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Journal of Chromatography A, 665 (1994) 243–251

JOURNAL OF CHROMATOGRAPHY A

On-line sample handling of water-soluble organic pollutants in aqueous samples using porous graphitic carbon

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Abstract

An on-line technique coupling preconcentration via a precolumn packed with porous graphitic carbon (PGC) and liquid chromatography with a PGC analytical column was investigated and found to be a very simple and efficient system for the trace-level determination of some very polar and water-soluble organic pollutants (characterized by logarithms of their water–octanol partition coefficients below 1) from environmental waters. As these analytes are much more retained by PGC than they are by C_{18} silica, preconcentration on a PGC precolumn cannot be coupled on-line with the widely used and more efficient C_{18} silica analytical columns, but with a PGC analytical column. Applications are presented for the trace-level determination of some organic compounds included in the EEC environmental priority pollutant list such as 2-chloro-4-aminophenol, chloroanilines, aminophenols and cyanuric acid. The influence of the sample matrix was investigated with drinking and river water samples.

1. Introduction

The determination of trace amounts of organic compounds in environmental aqueous samples requires a preconcentration step before the chromatographic analysis. Polar and water-soluble compounds cannot be determined at trace levels in these media because no simple method exists for their extraction from water samples. These compounds are characterized by weak hydrophobicity, as measured by values of the logarithms of their water–octanol partition coefficients (log P_{oct}) lower than 1, or they are hydrophilic with log $P_{oct} < 0$.

Trace enrichment is still often carried out by means of liquid–liquid extractions in many environmental procedures; nevertheless, recoveries are low for polar analytes and this technique cannot be applied to hydrophilic analytes which are more soluble in water than in usual organic solvents. Solid-phase extraction (SPE) techniques have grown in interest as an alternative to the laborious and time-consuming liquid–liquid extractions. SPE can be considered as a simple chromatographic process and retention of analytes by the sorbent occurs provided they are not eluted by the sample water. Consequently, reversed-phase sorbents and ion exchangers are convenient sorbents for the extraction of organics from water. The key parameter in SPE is the sample volume that can be handled without any breakthrough. In a first approximation, the breakthrough volume can be calculated from the capacity factor of analytes in water, k'_w. In general, C_{18} silicas are convenient sorbents for the trace determination of apolar compounds

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0021-9673/94/$07.00
SSDI 0021-9673(93)E0027-R

(*i.e.*, log $P_{oct} > 3$). Nevertheless, the capacity factors of moderately polar analytes (*i.e.*, log $P_{oct} = 1–3$) are too low with C_{18} silica to allow the handling of a sufficiently large volume. The retention of organic compounds in water is about 25–40 times higher with apolar copolymers such as PRP-1 or PLRP-S, so that these sorbents are more convenient for the preconcentration of moderately polar compounds [1–3]. As an example, the breakthrough volume of aniline (log $P_{oct} = 0.9$) was measured as 180 ml using a large precolumn (9 cm × 0.46 cm I.D.) packed with the PRP-1 copolymer [4]. This sorbent cannot be used for on-line preconcentration of more polar compounds, because small-sized precolumns are required.

Previous studies have shown that the retention of some polar compounds in water can be very high using porous graphitic carbon (PGC), available recently as a stationary phase for LC [3]. The capacity factors in water of 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene were measured as 21 and 3, respectively, with PRP-1 and as 331 and 1050, respectively, with PGC [5]. PGC shows a highly ordered crystalline structure with large bands of delocalized electrons, so that the retention mechanism is a mixture of hydrophobic and electronic interactions and is very different from that observed with C_{18} silicas and PRP-1 copolymers [5–9]. PGC is a reversed-phase sorbent and it is observed that the retention of compounds decreases when the organic content of the mobile phase increases. However, for some planar molecules such as benzene derivatives, the retention increases with increasing number of polar substituents on PGC whereas it decreases with the other two reversed-phase sorbents.

The aim of this work was to investigate the potential of PGC for both extracting and determining some water-soluble compounds in aqueous samples. An on-line approach coupling SPE and LC was studied. In contrast to off-line procedures, the advantages are that (i) there is no risk of loss and contamination as there is no sample manipulation between preconcentration and analysis, (ii) more quantitative results are expected and (iii) the entire sample is transferred and analysed, which allows the handling of a smaller sample volume. As many polar analytes are slightly volatile or are partly degraded when heated, on-line procedures are often more convenient for such analytes.

2. Experimental

2.1. Apparatus

A Model 5060 liquid chromatograph equipped with a UV 200 variable-wavelength spectrophotometer (Varian, Palo Alto, CA, USA) was used for direct injections and precolumn elution. On-line percolation of samples was performed using a Varian Model 2010 pump. Precolumn and analytical column switching were connected with two Rheodyne (Berkeley, CA, USA) valves. Quantitative measurements of peak areas were provided by a CR 3A integrator–computer (Shimadzu, Kyoto, Japan).

2.2. Stationary phases and columns

A C_{18} analytical column (25 cm × 0.46 cm I.D.) prepacked with Whatman Spherisorb ODS-2 (Nagel, Düren, Germany) and a column prepacked with Hypercarb porous graphitic carbon (10 cm × 0.46 cm I.D.) (Shandon, Runcorn, UK) were used. Preconcentrations were made through experimental stainless-steel precolumns (1 cm × 0.46 cm I.D.) prepacked with 10–15-μm Hypercarb PGC (Shandon). A 1 cm × 0.2 cm I.D. column available from Chrompack (Middelburg, Netherlands) was laboratory packed with C_{18} silica RP18 from Merck (Darmstadt, Germany) and used in series with the PGC precolumn. Off-line cartridges were packed with experimental 40–60-μm PGC material provided by Shandon.

2.3. Chemicals

HPLC-grade acetonitrile was obtained from Rathburn (Walkerburn, UK) and methanol from Prolabo (Paris, France). LC-grade water was prepared by purifying demineralized water in a

Milli-Q filtration system (Millipore, Bedford, MA, USA). Other chemicals were obtained from Prolabo, Merck or Fluka (Buchs, Switzerland). Stock standard solutions of selected solutes were prepared by weighing and dissolution in methanol or in water. The final standard solutions did not contain more than 0.5% of methanol.

3. Results and discussion

3.1. On-line methodology using a PGC precolumn

On-line coupling of SPE to LC is easily performed in any laboratory and automatic devices are now commercially available. In its simplest form, the extraction precolumn is placed in the sample-loop position of a six-port switching valve. After conditioning, sample application and cleaning via a low-cost pump, the precolumn is coupled to an analytical column by switching the valve to the inject position. The extracted compounds are then eluted directly from the precolumn to the analytical column by a suitable mobile phase which also permits the chromatographic separation of trapped compounds. The LC system is often run in the reversed-phase mode with a C_{18} analytical column and acetonitrile or a methanol–water gradient because the residual water does not have to be removed before desorption.

Band broadening

The size of the precolumn is an important parameter in the coupling because the profile of concentrated species transferred from the precolumn to the analytical column should ideally be as narrow as possible at the beginning of the separation. Consequently, the precolumn dimensions should be as small as possible and adapted to those of the analytical column [10,11]. For a classical analytical column of 15 cm × 0.46 cm I.D., the length of the precolumn should be a maximum of 1 cm and the diameter smaller than 0.46 cm. On another hand, if solutes are slightly retained by the sorbent, it is necessary to increase as much as possible the amount of sorbent and therefore the precolumn dimensions, in order to obtain breakthrough volumes as high as possible. For this reason, precolumns of 1 cm × 0.46 cm I.D. prepacked with 10–15-μm PGC were selected.

Chromatograms obtained by direct loop injection (20 μl) of a benzene solution on to a 10-cm long analytical column prepacked with 7-μm PGC (Hypercarb) and by preconcentrating a 5-ml water sample spiked with 20 μl of the same benzene solution are represented in Fig. 1a and b. The band broadening was assessed by calculating the number of plates from chromatograms corresponding to three replicate direct injections and on-line preconcentrations (Table 1). First, it can be seen that the plate number in the PGC column is low, around 1000, whereas the test carried out with xylenol having a similar k', but in a mobile phase containing 95% of methanol, gave around 3000 plates for the same column. This decrease is due to the high proportion of water (56%) in the mobile phase. When comparing efficiencies obtained by direct injection and via the precolumn, a decrease in the plate number of about 20% is observed and the peak-height ratio is 0.45. A similar decrease was observed when desorbing the precolumn in the opposite way to the percolation (backflush desorption). One reason is that the dimensions of the precolumns are too large in comparison with those of the analytical column, but no analytical column longer than 10 cm is available. The same precolumn was coupled to a 25-cm long analytical column packed with C_{18} silica. The mobile phase was adjusted in order to give the same retention time of benzene (Fig. 1c) and the experiments described above were carried out (Fig. 1d). Comparison of the efficiencies reported in Table I shows that no band broadening is obtained for benzene when the analytical column is longer. Despite equal efficiencies, the peak heights are different and the ratio between direct injection and on-line preconcentration of the same amount of benzene is 0.68. This is explained by the calibration of the loop which is specified to an average accuracy of 20%. Calibration of the loop is a delicate operation and was not performed in this study.

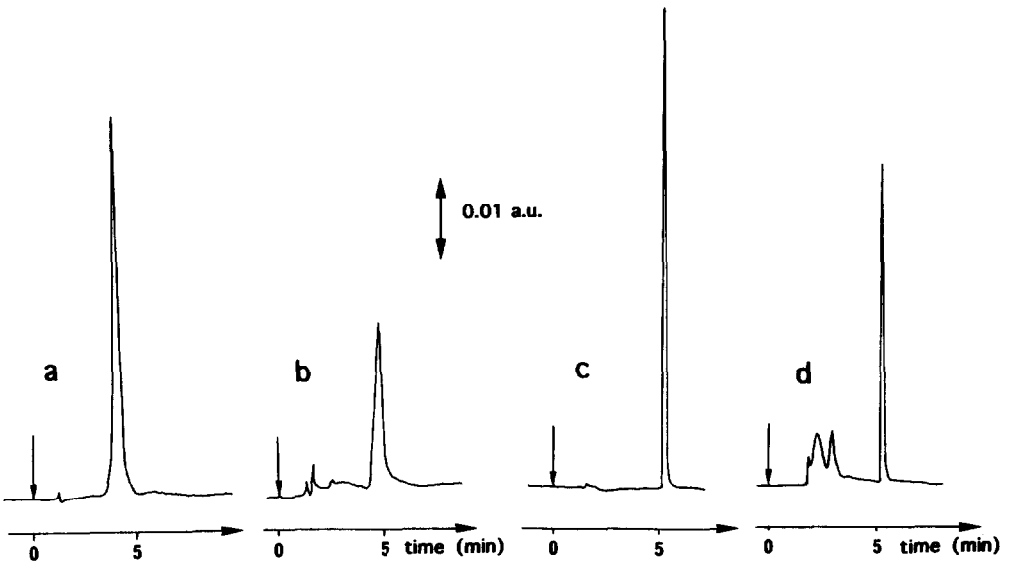

Fig. 1. Chromatograms obtained by direct injection on to PGC and C_{18} columns and by on-line preconcentration with a PGC precolumn. (a) Direct injection of 20 μl of a 10 mg/l benzene solution on to a 10 cm × 0.46 cm I.D. Hypercarb column. Mobile phase, methanol–water (44:56, v/v); flow-rate, 1 ml/min; UV detection at 254 nm. (b) On-line preconcentration of a 5-ml water sample spiked with 20 μl of the 10 mg/l benzene solution. Precolumn, 1 cm × 0.46 cm I.D. packed with PGC; elution in the same column and under the same experimental conditions as in (a). (c) Direct injection of 20 μl of a 10 mg/l benzene solution on to a 25 cm × 046 cm I.D. C_{18} Spherisorb ODS column. Mobile phase, acetonitrile–water (64:36, v/v); flow-rate, 1 ml/min. (d) On-line preconcentration of a 5-ml water sample spiked with 20 μl of the 10 mg/l benzene solution. Precolumn, 1 cm × 0.46 cm I.D. packed with PGC; elution in the same column and under the same experimental conditions as in (c).

Sorbent compatibility

Band broadening can also occur when the analyte is more retained by the sorbent of the precolumn than it is by that of the analytical column [1]. Nevertheless, many examples have been presented using a PRP-1 or PLRP-S precolumn and a C_{18} analytical column. The potential of PGC is in the extraction of compounds that cannot be extracted by C_{18} silica because of insufficient retention. Separation of polar analytes on C_{18} silica is usually achieved with water or water-rich mobile phases which are unable to desorb analytes that are more retained by the PGC precolumn. This is illustrated in Fig. 2 for the trace determination of polar aniline derivates included in the EEC priority pollutant list. On C_{18} silica, the more polar 2-chloro-4-aminophenol (log $P_{oct} = 1.16$) is eluted before the monochloroanilines (log $P_{oct} = 1.8$) and separation is achieved with a mobile phase containing 33% of acetonitrile (Fig. 2a). When the same mixture is analysed on-line via the PGC precolumn (Fig. 2b), a large band broadening occurs for 2-chloro-4-aminophenol. A similar separation including also a chloromethylaniline and a dichloroaniline was performed on the PGC col-

Table 1
Peak heights (h) and column efficiencies (plate number, N) measured with (a) direct injections of benzene and (b) on-line preconcentration with the PGC precolumn (mean values of three experiments)

Material	h(a)	h(b)	h(b)/h(a)	N(a)	N(b)
PGC	9.1 ± 0.2	4.1 ± 0.3	0.45	1260 ± 60	960 ± 50
C_{18} silica	11.4 ± 0.2	7.8 ± 0.3	0.68	10900 ± 400	11100 ± 600

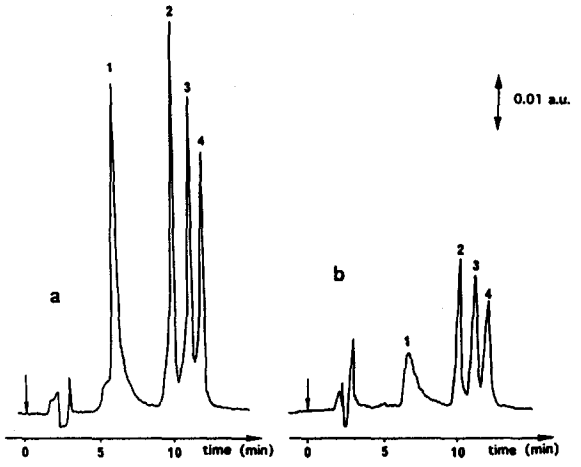

Fig. 2. Chromatograms obtained by direct injection and on-line preconcentration using a C_{18} analytical column. (a) Direct injection of 20 μl of an aniline derivative solution at 10 mg/l on to a 25 cm × 0.46 cm I.D. C_{18} Spherisorb ODS column. Mobile phase, 33% of acetonitrile and 67% of a 0.05 *M* sodium acetate–acetic acid solution at pH 4.6; flow-rate, 1 ml/min; UV detection at 240 nm, 0.1 AUFS Solutes: 1 = 2-chloro-4-aminophenol; 2 = 2-chloroaniline; 3 = 3-chloroaniline; 4 = 4-chloroaniline. (b) On-line preconcentration of a 10-ml water sample spiked with 20 μg/l of each compound. Precolumn, 1 cm × 0.46 cm I.D. packed with PGC; on-line elution into the C_{18} column under the same experimental conditions.

umn (Fig. 3a) and the more polar 2-chloro-4-aminophenol is eluted after the monochloroanilines. The mobile phase allowing the separation of the first compounds contains 68% of methanol. Fig. 3b illustrates clearly that when the sorbents in the precolumn and the analytical column are the same, the band broadening is decreased. Comparison between Fig. 2 and 3 indicates also that the difference in efficiencies between PGC and C_{18} silica is not as large for the aniline derivatives as it was for benzene, because in that example the mobile phase used with PGC contained a higher content of organic solvent than that with C_{18} silica.

It is concluded that for more polar analytes with log $P_{oct} < 1$, the direct coupling of a PGC precolumn and a C_{18} analytical column is impossible unless water is added to the mobile phase after the desorption of the precolumn via another pump. However, coupling with a PGC analytical column is easy.

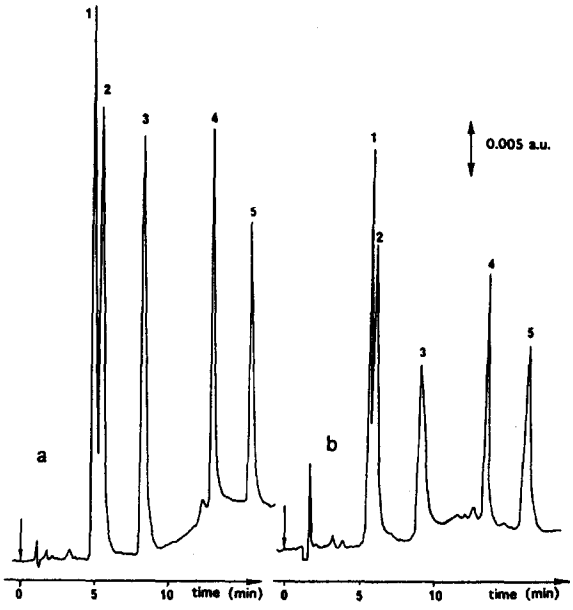

Fig. 3. Chromatograms obtained by direct injection and on-line preconcentration using a Hypercarb analytical column. (a) Direct injection of 20 μl of a solution containing 2-chloro-4-aminophenol of 64 mg/l and other aniline derivatives at 20 mg/l on to a 10 cm × 0.46 cm I.D. Hypercarb column. Mobile phase, methanol gradient with 0.05 *M* sodium acetate–acetic acid solution at pH 4.6, 68% of methanol from 0 to 6 min and up to 91% at 9 min; flow-rate, 1 ml/min; UV detection at 240 nm, 0.05 AUFS. Solutes: 1 = 4-chloroaniline; 2 = 2-chloroaniline; 3 = 2-chloro-4-aminophenol; 4 = 5-chloro-2-methylaniline; 5 = 2,3-dichloroaniline. (b) On-line preconcentration of a 10-ml water sample spiked with 128 μg/l of 2-chloro-4-aminophenol and 45 μg/l of the other compounds. Precolumn: 1 cm × 0.46 cm I.D. packed with PGC; on-line elution into the Hypercarb column under the same experimental conditions.

Precolumn stability

The same precolumn was re-used about 30–50 times with drinking waters and was just washed with pure acetonitrile or methanol after each run. With surface waters, the precolumn was washed with water–tetrahydrofuran (50:50) containing 0.1% of perchloric acid after each run and was changed about after ten runs.

3.2. *Applications of water-soluble analytes*

Aminophenols

These products are important industrial chemicals and also degradation products of aniline and

Table 2
Water–octanol partition constants and retention in water of aminophenols on PRP-1 and PGC

Solute	Log P_{oct}	Log k'_w	
		PRP-1	PGC
2-Aminophenol	0.52	1.7	1.6
3-Aminophenol	0.17	1.3	1.7
4-Aminophenol	0.04	1.1	2.1

some pesticides. Their extraction from water is difficult owing to their high polarity, as shown in Table 2. A method has been described which involved the preparation of acetate derivatives before extraction with methylene chloride and a second derivatization with trifluoroacetic anhydride before GC analysis and electron-capture detection [12]. 4-Aminophenol is not retained on C_{18} silica and only slightly on PRP-1, but its retention on PGC is ten times higher. We especially studied the on-line determination of 3- and 4-aminophenol because 2-aminophenol is easily oxidized and some drastic experimental conditions have to be applied in order to avoid degradation of this isomer [13]. The analytical separation was obtained with a methanol gradient containing initially 30% of methanol and is shown in Fig. 4a. As the UV maxima are different for the two compounds, a change in the UV wavelength was made at 7.5 min. The retention order of the two isomers follows the decreasing polarity order indicated by the log P_{oct} values in Table 2. Sample volumes of 10 and 20 ml containing the same amount of analytes as the direct injection were analysed on-line (Fig. 4b and c). The peak height of 4-aminophenol is constant for 10 and 20 ml, whereas that of 3-aminophenol decreases between 10 and 20 ml, indicating that breakthrough occurred between

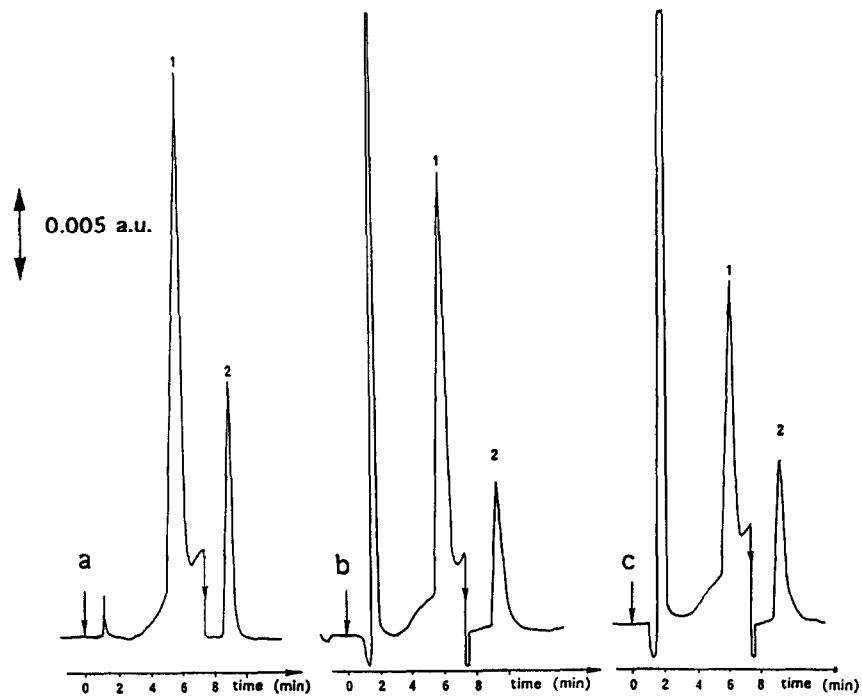

Fig. 4. On-line determination of aminophenols. (a) Direct loop injection of 600 ng of 3-aminophenol (solute 1) and 4-aminophenol (solute 2) in to the 10 cm × 0.46 cm I.D. Hypercarb column; (b) on-line analysis of a 10-ml sample spiked with 60 μg/l and (c) on-line analysis of a 20-ml sample spiked with 30 μg/l. Precolumn, 1 cm × 0.46 cm I.D. packed with PGC; analytical column, 10 cm × 0.46 cm I.D. Hypercarb; mobile phase, methanol gradient with a 0.05 *M* sodium phosphate solution at pH 7, 30 to 50% of methanol from 0 to 5 min; UV detection at 220 nm from 0 to 7.5 min and at 235 nm at 7.5 min (autozero at 7.8 min).

10 and 20 ml for the 3-isomer but not for the 4-isomer. The detection limit for these two compounds was measured as 2 μg/l in a 20-ml sample and can easily be lowered to the μg/l level using this simple on-line system with electrochemical detection, as a factor 500 has been reported between the electrochemical and UV responses [14].

Cyanuric acid

Another example is the trace-level determination of cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine). Cyanuric acid is the ultimate hydroxylated degradation product of some widely used triazine herbicides. Chlorinated derivatives of cyanuric acid are also used in swimming pools as disinfectants and are transformed into cyanuric acid, so that the residual cyanuric acid has to be controlled in pool waters. HPLC methods have been described for the characterization of this analyte with detection limits of the order of mg/l, but no preconcentration method has been reported [15–17]. The logarithm of the water–octanol partition constant was calculated relative to that atrazine (2.7), and was found to be −0.2, thus indicating a high polarity and solubility in water [18]. This analyte is very slightly retained by C_{18} silica in water ($\log k'_w = -0.3$) and not at all by PRP-1, whereas it is highly retained by PGC. Log k'_w was extrapolated from the linear relationship between log k' and the methanol content of the mobile phase to be 2.5 ± 0.2. This result is equivalent to that obtained for 1,3,5-trihydroxybenzene [5] and is another example of a water-soluble analyte that cannot be extracted from aqueous media by conventional sorbents or by liquid–liquid extraction.

Fig. 5a and b represent the direct injection of 20 μl of swimming-pool water on to the PGC analytical column and a C_{18} analytical column and the cyanuric acid concentration was measured to be about 4 mg/l. The difference in retention can be assessed by the difference in the mobile phase composition, pure water with the C_{18} column and 30% methanol for the PGC column. The effect of pH was studied on the PGC column and the retention did not vary between pH 3 and 8, despite the pK_a value of

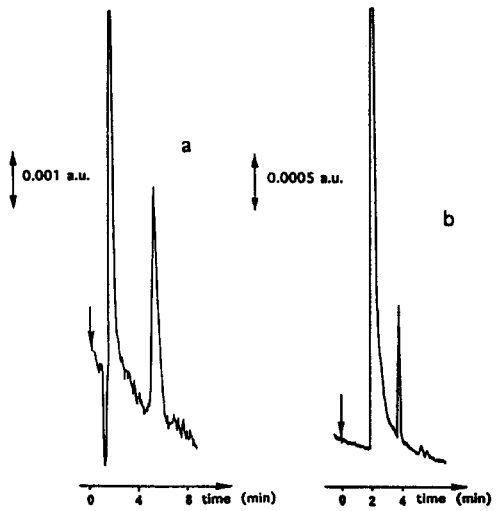

Fig. 5. Determination of cyanuric acid in a swimming pool water sample by direct injection of a 20-μl aliquot. (a) Analytical column, 10 cm × 0.46 cm I.D. Hypercarb; mobile phase, 30% of methanol with 70% of a 0.05 *M* sodium phosphate solution at pH 7, flow-rate, 1 ml/min UV detection at 220 nm, 0.01 AUFS. (b) Analytical column, 25 cm × 0.46 cm I.D. C_{18} Spherisorb ODS; mobile phase, water adjusted to pH 3 with perchloric acid; UV detection at 205 nm, 0.005 AUFS.

6.9. A 0.005 *M* sodium phosphate solution of pH 7 was selected as the mobile phase because it provided a sharper peak. As the UV spectrum of cyanuric acid does not show any absorbance above 220 nm, this compound cannot be identified in unknown samples using only diode-array UV detection and the retention times using the two different columns can serve as confirmation.

A lower detection level is obtained using the on-line preconcentration set-up. From the log k'_w found by extrapolation of the log k'–methanol content relationship, the breakthrough volume, V_b, was calculated to be between 25 and 70 ml. The V_b value was measured more accurately to be 50 ml by percolating increasing volumes of samples containing the same amount of cyanuric acid and by measuring the peak height on the chromatograms obtained by on-line elution as reported in Table 3 [2].

Fig. 6 represents the chromatograms obtained by on-line analysis of 50 ml of LC-grade drinking water and river water samples spiked with 3 μg/l

Table 3
Variation of peak heights (in cm) with the sample volume analysed on-line and corresponding recoveries (mean values of two experiments) according to ref. 2

Parameter	Sample volume (ml)							
	10	20	30	50	60	70	80	100
Concentration (μg/l)	85.6	42.8	28.5	17.1	14.3	12.2	10.7	8.6
Peak height	8.6	8.4	8.7	8.4	6.3	3.6	2.6	2.1
Recovery (%)	100	98	101	98	73	41	33	24

of cyanuric acid. The peak heights are equivalent for the different waters. An autozero has to be set at 3 min for river water owing to the larger amounts of interferences in these waters. A concentration of 3 μg/l is close to the detection limit in each water. If a lower detection level is required, the only means is to increase the amount of carbon in order to increase the breakthrough volume and an off-line procedure using a cartridge has to be applied. A cartridge was packed with 500 mg of 40–60-μm PGC sorbent and after conditioning with methanol and water a sample of 250 ml of drinking water spiked with 5 μg/l of cyanuric acid were percolated through it. Elution was carried out with 20 ml of methanol with subsequent evaporation to dryness. As cyanuric acid is more soluble in water than it is in methanol, injection of the extract reconstituted in 500 μl of methanol gave a bad peak shape, whereas reconstitution in 500 μl of water gave a correct peak. A mean recovery of 96% was measured with three replicate experiments by direct injection of 20 μl of the extracts corresponding to samples spiked at the 5 μg/l level. A volume of 500 μl was necessary to achieve total dissolution of the extract and 100 μl is the largest volume that can be directly injected into a 10-cm column. Therefore, it is obvious that the same detection limits are obtained using the on-line procedure with handling of a 50-ml sample volume and using off-line preconcentration with a 250-ml sample volume, as the injection of a 100-μl aliquot corresponds to a 50-ml fraction of the 250 ml of off-line preconcentrated solution. This problem was overcome by on-line analysing nearly the totality of the extract.

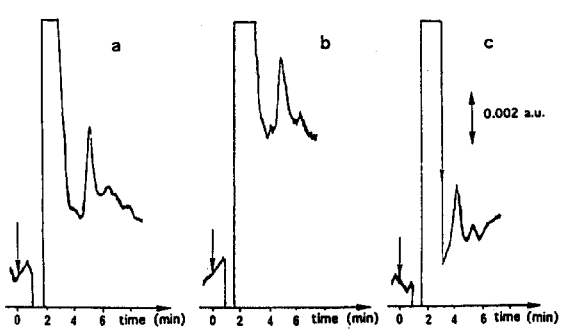

Fig. 6. On-line analysis of 50 ml of (a) LC-grade water, (b) drinking water and (c) river Seine water samples each spiked with 3 μg/l of cyanuric acid. Precolumn packed with PGC and other conditions as in Fig. 5a; UV detection at 220 nm, 0.02 AUFS.

After off-line preconcentration the dry extract was reconstituted in 30 ml of LC-grade water and 25 ml were analysed on-line, thus allowing the analysis of 83% of the extract from the 250 ml of sample concentrated in the cartridge. Using this coupling of an off-line extraction with on-line analysis, the chromatogram in Fig. 7 was obtained for the analysis of 250 ml of drinking water spiked with 5 μg/l of cyanuric acid. The UV attenuation is 2.5 times higher and the peak height much larger than in Fig. 6. The detection limit was 0.2 μg/l under these experimental conditions and can be easily lowered because the sample volume can be increased to 500 ml without breakthrough on a 500-mg cartridge and also because the extracts coming from two cartridges can be mixed together before on-line analysis. The on-line analysis of this extract was

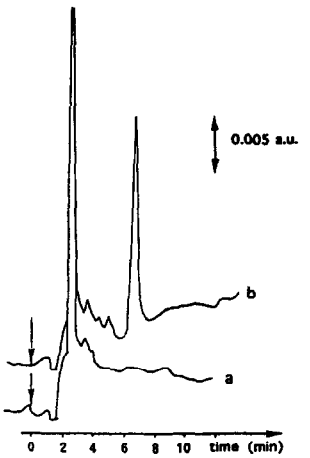

Fig. 7. On-line analysis of an off-line drinking water extract from 250 ml of drinking water, (a) non-spiked and (b) spiked with 5 μg/l of cyanuric acid. Dissolution of the dry extract in 30 ml of water and on-line analysis of a 25-ml aliquot (83% of the extract); other conditions as in Fig. 6; UV detection at 220 nm, 0.05 AUFS.

possible only because this analyte is water soluble.

4. Conclusions

The trace determination of some very polar and water-soluble organic pollutants in environmental waters requires specific strategies as illustrated in this study. On-line sample handling coupling the preconcentration of compounds using a 1-cm long precolumn packed with porous graphitic carbon and liquid chromatographic separation using a PGC analytical column is a very simple and efficient system for their trace-level determination, although smaller precolumns and more efficient analytical columns should be required. The potential of PGC as an extraction sorbent for water-soluble analytes will allow the study of the monitoring and behaviour of numerous compounds and degradation products in the environment.

5. Acknowledgements

This work was supported by the Environment R & D programme 1991-94 on the Analysis and Fate of Organic Pollutants in Water, from the Commission of European Communities (Contract N° EV5V-CT92-0114). Shandon HPLC from England and France are thanked for the supply of carbon materials.

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