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Mendeleev Commun., 2006, 16(2), 117–119
Mendeleev Communications

Polymethacrylate sorbent for the solid-phase extraction of amines

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DOI: 10.1070/MC2006v016n02ABEH002125

The use of solid-phase extraction with polymethacrylate for the gas chromatographic determination of dimethylamine, trimethylamine, ethylamine, triethylamine, propylamine, dipropylamine and tripropylamine in aqueous solutions was studied (detection limits of 0.7–1.0 μg dm^{-3}).

Aliphatic amines are of environmental importance because they are hazardous[1] and can be a source of nitrosamines.[2] Amines are toxic water pollutants.[3] Underivatized amines were determined by capillary gas chromatography and liquid chromatography.[4–6] Most hyphenated chromatographic systems provide high sensitivity; aqueous samples still have to be concentrated to meet the desired detection limits. This can be performed by liquid extraction[7,8] and solid-phase extraction.[9–11] A relatively new approach for the preconcentration of amines using solid-phase micro extraction was described.[12] Sorptive extraction based on the use of polydimethylsiloxane and poly(butyl acrylate) as sorption phase with thermal desorption was proposed.[13,14] Various porous polymers are also widely used as sorbents for the preconcentration of organic compounds from water (PS-DVB, XAD and cyclodextrin polymers are used in solid phase extraction).[15–18]

Dimethylamine (DMA), ethylamine (EA), diethylamine (DA), triethylamine (TEA), propylamine (PA), dipropylamine (DPA) and tripropylamine (TPA) were purchased from Sigma. Standard solutions (1 g dm^{-3}) were prepared in Milli-Q water (Millipore) and stored at 6 °C. Working solutions (50 μg dm^{-3}) were prepared by diluting the standard solutions with double-distilled water. Buffer solutions (pH 9.0) were prepared by mixing appropriate volumes of 0.1 M potassium dihydrogen phosphate and sodium hydroxide. HCl (Fluka) was added to adjust pH < 4. Polymethacrylate (PMA) with a particle size of 0.1–0.15 mm was prepared as described previously[18] and rinsed with propan-2-ol and diethyl ether.

GC analysis was performed on a Shimadzu GC-9A (Japan) gas chromatograph with an Automass II mass spectrometer (JEOL, Japan) and a SE-30 capillary column (25 m; film thickness of 0.3 μm). The injector and the detector temperatures were 200 °C. The column temperature was programmed as follows: 70 °C for 1 min, heating at 5 K min^{-1} to 200 °C and holding at the final temperature for 3 min. The flow manifold used comprised a Gilson Minipuls-2 pump. The injected volume was 2 μl.

The sorbent was packed in a 10×5 mm i.d. stainless precolumn. The standard solution was passed through the sorbent at different flow rates. After the amines were trapped on the sorbent, the sorbent column was dried for 5 min with a stream

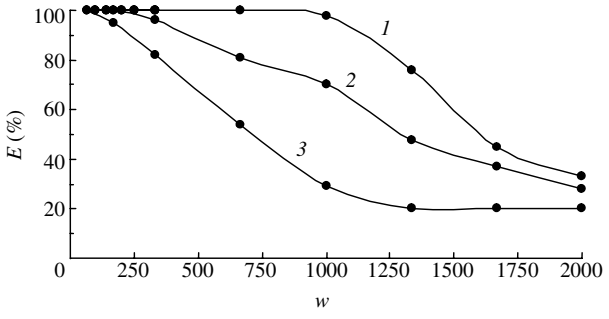

Figure 1 Influence of liquid to solid phase weight ratio on the extraction of amines: (*1*) DPA, (*2*) DEA and (*3*) DMA.

Table 1 Extraction of amines from 100 ml samples spiked at different pH (n = 3–4, P = 0.95).

Analyte	Extraction (%)		
	pH 4.0	pH 7.0	pH 8.5
Dimethylamine	28.2±2.6	55.8±3.4	98.9±3.6
Ethylamine	22.8±2.1	35.5±2.3	95.6±3.7
Diethylamine	15.5±1.3	49.7±3.2	102.3±3.4
Trimethylamine	18.4±1.5	68.4±3.4	94.0±3.2
Propylamine	10.6±0.9	24.5±1.6	88.2±3.6
Dipropylamine	25.1±2.1	52.1±3.4	94.3±3.6
Tripropylamine	16.3±1.4	22.6±1.1	98.9±3.4

of nitrogen and eluated with diethyl ether. The extract was dried over anhydrous sodium sulfate for 12 h, and the solution was concentrated using a rotary flash evaporator to approximately 0.5 ml. Further concentration to 100 µl was conducted under nitrogen.

DMA, EA, DA, TEA, PA, DPA and TPA were determined in model aqueous solutions. The aqueous standard solution at pH 9 was passed through the column. In order to determine the sorbent parameters, 10 ml of the sample was collected on passage through the sorbent column and simultaneously 10 ml of original sample was taken. Both samples were extracted with 1 ml of diethyl ether, and the extracts were dried over anhydrous sodium sulfate. Finally, aliquots of the extract were injected into the chromatograph for analysis. The difference between the chromatographic signals obtained gave the sorption efficiency of the sorbent. PMA exhibited a sorption efficiency close to 100% at pH 9. Chromatographic peaks of amines were not detected for a sample collected from the sorbent column. On the other hand, the efficiency of PMA at pH 7 and 3 was only 22–58 and 11–28%, respectively. The polarity of PMA resulted in a greater number of the polar interactions with amines and, consequently, high recoveries at high pH. Further, the percentage recovery of amines was calculated by comparing the peak areas. Recoveries were calculated as mean values of three analyses. Low RSDs (less than 12%) illustrate the repeatability of the procedure (Table 1).

In order to obtain optimum conditions for amine recovery, the following recovery experiments were performed using a standard solution containing 50 µg dm^{-3} of each amine. First, the liquid to solid phase ratio w = (sample weight)/(sorbent weight) varied from 67 to 2000 (Figure 1). Second, the amount of diethyl ether was the variable ranging from 0.5 to 10 ml while the sample (100 ml) and sorbent (400 mg) were constant.

When different amounts of the standard solution were used, a linear relation between the recovery of amines and amounts of the solutions used was obtained. The highest recovery was obtained from 80–100 ml sample solution amines. Consequently, 100 ml of the sample was used for further experiments. In the case of different amounts of sorbent used the recovery of amines did not show significant differences. The full extraction of amines was achieved when more than 0.4 g of the sorbent was used. Therefore, 400 mg of the sorbent was used for futher experiments. The optimum volume of diethyl ether was 2 ml.

The system was optimised and the best extraction was obtained when the flow rate of samples was 3 ml min^{-1}. The result in

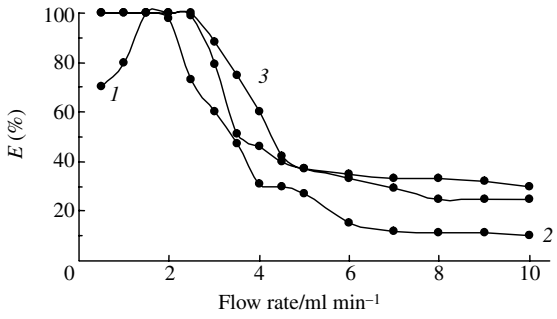

Figure 2 Influence of the flow rate of (*1*) DMA, (*2*) DEA and (*3*) DPA solutions on extraction.

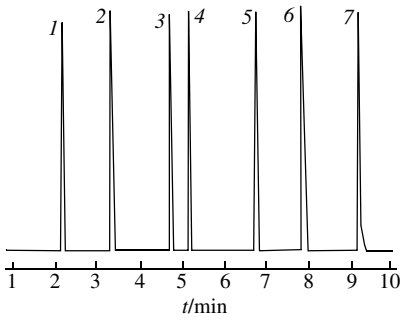

Figure 3 Chromatogram of the standard solution of amines (50 µg dm^{-3}) under optimal working conditions: (*1*) DMA, (*2*) EA, (*3*) PA, (*4*) DEA, (*5*) TEA, (*6*) DPA and (*7*) TPA.

Figure 2 indicates a local optimum flow rate of 2–3 ml min^{-1} for most amines and near 2 ml min^{-1} for DMA.

The extraction of amines from a polar aqueous solution into the hydrophobic PMA sorbent was low at a flow rate lower than 2 ml min^{-1} (Figure 3). The hydrophobic nature of the sorbent favoured the extraction of organic substances from aqueous solution. Extraction with the PMA sorbent can be divided into two broad steps.[19] In the first step, the aqueous sample containing the analyte is brought into contact with the sorbent, where some of the analyte is extracted into the sorbent surface. In second part, the analyte, which is dissolved in the sorbent, diffuses into the bulk of the sorbent. The flow rate of the high volume sample should correspond to optimum conditions. Figure 3 shows the chromatogram of the determination of amines in the standard solution after solid phase extraction with PMA under optimum conditions.

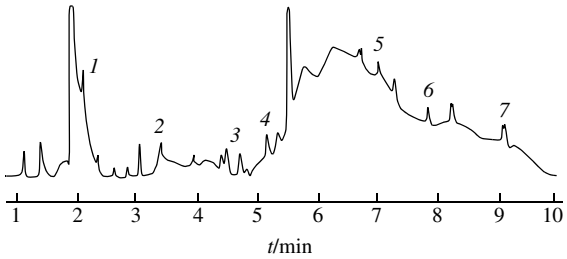

Figure 4 Chromatogram obtained in the analysis of river water spiked with amines (5 µg dm^{-3}): (*1*) DMA, (*2*) EA, (*3*) PA, (*4*) DEA, (*5*) TEA, (*6*) DPA and (*7*) TPA.

The detection limits at a signal-to-noise ratio of 3:1, which was obtained by measuring 100 ml samples containing 20 µg dm^{-3} of amines, were 0.7–1.0 µg dm^{-3}. The proposed preconcentration method was applied to the determination of amines in river water (Neckar, Germany). Samples were passed through a filter to remove particulates and pH 9 was adjusted before analysis. Because none of the amines was detected, the samples were spiked with amines. Figure 4 shows the chromatogram obtained for samples spiked with 5 µg dm^{-3} of amines under optimal working conditions.

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Received: 31st October 2005; Com. 05/2603