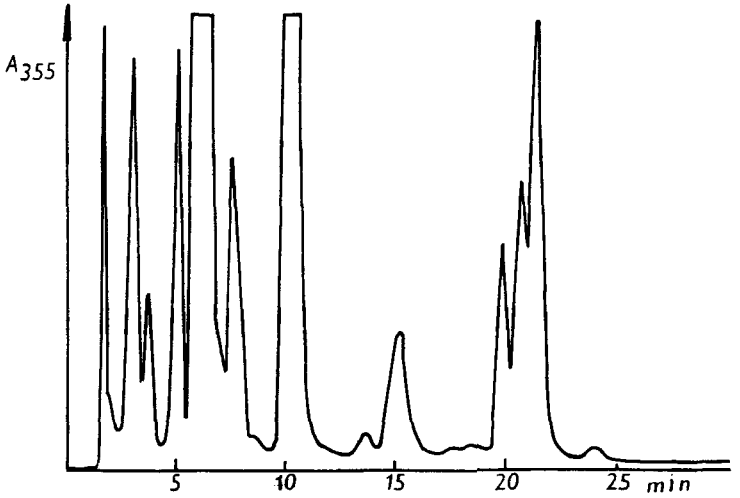

Fig.7.Chromatogram of the river water (Danube) with derivatization reagent after on-line preconcentration. (sampling volume 10 ml, pH = 7.
For the chromatographic conditions see Fig. 4.

gram of spiked redistilled water. A comparison of these chromatograms indicated that 2,4-dinitrophenylhydrazones can be detected in the lower ppb range. Retention times of 2,4-dinitrophenylhydrazones are reproducible with variations usually less than 5%. There is a slight baseline drift associated with the acetonitrile concentration but this does not contribute any additional uncertainties in the quantitative analysis.

Fig. 7 shows the chromatogram of Danube water with derivatization reagent and it is clear that there is no peaks of 2,4-dinitrophenylhydrazones of C_1- C_4 aldehydes. Fig. 8 clearly shows the absence of 2,4- dinitrophenylhydrazones and there can be seen several additional peaks in the spiked sample. This results has led to the conclusion that the additional peaks are the result of reaction

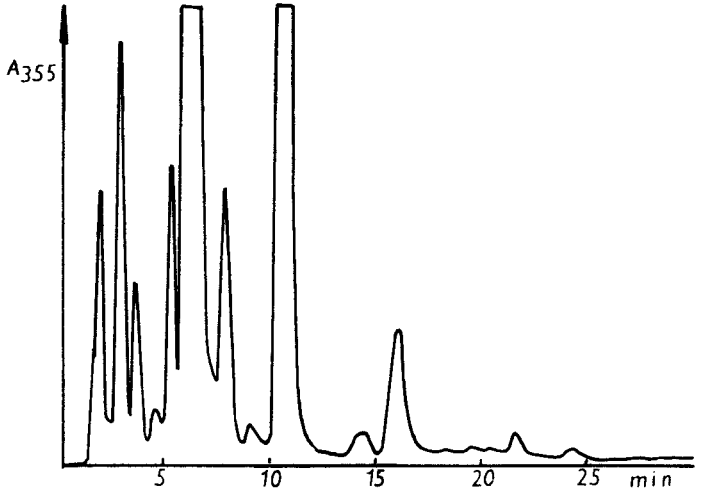

Fig.8.Chromatogram of the spiked river water (1 ppb of aldehydes) after derivatization, on-line preconcentration (sampling volume 10 ml, pH = 7).
For the chromatographic conditions see Fig.4.

products from the reaction of aldehydes with another compounds presented in the river sample. The same conclusion can be done in the case of the tap water where the reaction of aldehydes with chlorine (presented in tap water) can be assumed (at 1 ppb level of aldehydes).

Detection limits afforded by the HPLC method with on line preconcentration are of the order of a nanograms per litre. Lowest limits have been determined using a peak area integrator signal - to - noise ratio of 5. The analytical detection limits range from 50 ppt for formaldehyde to 200 ppt for butyraldehyde In practice, it is obviously extremely difficult to eliminate all impurities in the reagent at levels corresponding to these very low analytical detection limits.

RSD was also determined for quantitative analysis of calibration mixtures and samples prepared in the laborat-

ory. Triplicate injection yielded RSDs of about 10% for all aldehydes at 1 ppb level.

REFERENCES

1. Bailey R.A., Clark H.M., Ferris J.P., Krause S., Strong R.L., Chemistry of the Environment., Academic Pres, New York 1978.
2. Sitting M., Pollution Detection and Monitoring Handbook, Noyes Data Corp., Park Ridge, NJ, 1974.
3. Papa L.J., Turner L.P., J. Chromatogr. Sci., 10, 747 (1972)
4. Selim S., J. Chromatogr. 136, 271 (1977)
5. Kuwata K., Uebori M., Yamasaki Y., J. Chromatogr. Sci., 17, 264 (1979)
6. Carey M.A., Persinger H.E., J. Chromatogr. Sci., 10, 537 (1972)
7. Honed S., Kakehi K., J. Chromatogr. 152, 405 (1978)
8. Heath R.R., Tumlinson J.H., Doolittle R.E., Proveaw A.T., J. Chromatogr. Sci., 13, 380 (1975)
9. Fung.K., Grojean D., Anal. Chem., 53, 168 (1981)
10. Demko P.R., J. Chromatogr., 179, 361 (1979)
11. Nakamura K.I., Asami M., Orita S., Kawada K., J. Chromatogr., 168,221 (1979)
12. Vigh G., Varaga-Pouchy Z., Hlavay J., Petro-Tercza M., Szarfoldi-Salma I., J. Chromatogr., 193, 432 (1980)
13. Kuber R.J., Mopper K., Environ, Sci. Technol., 24, 1477 (1990)

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