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Evaluation of new polymeric sorbents with high specific surface areas using an on-line solid-phase extraction–liquid chromatographic system for the trace-level determination of polar pesticides

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Abstract

A styrene–divinylbenzene (PS–DVB) copolymer with a high specific surface area of about 1000 m^2/g was used for the on-line analysis of polar pesticides and compared with the similar PLRP-S polymer used previously in disposable on-line precolumns, but with a lower specific surface area of about 500 m^2/g. The retention of polar analytes was found to be higher, thus showing the possibility of using precolumns packed with this PS–DVB to extend on-line analysis to more polar pesticides. A problem encountered was the poor coupling of such precolumns with a C_{18} analytical column, because the mobile phase used for the analytical separation did not allow their correct transfer, thus causing band broadening of the peaks. The problem was solved by using a carbon-based analytical column which retains polar analytes; the results demonstrate the requirements for a similar retention by the sorbents used in the precolumn and in the analytical column for the on-line coupling of solid-phase extraction with liquid chromatography. Applications are given to the on-line trace determination of polar pesticides such as clopyralid, methomyl, monocrotophos, deisopropylatrazine, picloram with detection limits at the low 0.1 $\mu g/l$ level for 100-ml drinking water samples.

Keywords: Sorbents; Sample handling; Environmental analysis; Water analysis; Pesticides

1. Introduction

Polar pesticides are being increasingly applied in modern agriculture so that analytical methods are required for the trace-level determination of polar and partly water-soluble pesticides and/or degradation products. Liquid–liquid extraction is not an appropriate method for very polar compounds and solid-phase extraction (SPE) with the widely used C_{18} sorbents has been shown to be limited to the handling of moderately polar compounds because of the early breakthrough of polar and water-soluble analytes [1–3]. Among the reversed-phase stationary phases, apolar styrene–divinylbenzene (PS–DVB) copolymers or carbon-based sorbents have been shown to be more appropriate for the handling of polar analytes [2–7]. In recent years, apolar copolymers were not easily available in off-line cartridges, only in extraction disks. Most of the

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studies using apolar copolymers have been made with on-line techniques coupling the preconcentration and the separation by liquid chromatography (LC). Precolumns are usually packed with PRP-1 or PLRP-S and retention measurements by (LC) have shown that the retention factors of analytes were between 20 and 50 times higher using these copolymers instead of C_{18} silicas [2–5]. Therefore, it was possible to determine many pesticides with a wide range of polarity in 100–150-ml water samples with detection limits at the low 0.1 μg/l level in drinking water and at the 0.1–0.5 μg/l level in surface waters [8–16]. However, the precolumns used in automatic apparatus are typically 1 cm × 2 mm I.D. and the breakthrough volumes of polar degradation products such as deisopropylatrazine (DIA) and phenol are still too low (<30 ml) for accurate determination at low concentration [5,17].

PLRP-S and PRP-1 have specific surface areas of about 500 m^2/g. In recent years, PS–DVB polymers with higher specific surface areas of about 1000 m^2/g have become available from several companies for off-line preconcentration in disposable cartridges. The potential for higher retention was shown by the breakthrough volume of DIA, which was found to be higher than 1 l using 200 mg of sorbent.

As these new PS–DVB sorbents are pressure resistant, they can be used in on-line precolumns. The objective of this work was to investigate the potential of on-line techniques using precolumns packed with these PS–DVB sorbents for the on-line determination of very polar pesticides. Emphasis was placed on on-line coupling with C_{18} analytical columns, as previous work had shown that the coupling can be difficult or impossible when analytes are retained much more strongly by the sorbent in the precolumn than on C_{18} silica [17–19].

2. Experimental

2.1. Apparatus

A Model 9012 liquid chromatography equipped with a Model 9065 Polychrom diode-array detector (Varian, Palto, Alto, CA, USA) was used for direct injections of standard solutions and extracts obtained with off-line preconcentration and for precolumn elution.

On-line percolation of samples was performed with manually packed cartridges using a Varian Model 2010 pump or with disposable cartridges using the Prospekt system (Spark Holland, Emmen, Netherlands). The precolumn and analytical column switching was achieved by connection with two Rheodyne (Berkeley, CA, USA) valves. Quantitative measurements were provided by using the software of the Polychrom.

2.2. Stationary phases

A C_{18} analytical column (25 × 0.46 cm I.D., particle size 5 μm) from Supelco (Bellefonte, PA, USA) and a column packed with Hypercarb porous graphitic carbon (100 × 4.6 mm I.D., particle size 5 μm) from Shandon HPLC (Runcorn, UK) were used. Samples were preconcentrated on 200-mg cartridges prepacked with 43–123-μm SDB-1 PS–DVB copolymer kindly provided by J.T. Baker (Deventer, Netherlands), on 8 × 2 mm I.D. stainless steel precolumns manually packed with SDB-1 and on 8 × 3 mm I.D. precolumns prepacked by Spark Holland with PLRP-S (Polymer Labs., Church Stretton, UK).

2.3. HPLC conditions

The separation of thirteen pesticides was performed using the C_{18} analytical 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 to 72 min.

The separation of six polar acidic and neutral pesticides was performed using the Hypercarb analytical column with a mobile phase containing acetonitrile and $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7). The gradient was 10% of acetonitrile at 0 min, 15% at 5 min and 40% at 40 min.

2.4. Chemicals

HPLC-grade acetonitrile was obtained from Baker France (Noisy-le-Grand, France). LC-

grade water was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA).

Pesticides were supplied by Cluzeau (Sainte-Foy-la-Grande, France). Other chemicals were obtained from Prolabo, Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Stock standard solutions of pesticides were prepared by weighing and dissolving them in methanol. The standard solutions were stored at 4°C and were used for the preconcentration of diluted standard solutions and for spiking the water samples. The final spiked water samples did not contain more than 0.5% of methanol.

2.5. Extraction procedure

Cartridges packed with SDB-1 were first washed with 5 ml of methanol and conditioned with 10 ml of LC-grade water. Precolumns packed with SDB-1 and PLRP-S used for the preconcentration of acidic and neutral pesticides were conditioned with 10 ml of LC-grade water acidified at pH 3 with perchloric acid. The water samples were percolated at a flow-rate of 5–10 ml/min using the cartridges and 2 ml/min using the precolumns.

For cartridges, the residual water was removed by air aspiration. The pesticides were desorbed from SDB-1 with 2 ml of methanol–acetonitrile (50:50, v/v). The desorption solution was evaporated to dryness at 30°C with a gentle stream of nitrogen. The dry extract was dissolved in methanol–$5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7) (25:85, v/v). A 50-μl aliquot was injected. Using precolumns, the solutes were desorbed from the sorbent with the mobile phase, allowing the separation on the analytical column.

The test of volatility was performed by directly spiking the desorption solution with 50–100 ng of each analyte, then evaporating it to dryness and reconstituting the dry extract in the injection mixture as described above for the real samples.

Before preconcentration, river Seine samples were filtered through cellulose ester filters (HA type, diameter 47 mm, pore size 0.45 μm) from Millipore.

3. Results and discussion

3.1. Evaluation of PS–DVB polymer for the extraction of polar pesticides

The potential of the new PS–DVB sorbents for analysing very polar pesticides was first investigated using the available off-line cartridges and by determining the breakthrough volumes. Polar pesticides were first selected within the main chemical groups of pesticides which are characterized by low water–octanol partition coefficients ($\log P_{OCT} < 1.7$), as can be seen in Table 1. The evaluation of the PS–DVB sorbent was first carried out by measuring the recoveries using off-line extraction with a 200-mg PS–DVB cartridge and percolating 1 l of LC-grade water and drinking water both spiked with 0.1 μg/l of each pesticide. They were also measured with 200 ml of river water spiked with 1 μg/l of each pesticide. In LC-grade water, no breakthrough occurred with 1 l of sample, except for oxamyl with a recovery of 85%. The values of 80% for carbendazim and of 73% for aldicarb are not explained by breakthrough of the analytes but by losses due to the evaporation step. This was verified by carrying out a simple test of volatility, which consisted in spiking and evaporating the desorption solution made of 2 ml of methanol–acetonitrile (50:50, v/v). In three replicate experiments, the recoveries were in the range 95–103% for each analyte in Table 1 except carbendazim ($65 \pm 9\%$) and aldicarb ($71 \pm 3\%$). One must therefore take great care with the evaporation step using off-line extraction. Reproducibility of results cannot be guaranteed because it is difficult to perform the evaporation step with very reproducible conditions except when using automated procedures.

Despite these particular losses, Table 1 clearly shows the ability of PS–DVB to extract polar pesticides. The higher retention of PS–DVB compared with C_{18} silica for very polar pesticides is straightforward and, as comparison, we obtained recoveries below 30% for oxamyl, methomyl and DIA using a 500-mg cartridge packed with C_{18} silica and with the handling of 500-ml samples. The chromatogram corresponding to the analysis of 1 l of LC-grade water

Table 1
Log P_{oct} values and recoveries obtained by preconcentrating 1 l of LC-grade water spiked at 0.1 μg/l, 1 l of drinking water spiked at 0.1 μg/l and 200 ml of Seine river water spiked at 1 μg/l on a 200-mg SDB-1 cartridge

Compound	Type	Log P_{oct} [a]	Recovery (%) [b]		
			1 l of LC-grade water	1 l of drinking water	200 ml of river water
Oxamyl	Carbamate	−0.5	85	nd[c]	73
Methomyl	Carbamate	0.2–1.8	94	90	nd
DIA	Metabolite of atrazine	1.1	105	95	94
Monocrotophos	Organo phosphorus		103	102	90
Fenuron	Phenylurea	0.5–1.2	91	103	93
Metamitron	Triazinone	0.8	92	89	86
DEA	Metabolite of atrazine	1.5	98	115	106
Chloridazon	Diazine	1.1–2.2	94	nd	88
Carbendazim	Carbamate	1.4–1.6	80	nd	59
Aldicarb	Carbamate	0.9–1.6	73	76	79
Aminocarb	Carbamate	1.7	103	92	90
Metribuzin	Triazinone	1.6–1.7	102	93	97
Metoxuron	Phenylurea	1.6	84	79	98

[a] according Ref. [20].
[b] Mean values obtained from three determinations.
[c] nd = not detected.

spiked at the 0.1 μg/l level is presented in Fig. 1a, obtained using a C_{18} analytical column and an acetonitrile gradient for the separation. Very few extra peaks were detected and were due to the LC-grade water, so that we can conclude that the PS–DVB polymers cartridges are really clean and do not generate impurities upon desorption. Table 1 shows that similar recoveries are obtained in LC-grade and drinking water samples spiked at the same 0.1 μg/l level. The chromatograms corresponding to the non-spiked and spiked drinking water samples are shown in Fig. 1b and c, respectively. Interferences were detected at the retention times of oxamyl, chloridazon and DEA, so that recoveries could not be measured except for DEA, which was confirmed by UV diode-array detection (DAD) at a concentration of 15–20 ng/l. Carbendazim was not recovered in the drinking water extract and was certainly lost upon evaporation. Combination of Fig. 1a and c shows that detection limits below 0.05 μg/l are obtained for drinking water samples for each polar pesticide including the very polar carbamates, which can thus be simply detected and included in a multi-residue analysis. Aldicarb is more difficult to determine since its UV maximum is at 200 nm.

The chromatograms corresponding to the analysis of 200 ml of river Seine sample not spiked (Fig. 1d) and spiked with 1 μg/l of each pesticide (Fig. 1e) show similar fingerprint due to the interferences as for drinking waters. The sample volume was lowered to 200 ml to decrease the effect of interfering compounds because of the lack of selectivity of the PS–DVB packings. Only DEA was identified and confirmed by DAD at a concentration of 60 ± 10 ng/l and one interfering compound was detected at a similar retention to methomyl but was not confirmed. The average detection limits are between 0.1 and 0.3 μg/l in surface waters and are easily obtained with simple preconcentration of a 200-ml sample without any clean-up.

3.2. On-line preconcentration using a PS–DVB precolumn and a C_{18} analytical column

On-line solid-phase extraction has the advan-

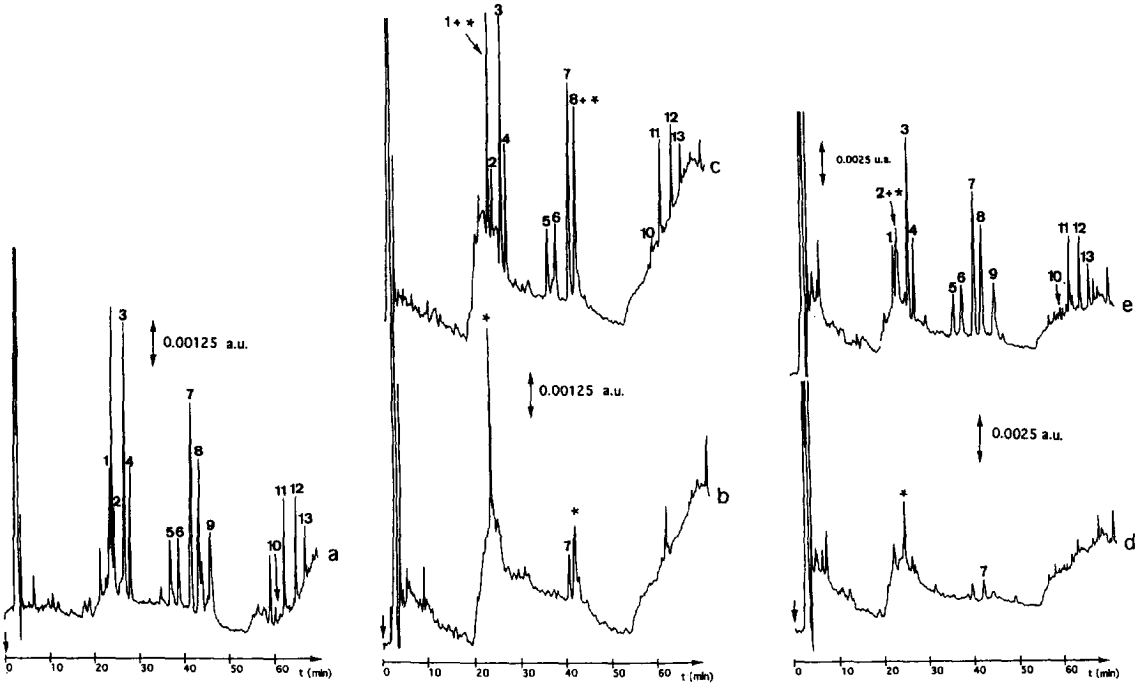

Fig. 1. Preconcentration of different aqueous matrices using a 200-mg SDB-1 cartridge: (a) 1 l of LC-grade water spiked at 0.1 μg/l; 1 litre of drinking water (b) not spiked and (c) spiked at 0.1 μg/l; 200 ml of river Seine water (d) not spiked and (e) spiked at 1 μg/l. Mobile phase: acetonitrile gradient 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. Flow-rate, 1 ml/min; UV detection at 220 nm. Compounds: 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.

tage of (i) avoiding any risk of loss and contamination that can occur during the transfer and evaporation step, (ii) providing more accurate results and (iii) allowing the handling of a smaller sample volume since the entire sample is analysed. A precolumn of 8×2 mm I.D. was packed with the same PS–DVB packing as used in disposable cartridges. First, emphasis was put on the on-line transfer. Fig. 2 shows the chromatogram obtained after the on-line preconcentration of 10 ml of LC-grade water spiked with 5 μg/l of each analyte using a 25 cm long C_{18} analytical column. All the peaks are broad in comparison with a direct injection as in Fig. 1a, for instance. Brouwer and Brinkman [19] have observed a similar band broadening on coupling a precolumn packed with a PS–DVB sorbent (ENVI-Chrom P with a surface area of 900 m^2/g) to a C_{18} analytical column for the analysis of phenolic compounds. The band broadening observed in Fig. 2 does not come from the fact that the PS–DVB particle size is large (40–120 μm). This was easily verified using a precolumn packed with a C_{18} silica sorbent with the same particle size, which did not cause any visible band broadening. Therefore, the band broadening originates from the too large difference in retention between the precolumn and the C_{18} analytical column. The mobile phase which allows the separation contains 10% of acetonitrile at the beginning of the gradient, and at this concentration it is unable to desorb and refocus the compounds at the beginning of the analytical column. A similar band broadening has been observed when coupling a precolumn packed with porous graphitic carbon (PGC) with a C_{18} analytical column [17]. In order to avoid this problem, one solution is to couple an analytical column which retains the analytes

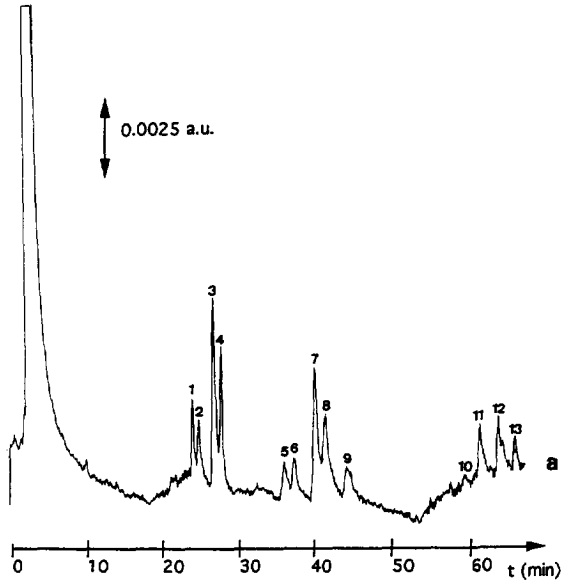

Fig. 2. On-line preconcentration of 10 ml of LC-grade water spiked at 5 μg/l with the thirteen pesticides using an SDB-1 precolumn coupled with a C_{18} analytical column. Experimental conditions as in Fig. 1.

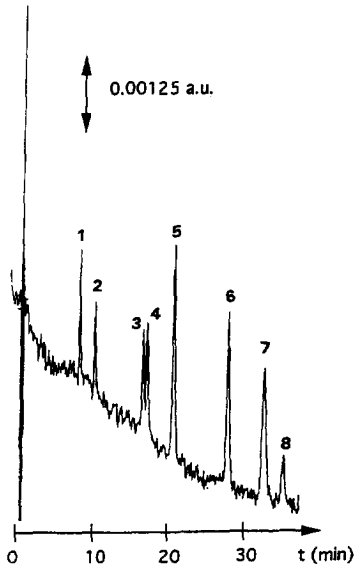

Fig. 3. Direct injection of eight polar acidic and neutral pesticides on a PGC analytical column. Mobile phase: acetonitrile gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7), 10% of acetonitrile at 0 min, 15% at 5 min, 40% at 40 min. Flow-rate, 1 ml/min; UV detection at 220 nm. Compounds: 1 = clopyralid; 2 = oxamyl; 3 = dicamba; 4 = monocrotophos; 5 = picloram; 6 = bentazone; 7 = DIA; 8 = fenuron.

more than C_{18} silica and which has a similar efficiency such as PGC analytical columns.

3.3. On-line preconcentration using a PS–DVB precolumn and a PGC analytical column

PGC has been available in recent years as a stationary phase for LC [21]. It has a very homogeneous carbonaceous structure made of large bands of delocalized electrons, so that the retention mechanism is totally different from that observed with C_{18} silicas or with apolar copolymers [21–26]. Its ability to retaining very polar compounds has been demonstrated [3,22]. However, since the retention is not based on hydrophobic interactions, it is not possible to separate all the polar pesticides reported in Table 1 in one run. For instance, compounds such as metoxuron, metribuzin and carbendazim are highly retained even with pure methanol as mobile phase [27]. In order to test the on-line coupling of a PS–DVB precolumn and a PGC analytical column, we selected polar pesticides which are separated on PGC with similar mobile phase conditions, such as clopyralid, dicamba, picloram and bentazone. An analytical separation using the PGC analytical column is shown in Fig. 3. Although the pH of the mobile phase is 7 and acidic pesticides (peak 1, 3, 5 and 6) are ionized, one can see their high retention, thus also showing the different retention mechanism. Fig. 4a represents the chromatogram obtained with the on-line preconcentration of 10 ml of LC-grade water at pH 6.5 and spiked with 2 μg/l of each pesticide using an SDB-1 precolumn and Fig. 4b the chromatogram obtain under similar conditions except that the sample was adjusted to pH 2 before the preconcentration. First, no band broadening is observed for the on-line coupling of an SDB-1 precolumn and a PGC analytical column, since the quality of these chromatograms is similar to that obtained by direct injection in Fig. 3. The mobile phase allowing the separation is rich enough in acetonitrile to allow the transfer and desorption of the analytes. Comparison of Fig. 4a and b indicates that

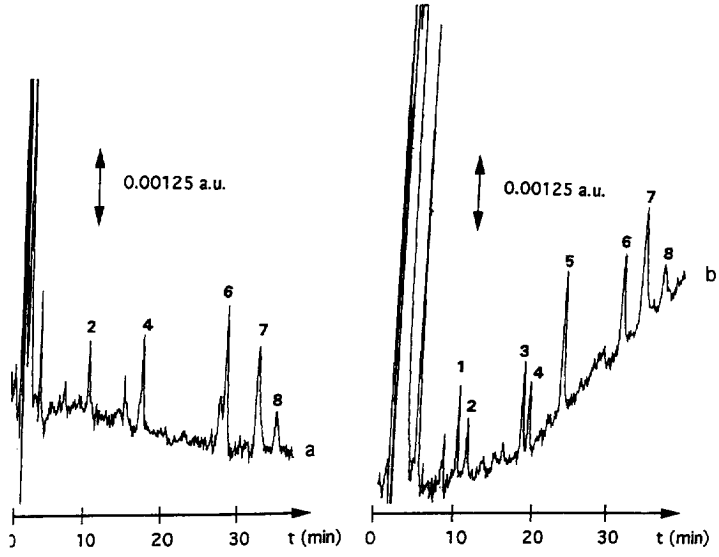

Fig. 4. Preconcentration of 10 ml of LC-grade water spiked at 2 μg/l with the eight pesticides, (a) not acidified and (b) acidified to pH 2 with perchloric acid. Experimental conditions as in Fig. 3.

breakthrough volumes depend on the sample pH.

Table 2 reports the recoveries obtained with acidified and non-acidified samples. The effect of the acidification of the samples was examined because when using off-line cartridges packed with 200 mg of the SDB-1 sorbent, a recovery of 100% was measured when 500 ml of water at pH 7 was percolated. The advantage was that humic materials were not co-extracted at pH 7 and the amount of interfering substances in surface water was low. Obviously, in on-line studies, there is insufficient sorbent to retain acidic compounds in their ionic form from a sufficient volume.

Table 2
Recoveries obtained by preconcentrating 10 ml of non-acidified spiked LC-grade water and 10 and 100 ml of spiked LC-grade water acidified to pH 2 with perchloric acid on an 8 × 2 mm I.D. SDB-1 precolumn and 50 and 100 ml of spiked LC-grade water acidified to pH 2 on an 8 × 3 mm I.D. PLRP-S precolumn

Compound	Recovery (%) ± S.D.				
	SDB-1			PLRP-S	
	10 ml of non-acidified water	10 ml of acidified water	100 ml of acidified water	50 ml of acidified water	100 ml of acidified water
Clopyralid	0	103 ± 4	97 ± 2	27 ± 3	13 ± 2
Oxamyl	90 ± 3	98 ± 1	99 ± 3	39 ± 2	14 ± 2
Dicamba	0	100 ± 2	95 ± 1	100 ± 3	93 ± 3
Monocrotophos	106 ± 5	100 ± 6	98 ± 4	31 ± 4	12 ± 3
Picloram	0	91 ± 5	97 ± 3	92 ± 4	35 ± 3
Bentazone	100 ± 3	99 ± 2	94 ± 3	101 ± 3	95 ± 2
DIA	105 ± 3	104 ± 5	97 ± 3	45 ± 3	14 ± 1
Fenuron	105 ± 6	98 ± 3	100 ± 4	96 ± 4	47 ± 3

3.4. Comparison of breakthrough volumes obtained on PLRP-S and SDB-1

Table 2 shows that the breakthrough volumes are higher than 100 ml for each pesticide when the sample is at pH 2 using an 8×2 mm I.D. SDB-1 precolumn. An 8×3 mm I.D. PLRP-S precolumn was also coupled to the PGC analytical column and 50- and 100-ml water samples adjusted to pH 2 and spiked were analysed in order to compare the breakthrough volumes. Although the amount of PLRP-S sorbent is higher owing to the difference in size of the precolumns, under acidic conditions breakthrough volumes lower than 50 ml for clopyralid, oxamyl, monocrotophos and DIA, between 50 and 100 ml for picloram and fenuron and higher than 100 ml for only dicamba and bentazone were obtained. These results clearly illustrate the increase in retention with SDB-1 to the higher specific surface area.

3.5. Matrix effect and application to real waters

Fig. 5 shows the chromatograms obtained after the preconcentration of 100 ml of LC-grade water not spiked and spiked with 0.1 μg/l of pesticides (Fig. 5a and b), 100 ml of drinking water not spiked with 0.2 μg/l (Fig. 5c and d) and 100 ml of river Seine water not spiked with 1 μg/l (Fig. 5e and f). All the samples were acidified to pH 2 before percolation with perchloric acid. Table 3 reports the recoveries obtained with the three types of samples, showing that the recoveries do not depend on the sample matrix.

The first chromatogram with LC-grade water samples indicates that on-line determination at the 0.1 μg/l level can be achieved, although some interferents show up in the blank of the LC-grade water. In drinking and surface waters, the effect of co-eluted humic and fulvic acids is visible in the large peak at the beginning of the

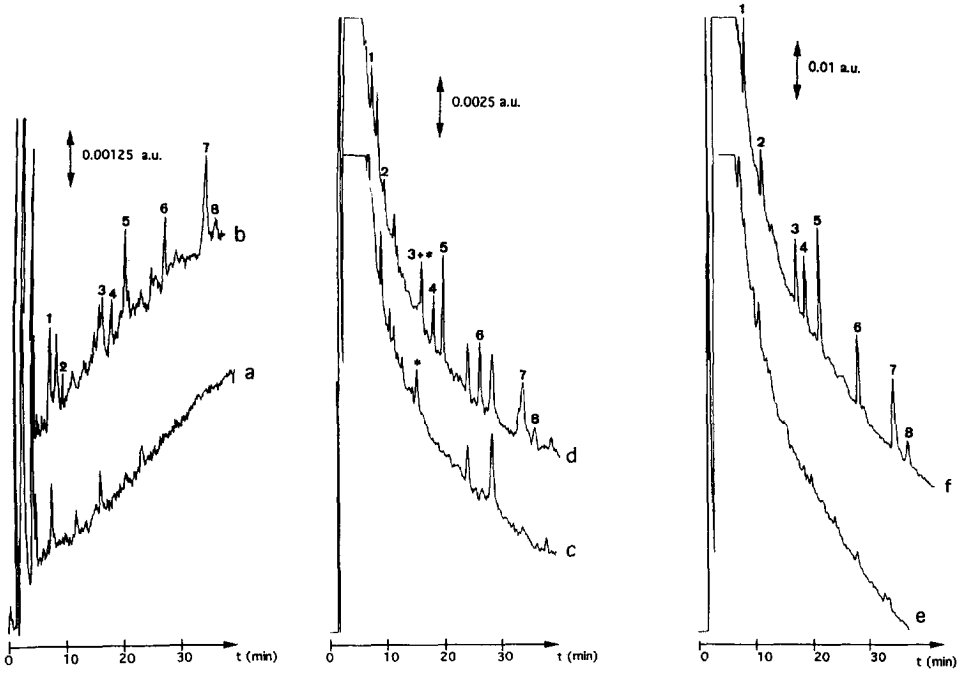

Fig. 5. On-line preconcentration of 100 ml of different aqueous samples acidified to pH 2 with perchloric acid on an SDB-1 precolumn coupled with a PGC analytical column. LC-grade water (a) not spiked and (b) spiked at 0.1 μg/l; drinking water (c) not spiked and (d) spiked at 0.2 μg/l; river Seine water (e) not spiked and (f) spiked at 1 μg/l. Experimental conditions as in Fig. 3.

Table 3
Recoveries obtained by preconcentrating 100 ml of LC-grade water spiked at 0.1 μg/l, 100 ml of drinking water spiked at 0.2 μg/l and 100 ml of river Seine water spiked at 1.0 μg/l

Compounds	Recovery (%)[a]		
	LC-grade water	Drinking water	River Seine water
Clopyralid	104	82	102
Oxamyl	102	73	102
Dicamba	94	97	99
Monocrotophos	104	105	99
Picloram	102	105	99
Bentazone	93	96	102
DIA	96	90	97
Fenuron	90	105	104

All the samples were acidified at pH 2 before preconcentration.
[a] Mean values from three replicate experiments.

chromatogram. However, clopyralid and oxamyl can still be detected. In drinking water, except for oxamyl, the other compounds can still be detected and quantified at the 0.1 μg/l level. In river Seine water samples, the amount of interfering compounds is larger, as seen by the different spiking level and the UV range used for detection. However, quantification can still be achieved at the 0.1–0.5 μg/l level depending on the analytes.

4. Conclusion

The potential of using PS–DVB copolymers with high specific areas for the extraction of polar pesticides has been demonstrated, thus increasing the range of analytes that can be monitored in water. This was clearly shown with off-line procedures. However, the on-line coupling of this new polymer with the efficient C_{18} analytical column is impossible if very polar analytes are to be determined. The on-line coupling requires analytical columns providing greater retention that C_{18} silicas. We have shown that the on-line coupling with a PGC analytical column can solve the analysis of some but not of all, polar analytes. The development of new, efficient, polymer-based analytical columns with relatively high specific surface areas is required.

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