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Short communication

Poly(allylamine) beads as selective sorbent for preconcentration of formaldehyde and acetaldehyde in high-performance liquid chromatographic analysis

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Abstract

Formaldehyde and acetaldehyde in water were determined by preconcentration with poly(allylamine) beads, derivatization with 2,4-dinitrophenylhydrazine (DPH) and analysis by HPLC. Poly(allylamine) beads (0.5 g) were used to adsorb formaldehyde and acetaldehyde at 1.2–150 $\mu g\ l^{-1}$ and 3.5–220 $\mu g\ l^{-1}$ from water (1 l). The concentration factor is 50 fold. The aldehydes were eluted and derivatized with 2 m*M* DPH in 0.5 *M* H_2SO_4 (10 ml). The time of analysis was 1 h. The detection limits ($S/N=3$) for formaldehyde and acetaldehyde were 0.6 and 2 $\mu g\ 1^{-1}$, respectively.

Keywords: Preconcentration; Poly(allylamine); Formaldehyde; Acetaldehyde

1. Introduction

Aldehydes are important pollutants of waters, being natural oxidation products of many organic compounds and products of many industrial processes. They are suspected carcinogens and mutagens in laboratory animal tests [1,2]. The most frequently used method for the determination of aldehydes in water involves derivatization with 2,4-dinitrophenylhydrazine (DPH) and analysis by HPLC [3–6]. These procedures are relatively easy to carry out, but they are not sensitive enough for direct analysis of the water samples; the detection limits for formaldehyde (FA) and acetaldehyde (AA) are about 20 $\mu g\ 1^{-1}$ [11]. The sensitivities were improved by a combination of HPLC and preconcentration by solid-phase extraction of the hydrazones with a C_{18} cartridge [7] and with a short column packed with zeolite [8], cation-exchange resins [9] or C_{18} beads [10,11]. Since in such preconcentration methods substances which have hydrophobic groups are non-specifically adsorbed on the adsorbents and the presence of a large amount of DPH interferes with the adsorption of the hydrazones, their recoveries were not always high (60–90%), and many peaks in complex chromatograms frequently obscured the analytes. For selective concentration of formaldehyde in water, poly(allylamine) beads (PA beads)

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have been proposed as an adsorbent for solid-phase extraction [12]. In the method, μg l^{-1} levels of formaldehyde in water were determined by preconcentration with the beads and analysis by flow-injection system with immobilized enzyme reactor and the detection limit was 0.3 μg l^{-1}.

The aim of this paper was the development of a selective and sensitive method for the HPLC determination of FA and AA in water. PA beads were evaluated as a selective sorbent for clean up/preconcentration of FA and AA. In the adsorption the aldehydes were trapped chemically from water as imines on the PA beads and the non-specifically adsorbed materials on the beads were removed by washing with aqueous acetonitrile.

$$HCHO, CH_3CHO + R\text{-}NH_2 = R\text{-}N{=}CH_2,$$

$$R\text{-}N{=}CHCH_3 + 2H_2O \ (R\text{-}NH_2; \text{poly(allylamine)}).$$

The conversion of the imines produced on PA beads to their corresponding hydrazones with acidic DPH solution was also studied.

$$R\text{-}N{=}CH_2, R\text{-}N{=}CHCH_3 + 2H^+ + 2\phi\text{-}NH\text{-}NH_2 = \phi\text{-}NH\text{-}N{=}CH_2 + \phi\text{-}NH\text{-}N{=}CHCH_3 + 2R\text{-}NH_3^+ \quad (\phi\text{-}NH\text{-}NH_2; \text{DPH}).$$

2. Experimental

2.1. Reagents

Poly(allylamine) beads (HCl salt, ca. 200 mesh, the amount of amine; 9.0 mequiv. g^{-1} of dry beads) were obtained from Nittobo (Tokyo, Japan). Formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazones (FA-DPHo and AA-DPHo) were purchased from Supelco (Bellafonte, USA). All other chemicals, which were from Nacalai Tesque (Kyoto, Japan), were of analytical-reagent grade. The water used throughout was prepared by distilling water according to the method given in Ref. [12]. The concentration of aldehydes in the purified water was checked by gas chromatography–mass spectrometry [13] and was <0.1 μg l^{-1}. The water and reagent solutions were stored in glass bottles with screw-caps to avoid contamination of aldehydes from air. DPH was purified as described by Cotsaris et al. [7]. FA solution (37.66%) was assayed by sulfite–HCl titrimetry [14].

2.2. HPLC

Chromatography was carried out with a Hitachi L-6000 pump, a Kyowa Seimitsu KHP-UI-130A injector with a 20 μl loop, a separation column (15 cm×4 mm I.D.) which filled TSKgel ODS8OTs (5 μm), a JASCO Uvidec-100-VI (360 nm), connected to a SIC SC77 signal cleaner and a System Instruments Chromatocorder II data processor. The column was held constant at 40°C in a column oven. The mobile phase was acetonitrile:water (55:45 v/v) at 0.90 ml min^{-1}.

2.3. Concentration and clean-up procedure

Water sample (1 l) was buffered at pH 10.5 by adding 4.8 g sodium carbonate and 0.8 g sodium hydrogen carbonate and PA beads (0.5 g) were added to the solution. The mixture was vigorously shaken (240 times min^{-1}) for 15 min at 60°C. After washing with acetonitrile–water mixture (55:45 v/v) (100 ml) and water (50 ml), the beads were transferred into a calibrated flask (20 ml). A DPH (2 m*M*) in 0.5 *M* sulfuric acid (10 ml) was added and the mixture was shaken for 20 min at 60°C. The mixture was diluted to the mark with tetrahydrofuran and agitated ultrasonically for 3 min. After centrifugation, 20 μl of the yellow solution was used for HPLC analysis.

A calibration graph for the determination of each aldehyde was prepared by using standard aldehyde solutions.

Under the conditions the concentration factor is 50 fold. The present method was compared with GC–mass spectrometry [13]. The derivatization reagent was *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine. A Shimadzu GCMS-QP5050 with a 25 m×0.32 mm I.D.×0.25 μm Ultra 1 column was used. The time of analysis was 2 h. The detection limits for FA and

AA were 0.1 and 0.8 μg l^{-1}, respectively, for a 5 ml water sample.

3. Results and discussion

3.1. Adsorption

The rate of aldehyde adsorption versus time was measured. The tests were performed by using 100 ml of aldehyde solution (1.00×10^{-5} *M* each) which was buffered with sodium carbonate–sodium hydrogen carbonate (pH 9.0–10.5) and 0.50 g of the beads at various temperatures (20–50°C). Solutions were harvested at different times (1–20 min, etc.) and the concentrations of nonadsorbed aldehydes in the solution were determined by using gas chromatography with a capillary column [15]. The rates were dependent on pH and temperature. For FA a linear relationship between log k' and $1/T$ was obtained at each pH medium as shown in Fig. 1; k' and T are the apparent kinetic constant and absolute temperature of the solution, respectively. For AA a similar relation was obtained, but the k' at each pH was one-sixth of that for FA; the carbonyl group in FA is more subject to nucleophilic addition than that in AA. For FA, the apparent rate constants calculated from the linear plot and the times required for completion of the adsorption (FA concentration to decrease to one-thousandth of its initial value) for pH 10.5 at 60, 70 and 80°C are 2.6, 3.8 and 5.8 min^{-1} and 6.0, 5.6 and 5.2 min, respectively. But, above 70°C the recovery of AA decreased because of its volatility. Above pH 11 media recoveries of aldehydes were decreased because aldehydes undergo the Cannizaro reaction [16,17]. Under the conditions of pH 10.5 at 60°C at shaking for 15 min the aldehydes will be trapped completely on the beads.

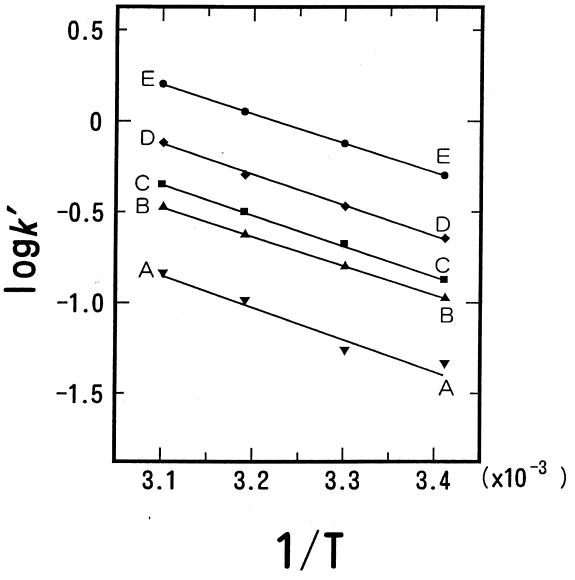

Fig. 1. Relationship between apparent kinetic constant (k') and absolute temperature (T) of the solution at each pH. (A) in water; (B) in pH 9.0; (C) in pH 9.5; (D) in pH 10.0; (E) in pH 10.5.

3.2. Desorption and derivatization

After adsorption of FA and AA (10^{-7} mol each), according to the concentration and clean-up procedure, the beads were treated with acidic DPH solution. Table 1 shows the effect of concentrations

Table 1
Peak heights of hydrazones in the chromatogram[a] showing the effect of concentration of acidic DPH solution used for desorption/derivatization[b]

Acidic DPH solution	FA-DPHo	AA-DPHo
0.5 m*M* DPH in 0.5 *M* H_2SO_4	155(5)[c]	29(2)[c]
1 m*M* DPH in 0.5 *M* H_2SO_4	164(5)	77(4)
2 m*M* DPH in 0.5 *M* H_2SO_4	164(5)	86(4)
3 m*M* DPH in 0.5 *M* H_2SO_4	125(10)	86(4)
4 m*M* DPH in 0.5 *M* H_2SO_4	UR[d]	82(6)
2 m*M* DPH in 0.1 *M* H_2SO_4	104(7)	12(2)
2 m*M* DPH in 0.3 *M* H_2SO_4	164(5)	75(4)
2 m*M* DPH in 0.7 *M* H_2SO_4	157(7)	83(4)
2 m*M* DPH in 1 *M* H_2S_4	93(10)	50(5)

[a] Peak heights for FA-DPHo and AA-DPHo in the mixed standard (5.00×10^{-6}*M* each) were 164 mm and 135 mm, respectively.

[b] Shaking time: 20 min, reaction temperature: 60°C.

[c] Average (mm) and relative standard deviation (%) of the peak height of 5 runs.

[d] UR; Peaks for DPH and FA-DPHo were unresolved.

of DPH and H_2SO_4 in the solution. For FA complete recovery was obtained with solutions ranging from 1 to 2 m*M* DPH (0.5 *M* H_2SO_4) and 0.3–0.5*M* H_2SO_4 (2 m*M* DPH). For AA the maximum recovery was 64±2% ($n=5$). The presence of larger quantities of DPH in the solution interfered with peaks for hydrazones in chromatograms; at 4 m*M* DPH peaks for DPH and FA-DPHo were unresolved, and moreover, the broad peak of DPH interfered with the peak for AA-DPHo. Above 0.7 *M* H_2SO_4 the hydrazones partially decomposed. A solution of 2 m*M* DPH and 0.5*M* H_2SO_4 was chosen as the optimum; the concentrations of DPH and H_2SO_4 in the final solution are 1 m*M* and 0.25 *M*, respectively.

The effect of the shaking period was studied over the range 5–60 min at 60°C. The recoveries for analytes increased with increasing shaking time from 5 and 20 min, first rapidly and then gradually. The equilibration period was between 20 and 25 min and above 30 min they decreased gradually because of the decomposition of hydrazones [7]. A shaking time of 20 min was chosen.

The temperature dependence of the recoveries was investigated over the range 30–80°C. The recoveries were increased exponentially from 30 to 55°C and maxima were obtained between 60 and 65°C. Above 70°C the hydrazones began to decompose. A reaction temperature of 60°C was chosen.

Though propionaldehyde, acrolein, glyoxal and methylglyoxal were trapped in above 90% yields as imines on the beads, the hydrazones were not produced under the condition described above; the imines are not appreciably hydrolyzed in the acidic solution.

3.3. Detection limits, linearity, and recovery

The detection limits for FA and AA, based on a S/N ratio of 3, were 0.6 μg l^{-1} and 2 μg l^{-1}, respectively, for a 1 l water sample. The relationship between the peak height and FA-DPHo or AA-DPHo concentration was linear from 1×10^{6} *M* to 2 m*M*.

The calibration graph of peak height for aldehyde concentration was linear over the range 1.2–150 μg l^{-1} with a correlation coefficient of 0.999 (11 data points) for FA and 3.5–220 μg l^{-1} with 0.991 (10 data points) for AA. The slope of the calibration curve for FA was 1.57 times that for AA.

Recovery of aldehydes was determined by seven replicate runs for standard solution ($1\times10^{7}M$ each, 1 l). Recoveries for FA and AA were 99–101% with a 2.4% relative standard deviation (RSD) ($n=7$) and 62–64% with a 4.7% RSD, respectively,

3.4. Application

The method was applied to the determination of aldehydes in mineral water and pond water. Results for four samples are reported in Table 2. A typical chromatogram of the pond water is shown in Fig. 2; there can be seen only two additional peaks. The results for pond water using the preconcentration-HPLC method compared well with those obtained by

Table 2
Aldehyde concentrations of mineral water and pond water

	Formaldehyde (μg l^{-1})		Acetaldehyde(μg l^{-1})	
	Proposed method	GC MS [13]	Proposed method	GC MS [13]
Mineral water in PET bottle[b]	2.9(3)[a]		nd[c]	
in paper package	1.7(3)		nd	
Pond water				
Ryuuga-ike	5.3(3)	5.8(4)	4.4(5)	4.7(5)
Shingen-bori	9.5(2)	9.1(4)	6.9(5)	7.2(5)

[a] Average and RSD (%) of 5 runs.
[b] PET: polyethylene terephthalate.
[c] ND; No peak detected (<2 μg l^{-1}).

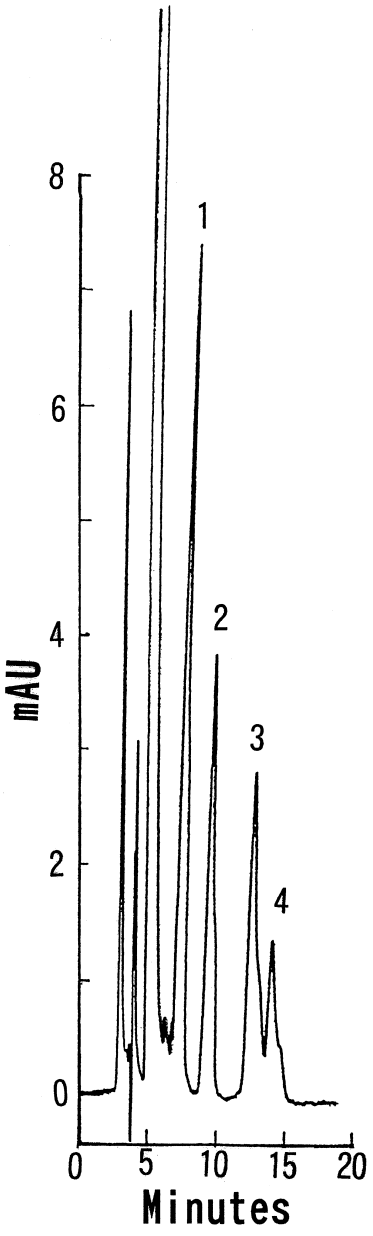

Fig. 2. Chromatogram of the pond water (Ryuuga-ike). Peaks: 1 = formaldehyde, 2 = acetaldehyde, 3,4 = unknowns.

GC–mass spectrometry [13]. Results for two samples are included in Table 2.

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