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BREAKTHROUGH VOLUMES INCREASED BY THE ADDITION OF SALT IN THE ON-LINE SOLID-PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY OF PESTICIDES IN ENVIRONMENTAL WATER

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The on-line isolation and trace enrichment of the pesticides simazine, atrazine, carbaryl, propanil, linuron and fenamiphos from different waters is described.

The pesticides were spiked at 0.05–0.5 $\mu\text{g L}^{-1}$ in mineral, tap, ground and sea water and were preconcentrated using on-line solid-phase extraction onto a C_{18} precolumn followed by column liquid chromatography-diode array detection (LC-DAD). The salting-out effect was studied in order to improve the breakthrough volumes. Detection limits lower than 0.1 $\mu\text{g L}^{-1}$ were obtained for all pesticides studied.

KEY WORDS: Pesticides, salt addition, on-line preconcentration, liquid chromatography, water.

INTRODUCTION

Pesticides are found in environmental waters at sub-microgram per liter (sub-ppb) levels. In Europe, the maximum allowable concentration for total pesticides in drinking water is 0.5 $\mu\text{g L}^{-1}$ and 0.1 $\mu\text{g L}^{-1}$ for individual pesticides¹, so that sample concentration techniques are required.

The preferred sample preparation technique is liquid-liquid extraction (LLE), but in the last years solid-phase extraction (SPE) has become an alternative.

Off-line SPE methodologies involve the use of packing materials which may contain functional groups of different polarity. C_8 - and C_{18} -bonded silica phases²⁻⁴, Amberlite XAD resins⁵⁻⁷ and graphitized carbon black⁸ have been used for the determination of a variety of pesticides. Empore membrane extraction discs are an alternative to cartridges⁹⁻¹².

SPE has been coupled to column liquid chromatography (LC) to produce an on-line system by adding an extraction precolumn to the sample-loop of a six-port injection valve. Different packing materials in the precolumn have been employed, such as C_8 - or C_{18} -bonded silica¹³⁻¹⁶ and PRP-1 or PLRP-S (styrene-divinylbenzene copolymers)¹⁷⁻²⁰. The on-line coupling of Empore extraction discs has also been used²¹⁻²⁴.

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PRP-1 and PLRP-S increase the breakthrough volumes of analytes²⁵ and although the combination of these materials in precolumns with C₁₈ analytical columns can produce band broadening, this problem can be solved with the application of a suitable mobile phase gradient¹⁸. Still, a slight band broadening can be observed for the first eluted peaks²⁶.

The aim of this work is to improve the breakthrough volumes of selected pesticides, used within Europe¹ that have different chemical functionalities, using a C₁₈-bonded silica precolumn by salt addition (salting-out effect). The effect of the concentration and type of salt added to the sample on breakthrough volumes of analytes was investigated by an on-line SPE method using a C₁₈-bonded silica precolumn followed by liquid chromatography-diode array detection (LC-DAD). The proposed method was applied to the determination of simazine, atrazine, carbaryl, propanil, linuron and fenamiphos in mineral, tap, ground and sea water. These pesticides were chosen because they are included in an European project to prepare a candidate certified reference material.

EXPERIMENTAL

Chemicals

High-purity Milli-Q water (Millipore), RS-grade methanol and acetonitrile (Carlo Erba) were passed through a 0.45 µm filter (Whatman) before use. Simazine, atrazine, carbaryl, propanil, linuron and fenamiphos were obtained from Riedel-de-Haën. Stock standard solutions (1000 mg L⁻¹) were prepared in acetonitrile and stored at -20°C.

Highly pure NaCl, MgSO₄ and Na₂SO₄ were purchased from Merck.

Chromatographic conditions

Eluent delivery was provided by a ConstaMetric 4100 Series high-pressure pump from Thermo Separations Products coupled with a SpectroMonitor 5000 photo diode-array detector from LDC Analytical. A Zorbax cartridge column (25 cm × 4.6 mm i.d.) packed with 5 µm Zorbax ODS from Phenomenex was used. Gradient elution was used with a mobile phase containing methanol-acetonitrile-water (25:25:50) up to methanol-acetonitrile (50:50) in 20 min; the isocratic mode was used for 10 min before returning to the initial conditions in 10 min. The flow rate was 1 ml min⁻¹.

Quantitative measurement of peak areas by LC-UV at 220 nm (simazine, atrazine, carbaryl) and 250 nm (linuron, propanil and fenamiphos) was carried out. These wavelengths were chosen in order to get the best selectivity and sensitivity.

Preconcentration conditions

The extraction and enrichment step was carried out using a Jones Chromatography precolumn (10 mm × 4.6 mm i.d.) packed with 5 µm Spherisorb ODS coupled to the loop of a Rheodyne 7725i injection valve. The preconcentration pump was a Waters Model 590 (Millipore).

The solid-phase extraction precolumn was first conditioned by flushing it with 10 ml of methanol and then 10 ml of Milli-Q water at 1 ml min⁻¹. Water sample (pH- 6–7) volumes of 200 ml, containing 10% (w/v) NaCl (140 ml without salt addition for sea

water), spiked with pesticides at concentrations of 0.05–0.5 $\mu\text{g L}^{-1}$ were filtered and were then preconcentrated on the precolumn at a flow-rate of 4 ml min^{-1} .

Following the preconcentration step, the injection valve was switched and the analytes were eluted in the back-flush mode and separated on the analytical column.

The precolumn was cleaned by flushing with 10 ml of methanol followed by 10 ml of water after each analysis.

RESULTS AND DISCUSSION

The selected pesticides are some of the most used in Europe, and displaying different chemical functionalities.

The precolumn conditioning procedure for the extraction of pesticides from water samples was based upon work of various other authors^{18–20}. The retention step was optimized for sample flow-rate, sample volume and the salting-out effect of different salts.

Preconcentration parameters

Preconcentration flow-rate Varying the preconcentration flow-rate between 1 and 4 ml min^{-1} did not influence the preconcentration of the pesticides on the column. A flow rate of 4 ml min^{-1} was chosen. Higher flow-rates are not recommended because channelling effects may occur²⁷.

Breakthrough volumes The effect of sample volume was studied at a constant pesticide mass of 160 ng, using 80, 100, 150 and 200 ml of Milli-Q water fortified with 2, 1.6, 1.06 and 0.8 $\mu\text{g L}^{-1}$, respectively.

The recoveries for the most polar pesticides (simazine, carbaryl and atrazine) are shown in Figure 1. The maximum volume of sample under these conditions was 100 ml. Larger volumes caused loss of simazine and carbaryl due to breakthrough.

Salting-out effect The addition of different types of salts was studied in order to improve the breakthrough volumes of simazine and carbaryl. NaCl, MgSO_4 and Na_2SO_4 were added covering the concentration range 1–10% (w/v). The breakthrough volumes obtained in the preconcentration of Milli-Q water spiked from 0.8–2 $\mu\text{g L}^{-1}$ for simazine and carbaryl are shown in Table I.

The addition of NaCl or Na_2SO_4 gave good results, and breakthrough volumes of 200 ml for carbaryl and 170 ml for simazine were obtained when adding 10% (w/v) NaCl.

On the other hand, the breakthrough volumes obtained for simazine with the addition of MgSO_4 decreased with the amount of salt added.

All salts tested did not affect the preconcentration of the rest of the pesticides.

It was decided not to use MgSO_4 and Na_2SO_4 due to their low solubility in water and to prevent possible overpressure on the preconcentration pump; so NaCl was used in the subsequent experiments.

Table II shows the recoveries obtained for all pesticides in mineral, ground and sea water by on-line SPE using the C_{18} precolumn, 200 ml of sample spiked with 0.15 $\mu\text{g L}^{-1}$ and 10% (w/v) of NaCl added. As can be seen in Table II, the on-line method allowed good recoveries for all pesticides. The relative standard deviations (RSD) were < 10%. These are acceptable values and prove the repeatability of the method.

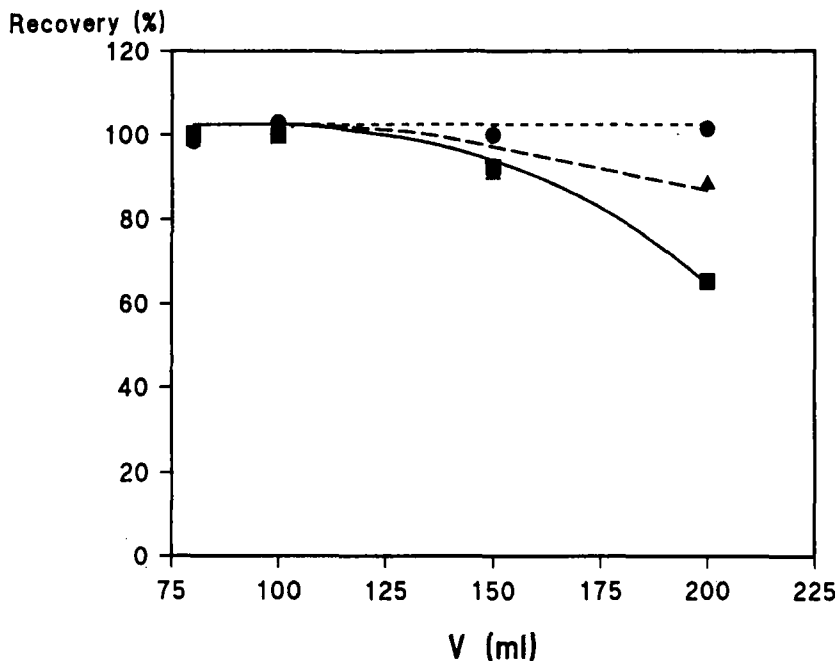


Figure 1 Experimental variations of recovery with percolated Milli-Q water samples having a constant amount (160 ng) of pesticides added. (■) simazine; (▲) carbaryl; (●) atrazine.

Table I Breakthrough volumes (ml) of simazine and carbaryl obtained on-line SPE on a C_{18} precolumn using Milli-Q water spiked from $0.8\text{--}2\ \mu\text{g L}^{-1}$ with salt addition.

	% NaCl			% $MgSO_4$			% Na_2SO_4		
	1	5	10	1	5	10	1	5	10
Simazine	120	140	170	110	80	n.d.	120	130	n.d.
Carbaryl	180	190	200	120	180	n.d.	140	200	n.d.

n.d.: not determined.

Table II Average recoveries (%) and RSDs ($n = 3$) of selected pesticides in on-line SPE on C_{18} precolumn of 200 ml of different water samples (10% NaCl added) spiked at the $0.15\ \mu\text{g L}^{-1}$ level.

Pesticide	Mineral water		Ground water		Sea water ^a	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
Simazine	88	6	81	9	73	6
Carbaryl	99	6	104	5	80	7
Atrazine	98	4	100	4	114	7
Propanil	104	7	105	8	96	10
Linuron	100	5	102	3	105	9
Fenamiphos	105	6	92	9	112	8

^a200 ml of sea water spiked at $0.5\ \mu\text{g L}^{-1}$ without salt addition.

Table III Calibration data for pesticide analysis (0.05–0.5 $\mu\text{g L}^{-1}$) after preconcentration of 200 ml of environmental waters (10% NaCl added).

Pesticide	Wavelength (nm)	Mineral water		Ground water		Tap water		Sea water ^a	
		Calibration equation ^b	R ²	Calibration equation ^b	R ²	Calibration equation ^b	R ²	Calibration equation ^b	R ²
Simazine	220	y = -244 + 24874x	0.9997	y = -89 + 62897x	0.9998	—	—	y = 512 + 477658x	0.9996
Carbaryl	220	y = 2720 + 60441x	0.9954	y = 9372 + 1052205 x	0.9998	y = 9289 + 949263x	0.9992	y = 1190 + 1643928x	0.9958
Atrazine	220	y = -2185 + 341113x	0.9935	y = 37547 + 953995x	0.9999	y = -7854 + 576634x	0.9960	y = 1718 + 1173409x	0.9901
Propanil	250	y = -11.5 + 130770x	0.9999	y = 5674 + 168457x	0.9996	y = -2985 + 23691x	0.9901	y = -4961 + 348962x	0.9928
Linuron	250	y = -542 + 194502x	0.9917	y = -925 + 303590x	0.9999	—	—	y = 1401 + 381808x	0.9999
Fenamiphos	250	y = -2121 + 95362x	0.9998	y = -5753 + 139570x	0.9994	—	—	y = -916 + 143971x	0.9992

^aSample volume: 140 ml without salt addition^by = peak area; x = concentration ($\mu\text{g L}^{-1}$).

Determination in different matrices

The proposed preconcentration and analytical procedure were applied to determine the polar test pesticides in several spiked waters. Equations of analytical calibration graphs for all analytes in mineral, tap, ground and sea water in the range $0.05\text{--}0.5\ \mu\text{g L}^{-1}$ used the same experimental conditions with a sample volume of 200 ml (140 ml for sea water) are shown in Table III. The correlation coefficients were satisfactory ($R^2 > 0.99$), which means that precise quantitative results can be obtained by the proposed method, except for simazine, linuron and fenamiphos in tap water where various interfering peaks were detected (Figure 2).

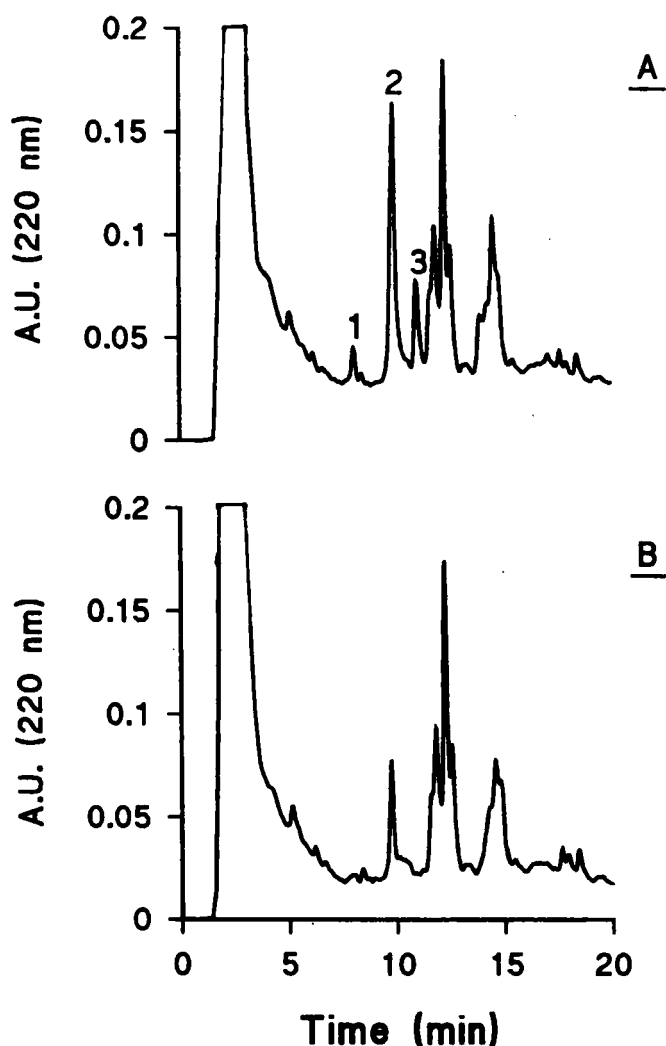


Figure 2 LC-UV chromatogram obtained after on-line preconcentration of 100 ml of tap water: (A) spiked at $1\ \mu\text{g L}^{-1}$; (B) not spiked. Peak numbers: see Figure 3. LC conditions: see experimental.

Figure 3 shows the chromatogram obtained in the on-line pre-concentration of 200 ml of ground water at 220 and 250 nm at a $0.15 \mu\text{g L}^{-1}$ spiking level. Figure 4 shows the chromatogram obtained in the on-line pre-concentration of 140 ml of sea water (Cantabrico Sea, Santander, Spain) spiked at the $0.1 \mu\text{g L}^{-1}$ level (Figure 4A) and not spiked (Figure 4B).

The detection limits obtained (IUPAC) are about $0.05 \mu\text{g L}^{-1}$ for simazine and lower for the rest of pesticides, which is the required level for the control of drinking water in Europe.

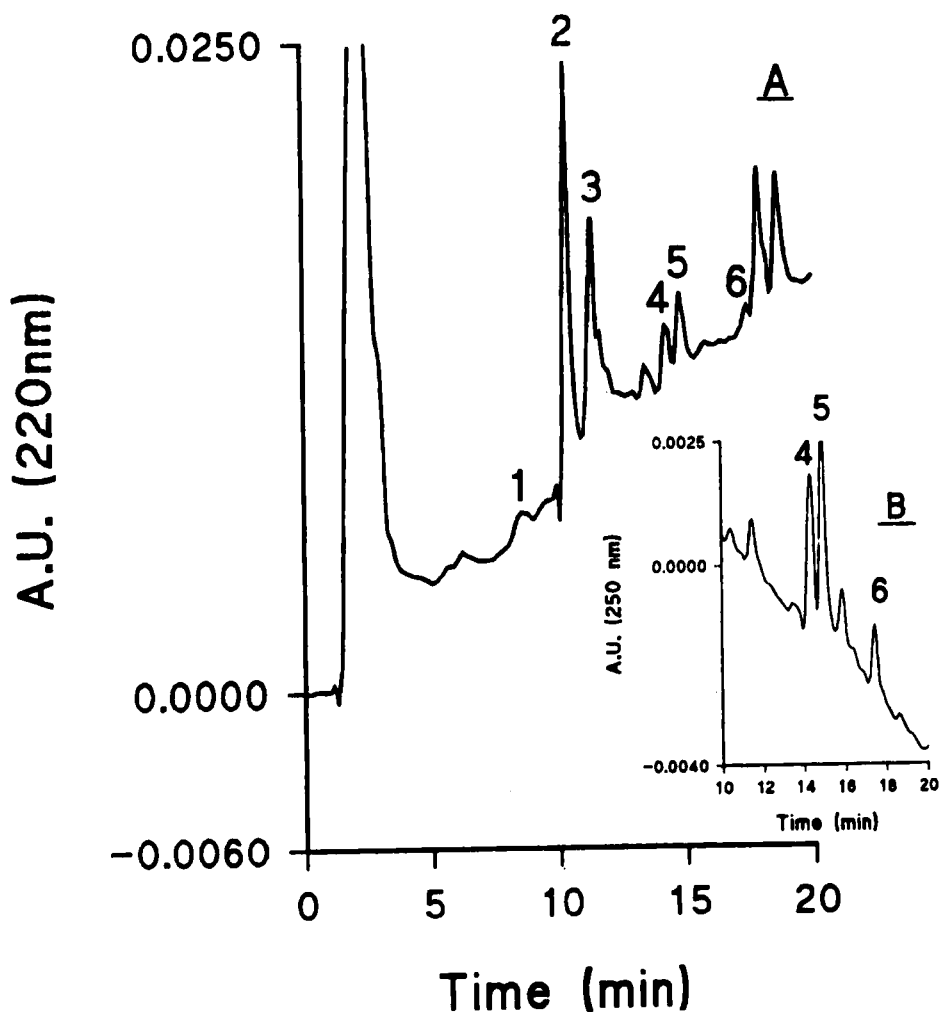


Figure 3 LC-UV chromatograms obtained after on-line pre-concentration of 200 ml of ground water spiked with $0.15 \mu\text{g L}^{-1}$ of pesticides and 10% (w/v) of NaCl added. (A) 220 nm; (B) 250 nm. Peak numbers: (1) Simazine; (2) Carbaryl; (3) Atrazine; (4) Propanil; (5) Linuron; (6) Fenamiphos. LC conditions: see experimental.

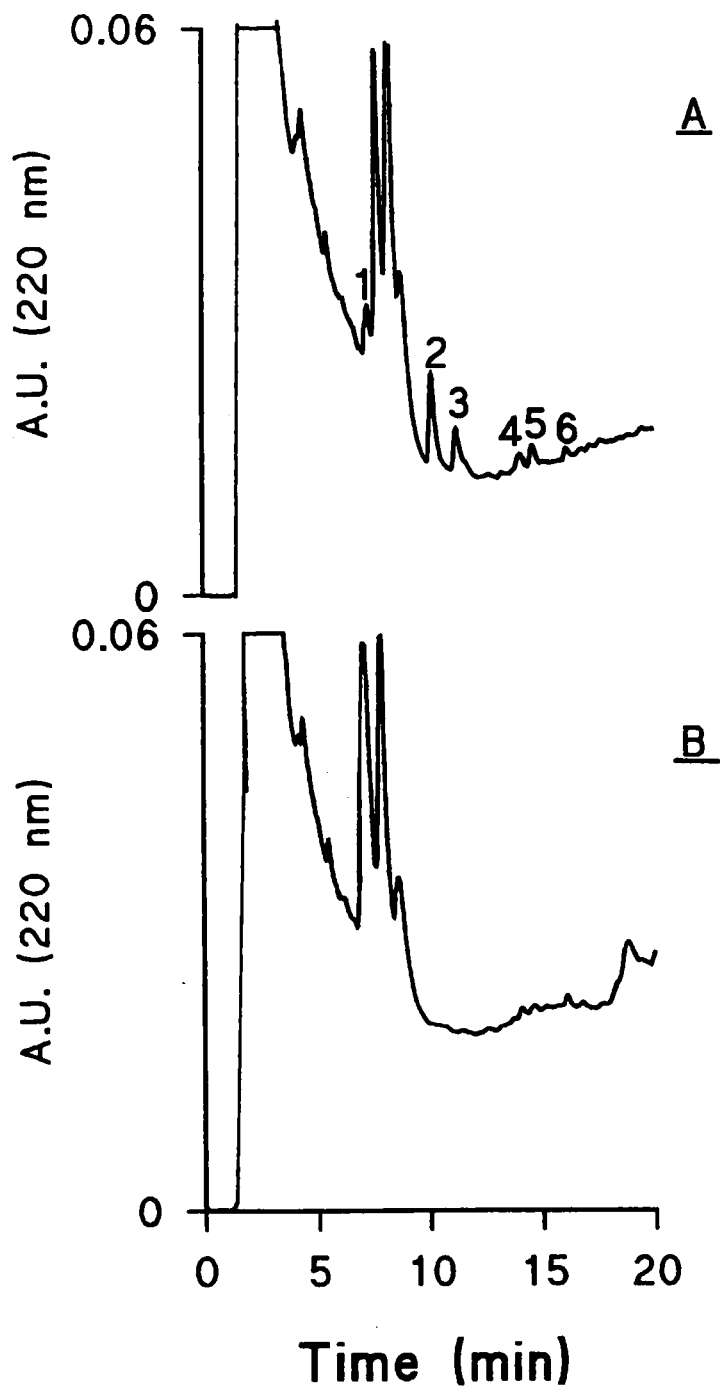


Figure 4 Chromatogram obtained after on-line pre-concentration of 140 ml of sea water (Cantabrico Sea, Santander, Spain): (A) spiked at $0.1 \mu\text{g L}^{-1}$; (B) not spiked. Peak numbers: see Figure 3. LC conditions: see experimental.

CONCLUSIONS

The addition of high amounts of salts (NaCl) significantly increases the breakthrough volumes for selected polar pesticides. Compared with 20 μ l loop injection, the preconcentration factor of the proposed on-line SPE method is about 10000. Preconcentration of 200 ml of sample allows quantification of all pesticides studied in water at the level required in Europe for the control of drinking water.

Future research will include the combination of salt addition and the use of on-line SPE using Empore extraction discs to improve the breakthrough volumes and to determine highly polar pesticides such as, e.g., deethylatrazine and deisopropylatrazine.

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