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Prediction from liquid chromatographic data of obligatory backflush desorption from solid-phase extraction cartridges packed with porous graphitic carbon

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Abstract

The potential of porous graphitic carbon sorbents (PGC) for extracting polar and water-soluble analytes from aqueous samples was demonstrated. However, even though breakthrough of analytes does not occur during the loading of samples, the recoveries are sometimes much lower than 100%, owing to the difficult desorption of some analytes from the solid-phase extraction cartridge. Extensive work was carried out to measure the retention factors of some polar and apolar analytes with analytical columns packed with the same PGC sorbent. Some analytes can be strongly retained in methanol, acetonitrile, tetrahydrofuran or dichloromethane, explaining why desorption from a cartridge used for solid-phase extraction with several millilitres of organic solvent is not as effective as from a cartridge packed with octadecylsilica (C_{18}). It is shown that the desorption volume required can be predicted from the data generated by liquid chromatographic measurements of retention factors in solvents. When compounds with a wide range of polarity are to be extracted, the desorption volume can be large, and it is obligatory to desorb the analytes from the cartridge by backflushing in order to have a 3–5-ml desorption volume. Then methanol can be used. Applications to the trace level analysis of polar pesticides in environmental waters are presented.

Keywords: Sorbents; Porous graphitized carbon; Environmental analysis; Water analysis; Sample handling; Pesticides

1. Introduction

The trace level determination of many organic pollutants in environmental waters requires a preconcentration step before the proper chromatographic analysis. Solid-phase extraction (SPE) is widely accepted as an alternative to laborious and time-consuming liquid–liquid extraction (LLE), which requires the use and disposal of large amounts of organic solvents.

The most widely used SPE sorbents up to now are alkyl-bonded, mainly C_{18}, silicas. However, their limitation has been demonstrated for trapping polar organic compounds from a sufficiently large sample volume which is usually necessary for trace determination at the μg/l level [1–3]. Apolar polystyrene–divinylbenzene (PS–DVB) copolymers and carbon-based sorbents were

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shown to be more appropriate for trapping polar analytes [1–9].

The similarity between the SPE process and the classical elution liquid chromatography (LC) has been pointed out [1–5,10,11]. Most of the parameters that describe a SPE sequence, i.e., nature and amount of sorbent, sample volume and elution conditions, can be predicted from data generated by LC. The parameter which has received most attention up to now is the breakthrough volume, V_b, which represents the sample volume that can be handled with a 100% theoretical recovery and which can be easily predicted from the retention factors in water.

Only a few carbon-based sorbents are available for SPE. The most common ones are graphitized carbon blacks (GCB), obtained by heating carbon blacks at high temperature (2700–3000°C) and characterized by a low specific surface area of around 100 m^2/g. As they are not pressure resistant, they cannot be used as LC stationary phases so that no data indicating the LC behaviour of solutes are available. In recent years, a porous graphitic carbon has been available in an SPE cartridge which has been derived from a carbon material especially made for LC [12]. It is characterized by a highly homogeneous and ordered structure and by a specific surface area of around 250 m^2/g. This sorbent can be used in the reversed-phase mode, but the retention mechanism has been shown to be very different from that observed on C_{18} or PS–DVB sorbents. Compounds are retained by hydrophobic and electronic interactions, so that apolar analytes, but also very polar and water-soluble analytes, can be highly retained from water [13–16]. A high retention has also been observed with pure organic solvents as mobile phase [15,16] and we can therefore predict that the desorption should not be as straightforward as on C_{18} silicas or on PS–DVB sorbents. Desorption problems were already obviously encountered with the GCB cartridges: pure methanol, acetonitrile or dichloromethane were shown to be unable to desorb many organic pollutants and dichloromethane–methanol (80:20, v/v) was recommended [7–9]. Whereas most pesticides and other organic pollutants were eluted using 6 ml of this eluting mixture with a 0.3-g SPE cartridge, this volume had to be strongly increased with a 1-g cartridge, so that a backflush desorption was used with 1-g GCB cartridges [9]. Special care also had to be taken when using this elution mixture owing to problems with double layers during the subsequent evaporation if water was not well removed before elution. In order to overcome this problem, it was recommended to wash the GCB cartridge with a small volume of pure methanol before applying the dichloromethane–methanol mixture, but then a risk of loss certainly exists for some weakly retained compounds [9,17].

In this work, the retention behaviour of some organic compounds was studied using an analytical LC column packed with PGC with various pure organic solvents as mobile phases in order to predict the elution conditions from SPE cartridges packed with the same PGC sorbent and to compare them with the real experimental conditions in the SPE sequence. The aim of this study was also to select elution solvents which are totally water miscible in order to ensure conplete compatibility with the aqueous sample and to avoid evaporation problems.

2. Experimental

2.1. Apparatus

A Model 9012 liquid chromatograph equipped with a Polychrom 9065 diode-array detector (Varian, Palo Alto, CA, USA) was used for direct injections of standard solutions and extracts obtained with off-line preconcentration. Quantitative measurements were provided by using the software of the Polychrom.

2.2. Analytical columns and cartridges

A commercial column packed with Hypercarb porous graphitic carbon (10 × 0.46 cm I.D., 7 μm particle size) from Shandon HPLC (Runcorn, UK) was used for retention measurements. The analytical separation of a mixture of thirteen pesticides was performed on a commercial column packed with C_{18} silica (25 × 0.46 cm I.D., 5

μm particle size). Supelcosil LC_{18}-DB from Supelco (Bellefonte, USA).

The void volume of this Hypercarb column was measured by injecting methanol, acetonitrile or tetrahydrofuran (THF) with a mobile phase composed of 100% of acetonitrile or THF. Cartridges were prepacked with 40–60-μm Hypercarb PGC provided by Shandon HPLC.

2.3. HPLC conditions

The separation of thirteen pesticides was performed using the Supelcosil LC_{18}-DB column at a flow-rate of 1 ml/min with a gradient of acetonitrile and $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7). The gradient was 5% of acetonitrile from 0 to 15 min, 10% at 20 min, 15% from 40 min to 50 min, 30% at 60 min and 35% from 65 min to 72 min.

2.4. Chemicals

Acetonitrile was purchased from Baker France (Noisy-le-Grand, France), methanol from Prolabo (Paris, France) and tetrahydrofuran, dichloromethane, chloroform and ethyl acetate from SDS (Peypin, France). LC-grade water was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA).

Pesticides were supplied by Riedel-de Haën (Seelze, Germany) or Cluzeau (Sainte-Foy-la-Grande, France). Other chemicals were from Prolabo, Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland).

Stock standard solutions of selected solutes were prepared by weighing and dissolving them in methanol. LC-grade water samples were spiked with these solutions. The final standard solutions did not contain more than 0.5% of methanol.

2.5. Extraction procedure

Cartridges containing 100 and 500 mg of PGC were used for preconcentration. The PGC cartridge was first washed with 5 ml of methanol and conditioned with 10 ml of LC-grade water. The water samples were percolated through the cartridge at a flow-rate of 5–10 ml/min using vacuum aspiration. The residual water was removed by air aspiration. The experimental desorption volume of atrazine was performed with subsequent fractions of pure methanol which were analysed separately. For the mixture containing thirteen pesticides, the desorption was performed in the same way as the percolation of samples (forward desorption) or in the opposite way (backflush desorption).

The desorption solution was evaporated to dryness at 30°C with a gentle stream of nitrogen. The dry extract was dissolved in a mixture containing 50 μl of methanol and 150 μl of $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7). A 50-μl aliquot was injected. Recoveries were calculated by comparison with direct injection of the same amount of compounds as contained in the spiked sample. The test of volatility was performed by spiking the desorption solution directly with this same amount, by evaporating the solution to dryness and dissolving the residue in the injection mixture under the conditions as described above for the real samples.

3. Results and discussion

3.1. Prediction of SPE parameters from LC data

Fig. 1 represents a breakthrough curve that can be recorded by monitoring the effluent from an SPE cartridge when an aqueous solution spiked with an analyte at the trace level and having an initial UV absorbance A_0 is percolated

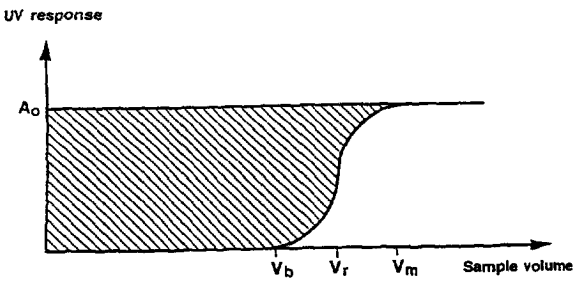

Fig. 1. Theoretical breakthrough curve obtained by percolation of a spiked sample (UV absorbance A_0) through a precolumn.

through it. The breakthrough volume V_b is usually defined at the 1% of the initial absorbance A_0, and after a volume V_m the effluent has the same composition as the sample. Under ideal conditions and if the precolumn is not overloaded, this curve has a bilogarithmic shape, the inflection point of which is the retention volume V_r of the analyte, which should be measured in elution chromatography using the same cartridge as a LC column with water as mobile phase. The measurement of V_r values has been used to estimate V_b values with acceptable accuracy for an SPE process [2–4].

High enrichment factors are obtained with large aqueous sample volumes without breakthrough volumes (meaning large V_b values) and as low as possible elution volumes for the desorption of the analytes. With C_{18} sorbents, the conditions of the desorption step have received little attention, since most of the organic compounds are not retained with pure acetonitrile or pure methanol. The volume of the desorption solution is usually set at two or three times the void volume of the cartridge. The choice of the desorption solvent is guided by the solubility of the analytes in the organic solvents [2].

If compounds are expected to be retained by organic solvents, the same approach as that represented in Fig. 1 can be taken. However, the elution volume required to ensure total desorption is the volume V_m, which can be also estimated from V_r values or retention factors in pure organic solvents. The value of the volume V_m (at around 99% of the front) can be calculated by the equation $V_m = V_r + 2\sigma_v$, σ_v being the standard deviation depending on the axial dispersion of solute along the cartridge. The value of σ_v is related to the theoretical plate number in the cartridge:

$$\sigma_v = \frac{V_0}{\sqrt{N}} \cdot (1 + k')$$

V_0 being the void volume of the cartridge [18].

3.2. Retention factors in pure organic solvents

With C_{18} silicas, the elution strength of common organic solvents is well known and follows the solubility parameter order of the solvents. The retention factor decreases in the order methanol, acetonitrile, THF, dichloromethane and hexane. With PGC, very few studies have been carried out on this topic and the first experimental results have not shown clear evidence for an eluotropic series. THF appeared to be a stronger eluting solvent than methanol or acetonitrile [19–22]. Table 1 lists some compounds, pesticides, chlorophenols and anthracene, ordered in an approximative hydrophobic order as given by the water–octanol partition coefficients, log P_{oct} [23]. The logarithm of the retention factors, log k', were measured on a PGC column with pure methanol, THF or dichloromethane and reported. First, it is obvious that the retention factor is not related to the hydrophobicity of the compound, as can be observed with reversed-phase C_{18} silicas. Both hydrophobic compounds such as tri- and pentachlorophenol, anthracene and diuron and more polar compounds such as metamitron, carbendazim and metoxuron have log k' values >1 in pure methanol. As a comparison, on a C_{18} silica column eluted with methanol, the log k' of anthracene and diuron were measured to be −0.33 and −1.1, respectively, and pentachlorophenol was eluted very close to the void volume. Although not presented here, the log k' values obtained with the PGC column when the compounds were eluted with acetonitrile were close to those obtained with methanol. THF was also studied and, as expected, all the compounds were less retained than in methanol, the retention order being similar as that observed with methanol. However, some compounds such as metamitron, carbendazim, pentachlorophenol and anthracene are still strongly retained in pure THF. Dichloromethane was found to be a less strong eluting solvent than THF and, as it is not water miscible, THF should be certainly a better choice for desorption.

3.3. Comparison between predicted and experimental values

The data in Table 1 explain clearly why the desorption of analytes cannot be performed

Table 1
Log P_{oct} values, log k' values measured on a PGC analytical column eluted with pure methanol, tetrahydrofuran and dichloromethane and calculated retention volume, V_r, with methanol on a cartridge packed with 500 mg of PGC (see text for calculation)

Compound	Log P_{oct} [a]	Log k'			V_r (ml)
		MeOH	THF	CH_2Cl_2	
Oxamyl	−0.5	−0.51	−1.42	−1.22	2
Methomyl	0.2–1.8	0.04	−0.92	−1.01	3
Metamitron	0.8	>1.4	0.23	0.26	>34
Fenuron	0.5–1.2	0.28	−0.56	−0.66	4
DIA	1.1	0.57	−0.71	−0.28	6
DEA	1.5	0.22	−1.01	−1.04	3
Metoxuron	1.6	1.28	0.05	−0.02	26
Aldicarb	0.9–1.6	−0.73	−1.22	−1.35	2
Monocrotophos		−0.24	−1.35	−1.42	2
Metribuzin	1.6–1.7	−0.35	−1.42	−1.04	2
Aminocarb	1.7	−0.25	−1.35	−1.01	2
Carbendazim	1.4–1.6	>1.4	0.79	nd	>34
Chloridazon	1.1–2.2	0.96	−0.13	−0.05	13
Simazine	1.5–2.3	0.97	−0.49	−0.39	13
Atrazine	2.2–2.8	0.62	−0.82	−0.85	7
Diuron	2.8	>1.4	0.17	nd	>34
Linuron	2.8	1.38	−0.10	−0.16	32
3,5-Dichlorophenol	3.6	0.52	−0.73	−0.51	6
2,4,5-Trichlorophenol	4.1	0.99	−0.12	0.20	14
Anthracene	4.7	>1.6	1.21	nd[b]	>34
Pentachlorophenol	5	>1.4	0.81	nd[b]	>34

[a] According to Ref. [23].
[b] Not determined.

using methanol or acetonitrile and why a PGC cartridge cannot be handled as a simple C_{18} cartridge. As an application of Fig. 1, the retention volumes V_r were calculated with methanol for a cartridge packed with 500 mg of PGC, using the equation $V_r = V_0(1 + k')$, V_0 being the void volume of the cartridge and having been estimated from the V_0 value of the 10-cm PGC analytical column (0.26 ml per 100 mg of sorbent). The calculated V_r values are high, e.g., 13 and 34 ml for simazine and diuron, respectively.

The experimental desorption profile was studied with atrazine with two cartridges, one packed with 500 mg and the other with 100 mg of PGC. Previous studies using PGC or GCB cartridges have shown that 500 mg of sorbent could be necessary to retain some pesticides and metabolites [9,16]. A sample volume of 50 ml of LC-grade water spiked with 40 μg/l of atrazine was percolated and desorption was performed with fractions of 1 ml of methanol for the 100-mg cartridge and of 2 ml for the 500-mg cartridge. Each fraction was analysed separately and Fig. 2 shows the desorption profile obtained as total percentage recovery versus desorption volume. The shape of the curve is good, the front being sharper for the 100-mg than for the 500-mg cartridge. According to Fig. 1, the V_r values were measured for a recovery of 50% and were found to be 1.5 and 8 ml for the 100- and 500-mg cartridge, respectively. The relationship with the amount of sorbent in the cartridge is therefore verified. The predicted value reported in Table 1 for atrazine was 7 ml for a 500-mg cartridge, so that the agreement is correct between values predicted from LC data and experimental values. However, a desorption volume equal to V_r is not sufficient to provide a 100% recovery, and owing

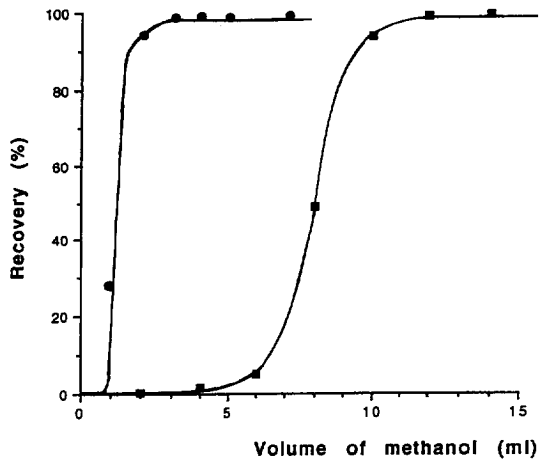

Fig. 2. Desorption profile of atrazine using methanol: ● = on a 100-mg PGC cartridge; ■ = on a 500-mg PGC cartridge.

to the spreading of the front, a desorption volume of ca. 12–14 ml of methanol is required. With an estimated number of only ten plates in the cartridge owing to the volume of the frits and connections, the calculation of V_m at around 99% gives 12.3 ml. Since many pesticides are more retained by methanol than is atrazine, it is obvious that a very large volume of methanol should be required for total desorption of all the compounds.

These results illustrate (i) the good agreement between predicted values calculated from LC data, (ii) that V_r calculations are only an estimation and the less retained the compound is, the sharper the front is and the better the estimation is, and (iii) that for more retained compounds, the desorption volume can be much more higher than V_r values.

3.4. Backflush desorption

Table 1 indicated that methanol or acetonitrile should not be used as a desorption solution. THF can be considered because it ensures lower retention factors, although some compounds, such as carbendazim ($\log k' = 0.79$), are more retained than atrazine was in methanol ($\log k' = 0.62$). However, THF is toxic and unstable.

Even with a 100- or 200-mg PGC cartridge, we can predict a too large desorption volume, since more than 10 ml should not be obtained for further evaporation. With GCB cartridges, the desorption of many analytes occurred with 6 ml of dichloromethane–methanol with 250 mg of sorbent and the backflush desorption was only recommended for the 1-g cartridges. We do not know the retention behaviour of analytes on GCB, but we can at least say that the retention is expected to be higher on PGC just because of the difference in specific surface area.

As it is not really straightforward to predict the compounds which will be strongly retained by PGC in both water for determining the aqueous sample volume and in THF for determining the desorption volume, the only solution is to desorb the compounds in the opposite way to the sample application. With this solution, other organic solvents may be used. We tested the use of methanol for backflush desorption when determining the concentration of a water sample spiked with thirteen polar pesticides as listed in Table 2.

Since another cause of incomplete recovery can be a loss during the evaporation of the desorption solution, we first studied this step. The volatility test consisted simply in spiking 5 ml of methanol with the analytes, evaporating to dryness and reconstitution in the mobile phase before injection. The recoveries were measured and Table 2 indicates that only losses for carbendazim and aldicarb were observed owing to evaporation of extracts.

Forward desorption was performed with 15 ml of methanol and, as can be predicted from the $\log k'$ values in methanol, most of the compounds are not desorbed. When carrying out a backflush desorption with only 5 ml of methanol, all the compounds are desorbed with recoveries of ca. 100%, including the compounds that were not desorbed in the forward desorption. The lowest recoveries observed for carbendazim and aldicarb are explained by the loss upon evaporation, as shown by the volatility test. Since the list of pesticides contains four compounds having $\log k'$ values in methanol of ca. 1, this result shows that using a 500-mg cartridge, a reasonable volume (5 ml) of methanol can be used for desorption, with the advantage of it being a

Table 2
Recovery data for the volatility test and when the desorption is performed in the same way (forward) or in the opposite way (backflush) as the percolation of the sample (LC-grade water spiked with 3 μg/l of thirteen polar pesticides) through a 500-mg PGC cartridge

Compound	Recovery ± S.D. (%)[a]		
	Test of volatility	Forward desorption (V_{MeOH} = 15 ml)	Backflush desorption (V_{MeOH} = 5 ml)
Oxamyl	100 ± 3	91 ± 8	101 ± 5
Methomyl	95 ± 3	94 ± 6	99 ± 4
DIA	103 ± 2	103 ± 4	102 ± 6
Monocrotophos	102 ± 3	105 ± 5	100 ± 5
Fenuron	95 ± 4	95 ± 3	101 ± 5
Metamitron	95 ± 3	Not desorbed	99 ± 3
DEA	103 ± 2	100 ± 3	101 ± 4
Chloridazon	105 ± 2	Not desorbed	106 ± 5
Carbendazim	65 ± 9	Not desorbed	58 ± 7
Aldicarb	71 ± 3	80 ± 5	79 ± 6
Aminocarb	103 ± 3	Not desorbed	103 ± 3
Metribuzin	102 ± 3	Not desorbed	101 ± 6
Metoxuron	98 ± 4	Not desorbed	101 ± 5

[a] Values from three replicate experiments.

Table 3
Effect of the matrix of the samples on recovery data

Compound	Recovery (%)[a]		
	Ultrapure water[b] (1 l)	Drinking water[b] (1 l)	River water[c] (200 ml)
Oxamyl	75	nd	95
Methomyl	95	100	84
DIA	97	nd	88
Monocrotophos	100	106	88
Fenuron	95	106	87
Metamitron	90	90	87
DEA	98	128[d]	95
Chloridazon	75	nd[e]	98
Carbendazim	53	nd[e]	53
Aldicarb	75	68	54
Aminocarb	106	nd	91
Metribuzin	93	52	84
Metoxuron	103	90	87

[a] Mean values calculated from three determinations.
[b] Sample spiked with 0.1 μg/l.
[c] Sample spiked with 1 μg/l.
[d] Compound present in non-spiked water.
[e] Not determined.

non-toxic organic solvent, totally water miscible and easy to evaporate.

3.5. Application to the trace level determination of polar pesticides in drinking and surface waters

Once the desorption conditions had been set up, we measured the recoveries obtained when percolating 1 l of LC-grade water spiked with 0.1 μg/l of thirteen pesticides and of drinking water spiked at the same level. The recoveries are reported in Table 3. For the LC-grade water sample, the recoveries are higher than 90% for most of the pesticides except oxamyl, chloridazon and aldicarb (75%) and carbendazim (53%). Breakthrough occurs for oxamyl and explains the lower recovery. Losses during the evaporation explain the lower recoveries for aldicarb and carbendazim. The low recovery obtained for chloridazon may be due to a problem of stability of this compound in water and this is under study. With drinking water samples many compounds had the same retention times as some pesticides, so that it was not possible to measure the recoveries for some pesticides. Similar recoveries as in LC-grade water were obtained for the others. In River Seine samples, the sample volume was set at 200 ml and the recoveries were measured at the μg/l level. Good recoveries were also obtained, showing that no matrix effect was observed.

Fig. 3 shows the chromatogram corresponding to 1 l of LC-grade water spiked with 40 ng/l of each pesticide. This chromatogram shows that only two or three extra peaks can be detected at 220 nm, thus showing the purity of the LC-grade water and also that no impurities, or very few, are generated by the carbonaceous sorbent. Detection at 200 nm shows more interferents but allows the detection of aldicarb. Fig. 4 shows (A) the chromatogram corresponding to 1 l of drinking water (Fig. 4), (B) the chromatogram corresponding to the same drinking water spiked at the 0.1 μg/l level and detected at 220 nm and (C) part of the chromatogram of the same spiked sample detected at 200 nm. The real sample contains few compounds, some of them (marked with asterisks) having similar retention times to compounds of Table 3. Only deethylatrazine (DEA) was detected and identified by the diode-array detector at a concentration lower than 10 ng/l. Fig. 4 shows that the UV detection of some polar carbamates can be achieved below the 0.1 μg/l level.

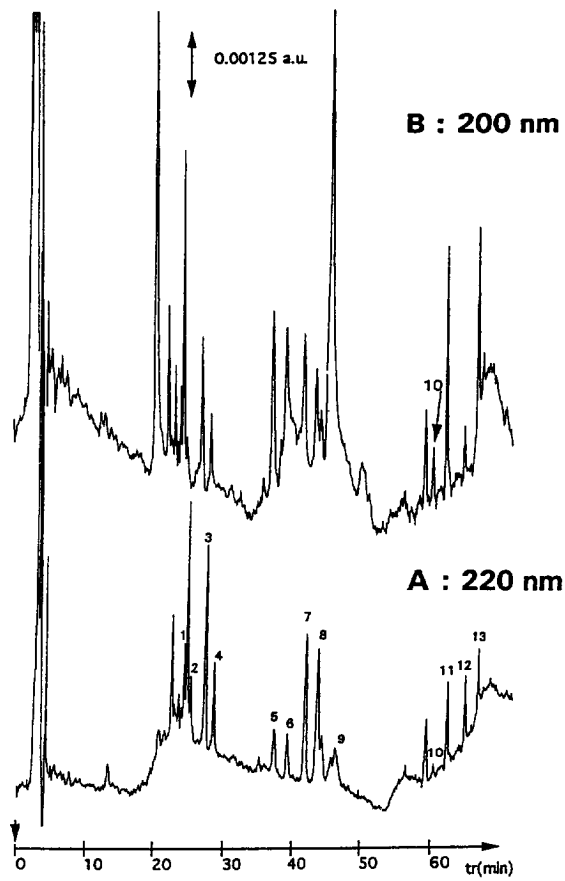

Fig. 3. Preconcentration of 1 l of ultrapurified water spiked with 0.04 μg/l of each pesticide on a 500-mg PGC cartridge. Analytical column, 25 × 0.46 cm I.D. Supelcosil LC_{18}-DB; mobile phase, acetonitrile gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7), 5% of acetonitrile from 0 to 15 min, 10% at 20 min, 15% from 40 min to 50 min, 30% at 60 min, 35% from 65 min to 72 min; UV detection at (A) 220 and (B) 200 nm. Solutes: 1 = oxamyl; 2 = methomyl; 3 = DIA; 4 = monocrotophos; 5 = fenuron; 6 = metamitron; 7 = DEA; 8 = chloridazon; 9 = carbendazim; 10 = aldicarb; 11 = aminocarb; 12 = metribuzin; 13 = metoxuron.

Fig. 5 corresponds to the analysis of a River Seine sample (a) not spiked and (b) spiked with 1

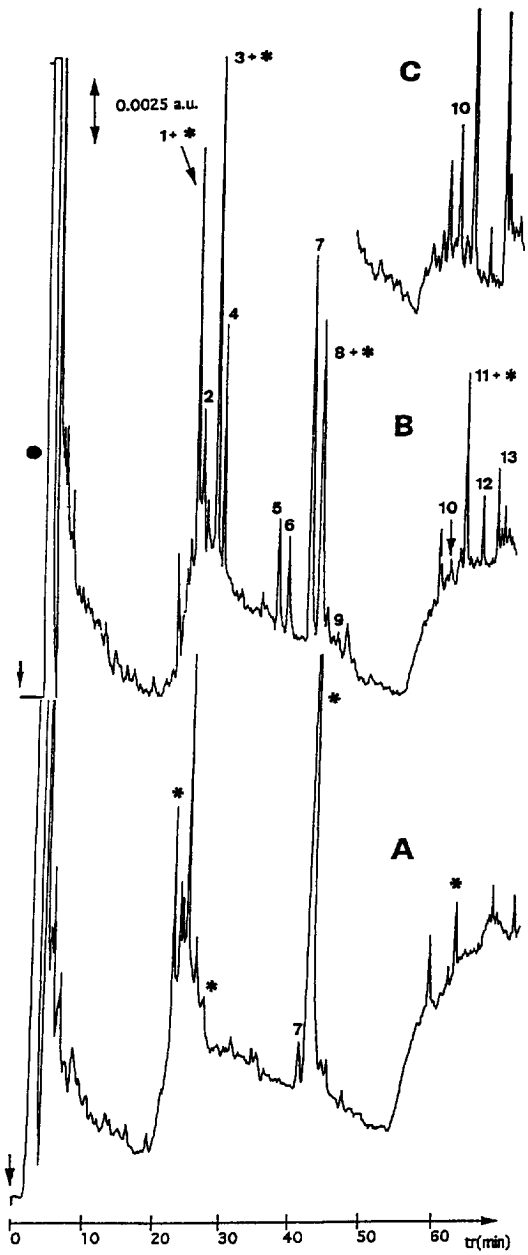

Fig. 4. Preconcentration of 1 l of drinking water on a 500-mg PGC cartridge. (A) Non-spiked water, UV detection at 220 nm; (B) water spiked with 0.1 μg/l of each pesticide, UV detection at 220 nm; (C) water spiked with 0.1 μg/l of each pesticide, UV detection at 200 nm. Other analytical conditions as in Fig. 3.

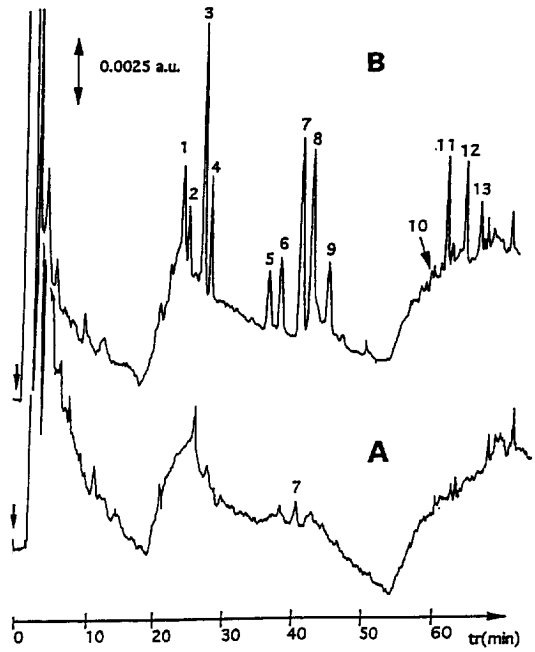

Fig. 5. Preconcentration of 200 ml of River Seine water on a 500-mg PGC cartridge. (A) Non-spiked water; (B) water spiked with 1 μg/l of each pesticide. Other analytical conditions as in Fig. 3.

μg/l of each pesticide. Only DEA was identified. Detection limits are at the 0.05–0.3 μg/l level in surface waters for these polar pesticides.

4. Conclusion

Many polar pesticides and polar degradation products can be quantified at the 0.1 μg/l level using PGC sorbent for their extraction from aqueous samples, whereas C_{18} silica cannot be used. However, owing to the different retention mechanism, compounds can be highly retained in water, but also in organic solvents. From LC data, desorption may not be straightforward unless a backflush desorption is performed. This backflush desorption allows the use of methanol (or acetonitrile) with the advantage of being a water-miscible solvent. This work has indicated that the knowledge of the retention behaviour of analytes in LC with new sorbents allows the prediction of the conditions for their use as solid-

phase extraction sorbents. More work should be performed in that field in the future to widen the range of analytes that can be analysed at trace levels in aqueous (or organic) matrices. In particular, more attention should be devoted to very polar and water-soluble analytes.

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