

Comparison of sorbents for solid-phase extraction of polar compounds from water

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ABSTRACT

Octadecyl-bonded silica, styrene-divinylbenzene and hydroxyethyl methacrylate-ethylene dimethacrylate sorbents were tested for their ability to preconcentrate aniline, benzothiazole, cyclohexanone and cyclohexanol. Breakthrough curves for these compounds were measured for aqueous solutions at pH 5.8 and 10.0 by gas chromatographic analysis of fractions of the aqueous effluents. Elution curves of the analytes in methanolic eluates were obtained in order to determine the optimum volume of the eluate. Using breakthrough volumes and widths of the elution curves, theoretical preconcentration factors were calculated for all analyte-aqueous sample-sorbent systems tested. Octadecyl-bonded silica and styrene-divinylbenzene sorbents were found to be suitable for the preconcentration of weakly polar to polar compounds for practical water quality control purposes.

INTRODUCTION

Sample preparation is an important step in the analysis of complex water matrices for organic pollutants. Many techniques are available for the isolation and preconcentration of these compounds, and solid-phase extraction is currently being intensively developed. Many examples of the use of solid sorbents for the accumulation of organics from aqueous solutions can be found in the literature and have been well reviewed^{1–5}.

With regard to general methodology, solid-phase extraction (SPE) procedures can be performed in two ways: off-line using disposable cartridges and on-line via pre-column switching. Although automation of the sorbent extraction techniques,

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incorporating them into multi-dimensional chromatography/column switching systems, offers a very effective tool for analyses of water samples, for some applications of trace enrichment disposable cartridges still have significant advantages owing to their ease of handling and portability. The easy manipulation of these cartridges permits processing of the samples in the field, which avoids the transport and possible breakage of samples in glass containers. Moreover, the sorbed organic compounds are well preserved against breakdown by bacteria⁶.

The solid supports mostly used in the SPE are bonded silicas and various polymeric resins. Their application includes the preconcentration of polycyclic aromatic hydrocarbons⁷⁻¹⁰, pesticides¹¹⁻¹⁸, chlorophenols¹⁹⁻²¹, phenols^{9,21}, polychlorinated biphenyls¹³, priority pollutants²², organosulphur compounds²³, nitroaromatics²⁴, surfactants^{25,26}, chloroanilines²⁷ and nitrogen heterocycles⁹.

The polarity of accumulated compounds usually ranges from weakly polar to non-polar. Efforts to capture more polar compounds by means of hydrophobic sorbents often lead to a drastic decrease in recovery, so that for binding of these types of organic compounds other types of interactions (*e.g.*, ionic) have to be used.

The factor that most influences the accumulation of the analyte in the SPE column is its retention, which can be expressed as the capacity factor of the analyte in the water-stationary phase (sorbent) system. It has been well documented that even for columns that have a small number of theoretical plates, which is typical in SPE, high breakthrough volumes can be obtained if the retention is sufficiently high²⁸.

In order to obtain an effective preconcentration procedure, maximization of the amount of water sample and minimization of that of the eluting solvent are required. An approach to the development and verification of an SPE method has been reported¹⁷. Another possible approach is to measure the breakthrough curve for the analyte-water-sorbent system and concentration profile of the analyte in the organic eluent-sorbent system (*i.e.*, the retention characteristics of the sorbent bed in the presence of two extreme mobile phases). Having obtained information on these retention characteristics, suitable volumes of the water sample and the organic eluent can be determined.

The objective of this work was to evaluate, using the latter approach, two popular types of solid supports, octadecyl-bonded silica and styrene-divinylbenzene copolymer, for their capacity for selected polar compounds. Another solid polymer support, Spheron 100, a copolymer of hydroxyethyl methacrylate and ethylene dimethacrylate, which is more polar than styrene-divinylbenzene resin was chosen for testing as it was assumed that it would have higher affinity for polar molecules. In this instance, however, the presence of water as the competitive factor might play a negative role and this had to be taken into account.

EXPERIMENTAL

Materials

Model solutions of cyclohexanol, cyclohexanone, aniline and benzothiazole (Lachema, Czechoslovakia) in water were prepared from stock solutions in methanol (5000 ppm). These stock solutions were also used to spike industrial wastewaters with the pollutants for overall recovery tests and the same stock solutions were diluted with methanol to serve as a reference in all recovery tests. Deionized water was

obtained from a Rodem purifier system (OPP Tišnov, Czechoslovakia). Potassium chloride, potassium carbonate and dimethylaniline (Lachema), used as an internal standard, were of analytical-reagent grade.

Silica-Cart C₁₈ cartridges (60 μm) and empty polypropylene cartridges were obtained from Tessek (Prague, Czechoslovakia). Synachrom E 5 styrene-divinylbenzene resin was obtained from Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences (Prague, Czechoslovakia) and was ground and sieved to obtain a few grams of 40–71 μm particle size fraction. Spheron 100 hydroxyethyl methacrylate-ethylene dimethacrylate copolymer resin (25–40 μm) was purchased from Lachema. Polymer resins were wet-packed into polypropylene cartridges.

Apparatus

An FCC 60 fraction collector (Laboratory Instruments Works, Czechoslovakia) and an MMC-1 pump (Mikrotechna, Czechoslovakia) were used for collection of water fractions to measure breakthrough curves. Concentrations of analytes in water fractions were measured using a CHROM-4 gas chromatograph (Laboratory Instruments Works) equipped with a flame ionization detector. Integration was done on a CI-100 integrator (Laboratory Instruments Works). The chromatographic conditions were as follows: glass column, 2 m \times 3 mm I.D., packed with 10% Carbowax 20M on Inerton N-AW (0.125–0.160 mm) (Lachema); carrier gas, nitrogen at 30 ml/min; injector temperature, 160°C; column temperature, dependent on the compound; and volume injected (direct injection of water sample), 2 μl .

Desorptions were carried out using an M122 Doser pump (Mikrotechna) with glass syringe as a solvent reservoir. Analyses of methanolic eluates were done on a Hewlett-Packard (Waldbronn, F.R.G.) 5880 Level Four gas chromatograph equipped with a flame ionization detector and a split/splitless injector. The chromatographic conditions were as follows: 20 m \times 0.25 mm I.D. Carbowax 20M glass capillary column (Lachema); carrier gas, nitrogen at 3 ml/min; temperature programme, 10 min at 90°C, then increased at 6°C/min to 190°C; injector temperature, 210°C; and detector temperature, 250°C.

Procedure

The disposable cartridge with a volume of 1 ml containing C₁₈-silica, Synachrom E 5 or Spheron 100 sorbent was activated by rinsing with 15 ml of methanol, which was subsequently displaced with 3 ml of water. The conditioned cartridge was then used for breakthrough, desorption or overall recovery experiments. To measure a breakthrough curve, a 5 ppm aqueous solution of the analytes was pumped through the column at a flow-rate of 5 ml/min and the effluent was collected in glass vials. At the beginning, the volume of each water fraction collected was 5 ml. After 150 ml of effluent had passed through the column, the volume of the fractions collected was increased to 15 ml. A 2- μl aliquot of each fraction was analysed by gas chromatography (GC).

The breakthrough characteristics were measured for a solution in deionized water (pH 5.8) and for an aqueous solution with the pH adjusted to 10.0 with potassium carbonate. To permit the GC determination of cyclohexanone in an alkaline water fraction, this fraction had to be neutralized with a few microlitres of hydrochloric acid. To obtain the shape of a desorption curve, a cartridge with accumulated

analytes was used. For this purpose 50 ml of a 5 ppm aqueous solution of all four compounds were passed through an activated disposable column. The residual water was removed by drying the cartridge under vacuum for 25 min. The cartridge was then connected in the backward-flush mode to the luer of the glass syringe in the pump and to the outlet of this cartridge a thin needle with a cut end was attached. The methanolic effluent was collected in vial as ten-drop fractions. An average volume of ten drops of the methanolic fraction of *ca.* 60 μl was calculated from the average weight of ten drops and the density of methanol. Aliquots of 2 μl of the effluent fractions were analysed by GC. Quantitative analyses in the breakthrough and desorption experiments were performed via the calibration graph method.

For overall recovery tests, 30 ml (60 ml for Synachrom E 5 cartridges) of a 200 ppb^a solution of the analytes in deionized water was forced through the activated cartridge with suction at a flow-rate of 5 ml/min. The sorbed compounds were eluted with methanol. For desorption wet cartridges were used in order to prevent possible losses of cyclohexanone and cyclohexanol caused by drying, which had been observed in our previous work²⁹. The volume of the aqueous fraction of the eluate to be discarded was determined from the weight difference between wet and dry cartridges and was controlled during the elution. The second, methanolic, fraction (600 μl for C₁₈ and Spheron 100 and 1200 μl for Synachrom E 5) was collected separately and analysed.

Wastewater samples were adjusted to pH 10.0 with potassium carbonate and the necessary volume of stock solution was added to increase the analyte concentrations to at least 200 ppb. The subsequent sample processing was similar to that for model water samples. In overall recovery tests prior to the analysis, N,N-dimethylaniline was added to the methanolic eluate as an internal standard.

RESULTS AND DISCUSSION

Cyclohexanone, cyclohexanol, aniline and benzothiazole can be found in industrial wastewaters and can subsequently pollute surface waters. Their detection and quantification are important, *e.g.*, for testing water quality and for evaluation of wastewater treatment plant efficiency. Their isolation from aqueous solution using a hydrophobic medium (solvent or sorbent) can be problematic owing to their relatively high solubility in water (several grams per 100 g of water). Moreover, there is a possibility of ionization of aniline ($\text{p}K_{\text{b}} = 9.4$) and benzothiazole ($\text{p}K_{\text{b}} = 12.4$), which leads to a dependence of the recovery on the sample pH. These potential problems mean that the application of SPE in such instances has to be well verified so as not to obtain a method with poor reproducibility and low efficiency.

It is clear that the overall SPE recovery of an analyte is a function of both retention efficiency and elution efficiency. The most laborious but most exact approach to maximizing the overall efficiency is to measure the breakthrough curve and the analyte concentration profile in the eluate (elution curve). From the breakthrough curve the breakthrough volume can be calculated, which corresponds to the maximum volume of the water sample that can be forced through the column without losses of analytes. From the elution curve the minimum amount of eluent needed to

^a Throughout this article, the American billion (10^9) is meant.

remove the sorbed analyte quantitatively can be determined. Thus, for any SPE application, the maximum theoretical preconcentration factor can be found, given by $F = V_B/W$, where V_B (ml) is the breakthrough volume and W (ml) is the width of the elution curve.

Examples of the calculation of the breakthrough volume can be found in the literature^{28,30}. To obtain the width of an elution curve for calculating F , a volume interval of the eluate can be chosen that covers 99% (or 95%) of the total area below the elution curve, *i.e.*, a volume that contains 99% (or 95%) of the desorbed solute mass. In practice, however, where preconcentration of several compounds with different positions of the elution curve on the volume axis is the most common situation, the W value applied should include a volume interval containing all elution curves, otherwise losses of some compounds will occur. This concept, naturally, leads to a decrease in the actual preconcentration factor. Nevertheless, the proposed theoretical W value is useful for characterizing the sorbent as the average F value for any sorbent can serve for the approximate evaluation of its preconcentration efficiency towards a certain group of analytes (*e.g.*, polynuclear aromatic hydrocarbons, priority pollutants, polar compounds).

The breakthrough curves of the investigated polar compounds on C₁₈-silica, Synachrom E 5 and Spheron 100 are shown in Figs. 1–3, which were obtained from experiments with (a) non-buffered deionized water of average pH 5.8 and (b) buffered deionized water adjusted to pH 10.0. The pH of the pure deionized water samples was measured twice during a breakthrough experiment, first before the water sample had been forced through the column and then immediately after the sorption was finished. All the pH values were found to be constant within the range 5.7–5.9. The non-adjusted deionized water used in the first part of the experiments was chosen to exclude the influence of any possible interferences (*e.g.*, ions including those of buffer solutions). Moreover, the average pH of this non-adjusted water could be considered to be approximately the lowest end of the interval of pH values commonly occurring in real surface waters. The pH of 10.0 used in the second part of the breakthrough experiments to suppress the ionization included the upper end of that real pH interval, which is usually 6–8.

From the displayed breakthrough curves the maximum applicable volumes of the water sample can be calculated. The exact volume depends on what breakthrough level (the ratio of the outlet to the inlet concentration) is taken as the operational value.

The breakthrough curves shown in Figs. 1–3 represent mean values from three measurements. The relative standard deviation is 5–10% for each sorbent-analyte-sample pH system.

According to our assumptions, alkalization of a water sample should have resulted in an increase in the breakthrough volume for weakly basic benzothiazole and aniline owing to suppression of the ionization. The results obtained, however, did not confirm our expectations and the increase in retention did not occur. Moreover, particularly for benzothiazole, a considerable decrease in its retention on C₁₈ and Synachrom E 5 with increase in pH was observed. On the other hand, alkalization of the water sample led to a drastic increase in the breakthrough volume of cyclohexanone and the breakthrough curve of cyclohexanone in alkaline solutions was less steep than all the other curves. This behaviour might be a consequence of a keto–enol

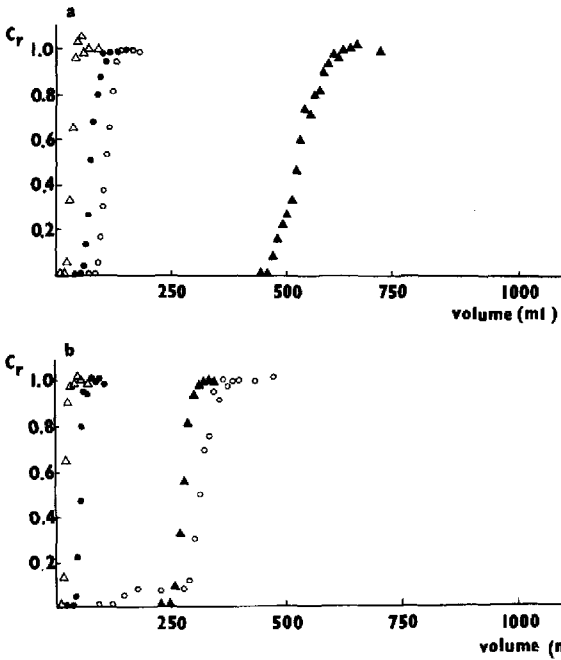


Fig. 1. Breakthrough curves of cyclohexanone (○), cyclohexanol (●), aniline (△) and benzothiazole (▲) on Silica-Cart C_{18} cartridge, measured as relative concentrations of these compounds in aqueous effluent fractions. $C_r = C_e/C_i$, where C_e and C_i are the concentrations of the analytes in the effluent and influent, respectively. pH of the water: (a) 5.8 and (b) 10.0.

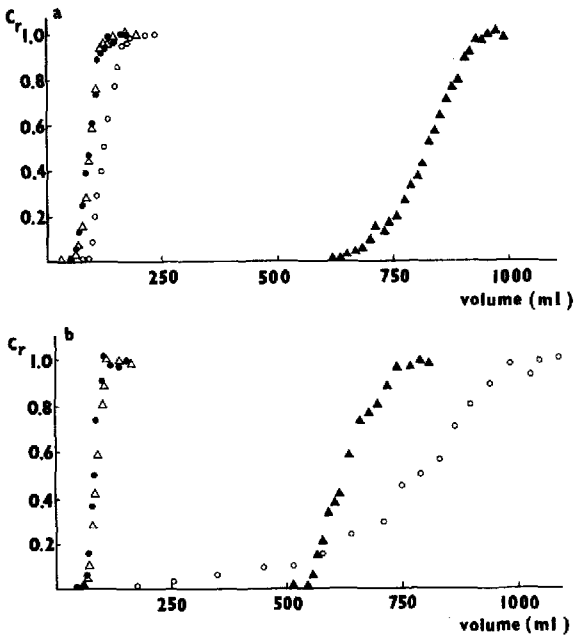


Fig. 2. Breakthrough curves of cyclohexanone (○), cyclohexanol (●), aniline (△) and benzothiazole (▲) on Synachrom E 5 cartridge. Details as in Fig. 1.

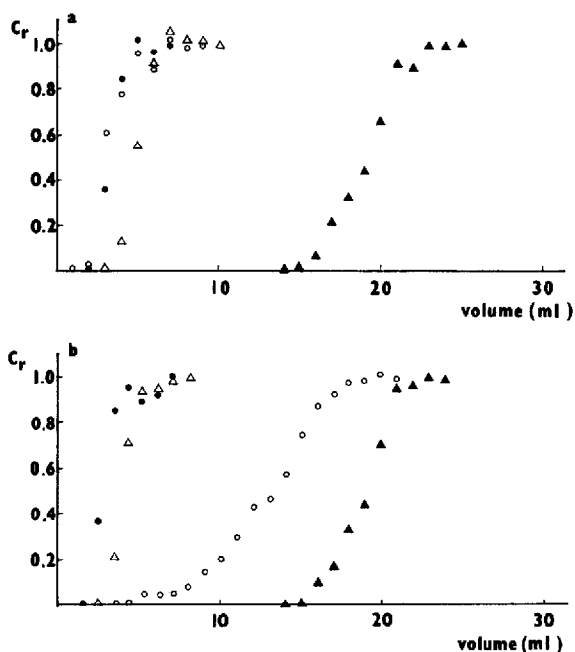


Fig. 3. Breakthrough curves of cyclohexanone (○), cyclohexanol (●), aniline (△) and benzothiazole (▲) on Spheron 100 cartridge. Details as in Fig. 1.

tautomerism of cyclohexanone. The enol-form, cyclohex-1-en-1-ol, should have a much higher affinity towards hydrophobic surfaces. The practical consequence of this phenomenon is much increased capacity for cyclohexanone.

From the comparison of investigated sorbents it is obvious that whereas Synachrom E 5 and C_{18} have similar retention properties, Spheron 100 is much less efficient. A possible reason for this behaviour is water acting as a competing agent during the sorption.

The elution curves of the investigated compounds (Figs. 4–7) begin on the volume axes in the first or second methanolic fraction, except for the curve for cyclohexanone on C_{18} -silica. (Fig. 4a). From the curves obtained it can be seen that the width of an elution curve could in some instances be considered to be proportional to the retention ability of a given sorbent determined from breakthrough experiments. The differences between these elution curve widths, however, are not as great as those between corresponding breakthrough volumes. On the other hand, this proportionality is not valid for the elution curves of cyclohexanone on Synachrom E 5 and aniline on C_{18} , where the relative retention in the methanol-sorbent system is higher than that in the water-sorbent system in comparison with other cases. The considerable tailing of aniline on C_{18} might be ascribed to a secondary retention mechanism between residual silanol groups on chemically bonded silica and amines.

Theoretical preconcentration factors for the studied organic compounds were calculated according to the above equation $F = V_B/W$. Breakthrough volumes were calculated for a breakthrough level of 10%. Widths of the elution curves were obtained as the interval containing 99% of the area below the curve. Calculated F values

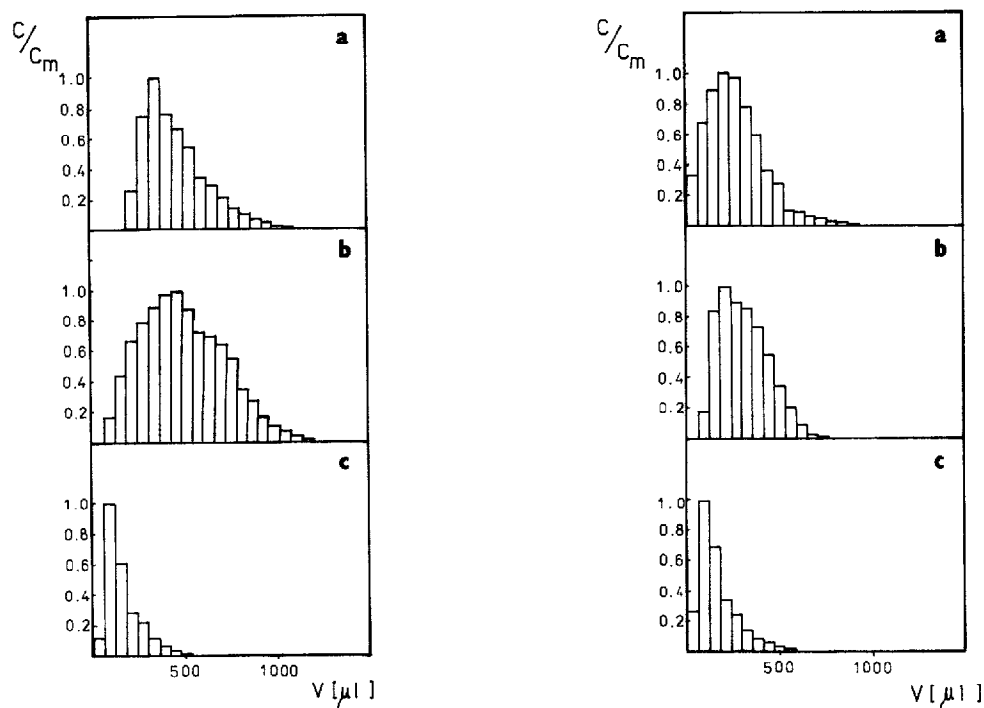


Fig. 4. Elution curves of cyclohexanone on (a) C_{18} , (b) Synachrom E 5 and (c) Spheron 100, measured as its concentration in methanolic effluent fractions. C and C_m are the concentration of cyclohexanone in a particular fraction and the maximum concentration of cyclohexanone in the particular fraction, respectively.

Fig. 5. Elution curves of cyclohexanol. Details as for cyclohexanone in Fig. 4.

for non-alkalinized and alkalinized samples and the mean values for each sorbent are listed in Tables I and II. These mean preconcentration factors reflect the general ability of the sorbent used to preconcentrate a given group of compounds. For our small group of compounds they serve only as an illustrative example, but they can help in establishing the general suitability of a chosen sorbent for the preconcentration of a large group of analytes.

To confirm the real preconcentration capabilities of the tested sorbents, the overall recoveries of the studied polar compounds from both non-alkalinized and alkalinized water samples were measured. As an additional test, the influence of the salting-out effect on the overall recovery was studied, 40 g/l of potassium chloride being added to an alkalinized sample. Table III shows the results of these experiments which confirmed C_{18} and Synachrom E 5 to be suitable for the preconcentration of the studied compounds. Except for aniline, the recoveries on C_{18} are similar for alkalinized and non-alkalinized samples, the differences being within the standard deviation range. Adjusting the pH to 10.0 did not result in any substantial change in the overall recoveries on Synachrom E 5. The low recoveries observed with Spheron 100 were caused by lower breakthrough volumes in comparison with the volume of

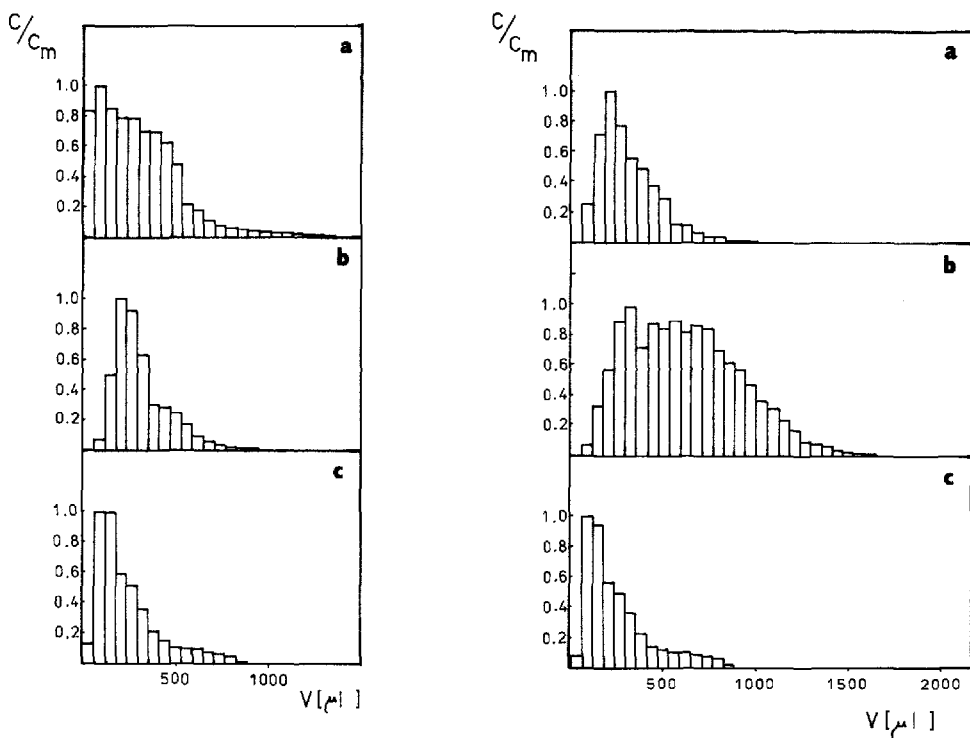


Fig. 6. Elution curves of aniline. Details as for cyclohexanone in Fig. 4.

Fig. 7. Elution curves of benzothiazole. Details as for cyclohexanone in Fig. 4.

water applied. For the recovery of aniline on C_{18} , it is interesting that the alkalization of the water sample led to an increase in the recovery of aniline and, moreover, to a large increase in the reproducibility of the recovery, even though the breakthrough volumes in both instances were similar (for non-alkalinized water samples the average reproducibility of the recovery of aniline was 8–9 times worse than those observed for the other compounds, which were usually 3–5%). This behaviour could be ascribed to the different reactivities of free silanol groups under these conditions, which might be

TABLE I

THEORETICAL PRECONCENTRATION FACTORS OF CYCLOHEXANONE, CYCLOHEXANOL, ANILINE AND BENZOTHAZOLE ON DIFFERENT SORBENTS AT pH = 5.8.

Values calculated according to the equation $F = V_B/W$.

Compound	C_{18}	Synachrom E 5	Spheron 100
Cyclohexanone	150	115	4
Cyclohexanol	100	140	4.5
Aniline	32	130	4.5
Benzothiazole	680	600	20
Mean	240.5	246.3	8.3

TABLE II

THEORETICAL PRECONCENTRATION FACTORS OF CYCLOHEXANONE, CYCLOHEXANOL, ANILINE AND BENZOTHAZOLE ON DIFFERENT SORBENTS AT pH = 10.0.

Values calculated according to the equation $F = V_B/W$.

Compound	C_{18}	Synachrom E 5	Spheron 100
Cyclohexanone	365	740	15
Cyclohexanol	60	120	4
Aniline	19	130	3.5
Benzothiazole	335	450	19
Mean	194.8	360	10.4

suppressed by increasing the pH. As can be seen in Table III, an increase in the ionic strength by means of potassium chloride caused no substantial changes in SPE recoveries.

Both C_{18} and Synachrom E 5 sorbents were used to preconcentrate benzothiazole, aniline, cyclohexanone and cyclohexanol from spiked treated wastewaters. The pH of all samples was adjusted to 10.0 with potassium carbonate to secure suitable conditions for accumulation of aniline. The results of these experiments (Table IV) confirmed that C_{18} and Synachrom E 5 are suitable preconcentrating media for studied polar compounds.

TABLE III

RECOVERIES OF CYCLOHEXANONE, CYCLOHEXANOL, ANILINE AND BENZOTHAZOLE FROM FORTIFIED WATER ON THE INVESTIGATED SORBENTS

The volume of the water samples was 60 ml for Synachrom E 5 and 30 ml for C_{18} and Spheron 100.

Sample	Compound	Recovery (%)		
		C_{18}	Synachrom E 5	Spheron 100
A ^a	Cyclohexanone	88	88	10
	Cyclohexanol	89	92	10
	Aniline	64	78	15
	Benzothiazole	84	75	60
B ^b	Cyclohexanone	92	93	30
	Cyclohexanol	93	90	10
	Aniline	92	90	15
	Benzothiazole	82	72	75
C ^c	Cyclohexanone	90	90	35
	Cyclohexanol	89	89	12
	Aniline	90	92	20
	Benzothiazole	81	70	75

^a Deionized water at pH 5.8.

^b Deionized water adjusted to pH 10.0 with K_2CO_3 .

^c Deionized water adjusted to pH 10.0 with K_2CO_3 , KCl added at a concentration of 40 g/l.

TABLE IV

RECOVERIES OF CYCLOHEXANONE, CYCLOHEXANOL, ANILINE AND BENZOTHAZOLE FROM SPIKED WASTEWATERS ON C₁₈-SILICA AND SYNACHROM E 5Wastewaters were adjusted to pH 10.0 with K₂CO₃. Volumes applied as in Table III.

Compound	Recovery (%)	
	C ₁₈	Synachrom E 5
Cyclohexanone	92	89
Cyclohexanol	88	91
Aniline	93	88
Benzothiazole	75	77

CONCLUSION

Of the sorbents tested, Synachrom E 5 and octadecyl-bonded silica showed adequate preconcentration capabilities for benzothiazole, aniline, cyclohexanol and cyclohexanone. Although the preconcentration factors obtained are not as large as those which can be achieved on these sorbents with non-polar compounds, they are sufficient for practical purposes of water quality control. The method for calculating theoretical preconcentration factors from measured breakthrough and elution curves gives better information on the preconcentration capabilities of a given sorbent and allows optimum conditions for SPE procedures to be chosen.

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