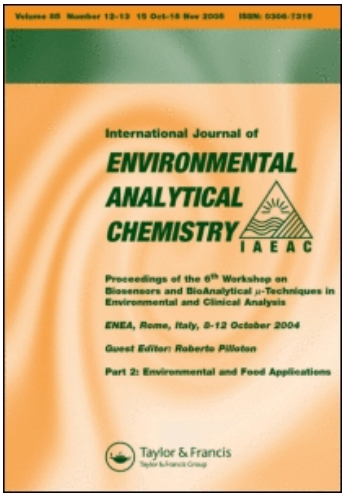

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Solid-Phase Extraction, Clean-pp and Liquid Chromatography for Routine Multiresidue Analysis of Neutral and Acidic pesticides In Natural Waters in One Run

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SOLID-PHASE EXTRACTION, CLEAN-UP AND LIQUID CHROMATOGRAPHY FOR ROUTINE MULTIRESIDUE ANALYSIS OF NEUTRAL AND ACIDIC PESTICIDES IN NATURAL WATERS IN ONE RUN

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Solid-phase extraction using C_{18} silica cartridges, liquid chromatography analysis and UV diode array detection were investigated for the routine trace-level determination of neutral pesticides over a wide range of polarity. Detection limits below the 0.1 µg/l range were easily obtained in drinking water. If neutral and acidic pesticides over a wide range of polarity have to be determined in the same run, samples have to be acidified to obtain good recoveries of extraction. The effect of the sample matrix was studied and detection limits in the 0.1 µg/l range were obtained in drinking water except for the more polar ones which are in the interfering peak of humic and fulvic acids. For surface water, a clean-up step using a Florisil cartridge has to be included in the procedure that allows detection limits in the range 0.05–0.3 µg/l.

KEY WORDS: Pesticides, solid-phase extraction, clean-up, water, multiresidue analysis.

INTRODUCTION

Many pesticides are now present in surface and ground waters all over the world, especially in agricultural areas[1,2]. Environmental programs are now setting up for the quality control of surface waters and regulations lay down the maximum allowed concentrations in drinking waters[3]. The more stringent regulations are in European countries with individual limits of concentration of 0.1 µg/l for each pesticide and 0.5 µg/l for their sum in drinking waters.

Trends in pesticide analysis are in multiresidue analyses using liquid-solid extraction with C_{18} silica sorbents. Liquid chromatography is largely employed due to its suitability for the direct analysis of pesticides over a wide range of polarities without any derivatisation step. This procedure allows the monitoring of a large number of pesticides at the same run, thus reducing the price and the number of analyses[4–9]. Automation is possible with special preparation units that sequentially extract the samples and prepare them for automatic injection.

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SPE procedures using C_{18} silica cartridges have been applied for the determination of neutral and basic pesticides in drinking waters and detection limits as low as 0.1 μg/l have been obtained without clean-up. However, there is an interest in multiresidue analysis including also acidic herbicides since they are often detected together with other neutral herbicides in ground and surface waters. The determination of acidic pesticides requires a previous acidification of samples before percolation, but a large non-resolved peak usually appears in the chromatogram due to the co-extraction of humic and fulvic acids in natural samples. This was shown using cartridges and also on-line techniques with precolumns[6,9–14]. As a consequence, the detection limits which are in the 0.1 μg/l range are higher in surface water, unless a clean-up step is added.

The aim of this paper is (i) to assess the limitation of using the C_{18} SPE cartridges depending on the polarity of pesticides, (ii) to examine the possibility of a multiresidue analysis at acidic pH, (iii) to measure the detection limits that can be reached without any clean-up and the possibility of identification by the LC-UV diode array detection system in both drinking and surface waters, (iv) to provide a clean-up procedure using SPE cartridges for contaminated surface water.

EXPERIMENTAL

Apparatus

LC analysis were performed with a Varian LC System Workstation including the Varian Star 9010 Solvent Delivery System and the 9065 Polychrom® diode array detector. The analytical column was connected to a Rheodyne valve (Berkeley, CA, USA). The extraction procedure was performed with a vacuum glass manifold Baker Spe-12 (J. T. Baker, Deventer, The Netherlands).

Stationary phases and columns

The analytical columns were a 25 cm × 4.6 mm I.D. prepacked with 5-μm octadecylsilica Supelcosil LC-18-DB (Supelco, Bellefont, PA, USA) for the separation of the mixture containing triazines and phenylureas and a 25 cm × 4.6 mm I.D. prepacked with 5-μm octadecylsilica Bakerbond Narrow Pore (J. T. Baker) for the separation of the mixture containing neutral and acidic compounds.

The cartridges used for the extraction were the 3-ml disposable extraction cartridges packed with 500 mg octadecylsilica Bakerbond (J. T. Baker) for the mixture of neutral and acidic compounds and the 6 ml disposable extraction cartridges packed with 500 mg of Supelclean™ Envi-18 (Supelco, Bellefont, PA, USA) for triazine and phenylurea pesticides. The cartridges used for the clean-up step were the 6 ml of 0.5 g Supelclean™ Envi™-Florisil® (Supelco).

Chemicals

HPLC-grade acetonitrile was from J. T. Baker and methanol from Prolabo (Paris, France). LC-quality water was prepared by purifying demineralized water in a milliQ filtration system (Millipore, Bedford, MA, USA). Other chemicals were from Prolabo, Merck or Fluka.

The various pesticides were supplied by Riedel-de Haën (Seelze, Germany), Promochem (Wesel, Germany) or Cluzeau (Sainte Foy La Grande, France). Stock solutions of selected solutes were prepared by weighing and dissolving them in methanol and stored at 4°C. The concentrated solution was used for the preparation of diluted standard solutions and for spiking water samples. No change in the chromatogram of the standard solutions was observed during the four months of this study. Final spiked samples did not contain more than 0.5% of methanol.

Procedures

Off-line extraction step was achieved by using a vacuum glass manifold Baker spe-12. The procedure used for the extraction step of triazines and phenylureas on C_{18} cartridges without a clean-up step were as follows: (1) conditioning the cartridge with 10 ml of methanol, (2) washing the cartridge with 10 ml of milliQ water, (3) percolating the sample, (4) washing the cartridge with 5 ml of milliQ water, (5) drying the cartridge with an air flow, (6) desorption of pesticides with 4 ml of methanol, (7) evaporation under a stream of nitrogen to dryness, (8) adding 500 µl of acetonitrile/milliQ water (2:8), (9) direct injection of 50 µl of the residue solution.

For neutral and acidic compounds, steps (1) to (6) are similar as above. But after the desorption, 50 µl of a mixture containing methanol and ammoniac (4:1) was added to the 4-ml methanol before the evaporation step. Under these basic conditions, acidic compounds are ionized and cannot be therefore volatilized during the evaporation step. After the evaporation under a stream of nitrogen (7), 200 µl of acetonitrile/milliQ water (2:8) were added (8), and 50 µl directly injected for the LC analysis (9).

The clean-up step of the dry extracts (obtained in the step 7 of the above sequence) was performed on a Florisil cartridge. The procedure was as follows: (1) adding 120 µl of isopropanol to the residue of the evaporation and 12 ml of hexane, (2) conditioning the cartridge of Florisil with 10 ml of methanol/ethyl acetate (1:1) and 10 ml of hexane, (3) percolating the sample, (4) drying the cartridge with an air flow, (5) eluting the pesticides with 12 ml of methanol/ethyl acetate (1:1), (6) evaporation of the sample under a stream of nitrogen, (7) adding 0.2 ml of acetonitrile/phosphate buffer at pH 3 (1:4), (8) injection of 50 µl of the residue solution.

RESULTS AND DISCUSSION

Determination of the SPE parameters using a C_{18} cartridge

A group of neutral pesticides including triazines, some of their degradation products and phenylureas has been selected and are reported in Table 1. Their water-octanol partition coefficient (P_{ow}) shows the wide range of hydrophobicity of the pesticides of interest, the more polar ones having log P_{ow} values lower than 2 and the non-polar ones values close to 4. As shown, very different values are found in the literature, depending on their determination method[15].

Separation by LC and detection limits. The analytical separation was carried out by reversed-phase chromatography using a C_{18} analytical column and an acetonitrile gradient with phosphate buffer at pH 7. Since the objective of this work is to demonstrate that SPE can be easily applied to pesticides with a large range of

Table 1 Characteristics of the studied compounds and recoveries obtained for the preconcentration of 500 ml of milliQ water spiked at 3 µg/l obtained by comparison to a direct injection of the standard solution at 3 mg/l (mean value of three replicates, R.S.D.: 3–7%). Log P_{ow} values reported by A. Noble[15] or by T. Brauman[16] (*).

No	*Compounds*	*Retention time (min)*	*Wavelength (nm)*	*log P_{ow}*	*Recovery (%)*
1	DIA	7.9	220	0.3–1.1	26
2	Fenuron	12.5	244	1.2	51
3	OHA	13.3	220	–	68
4	DEA	13.4	220	0.7–1.5	68
5	Hexazinone	21.9	244	–	98
6	Methoxuron	22.6	244	1.6	98
7	Simazine	23.7	220	1.4–2.3	96
8	Monuron	24.9	244	1.9	96
9	Cyanazine	26.4	220	1.6–2.2	81
10	Methabenzthiazuron	32.5	220	–	99
11	Simetryne	32.6	220	2.6–2.8	99
12	Atrazine	33.4	220	2.2–2.7	99
13	Chlortoluron	33.4	244	2.4	99
14	Fluometuron	34.6	244	2.4	101
15	Prometon	36.8	220	2.9–3.1	99
16	Monolinuron	37.1	244	2.3	107
17	Isoproturon	37.1	244	2.2	107
18	Diuron	37.4	244	2.68*	105
19	Difenoxuron	40.3	244	–	98
20	Sebutylazine	42.6	220	–	98
21	Propazine	43.5	220	2.5–3.0	94
22	Buturon	45.5	244	–	90
23	Terbutylazine	46.6	220	2.6–3.0	91
24	Linuron	49.1	244	2.7–3	96
25	Chlorbromuron	51.2	244	2.2	92
26	Chloroxuron	51.2	244	3.7	92
27	Diflubenzuron	58.9	244	–	94
28	Neburon	61.9	244	4.3*	95

polarities, the separation was not optimized. Moreover, the occurrence of each compound in the same sample is unlikely, so that only some target compounds have to be well separated on the basis of their usage and amount. In addition, as can be seen by the retention times that were reported in Table 1, co-eluted analytes do not belong to the same group and can easily be differentiated by the UV diode array detector (DAD).

Figure 1a represents the chromatograms obtained at 220 nm and 244 nm, corresponding to the direct injection of the mixture containing 5 ng of each pesticide. The limits of detection (LODs) defined as a signal-noise ratio of 3 are between 0.5 and 3 ng.

Sample volume for quantification at the 0.1 µg/l level. The sample volume that can be percolated through a C_{18} cartridge with theoretical recoveries of 100% depends on the amount of C_{18} silica and of the pesticides polarity, since no breakthrough should occur[6].

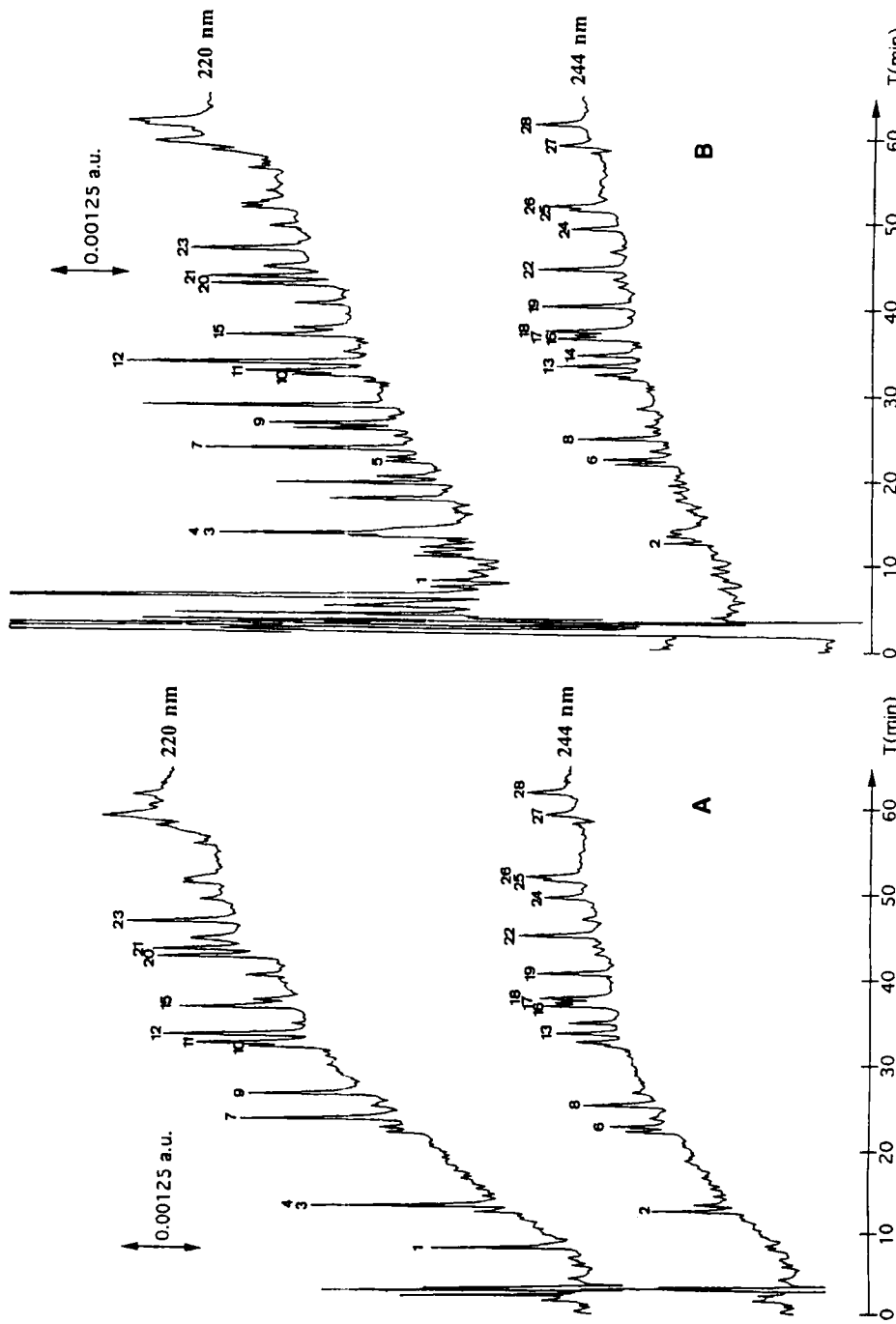

Figure 1 Comparison between (A) direct injection of 50 µl containing 5 ng of the 28 pesticides in the mix acetonitrile/water (2:8) and (B) the preconcentration of 500 ml of drinking water spiked at 0.1 µg/l. Analytical column: Supelcosil LC-18-DB 25 cm × 4.6 mm I.D.; flow rate: 1 ml/min; loop: 50 µl; mobile phase: acetonitrile gradient with 0.005 M phosphate buffer at pH 7; gradient: 15% to 60% acetonitrile from 0 to 70 min. For the peak names: see Table 1.

From the LOD values obtained by direct injection, one can easily calculate the sample volume to be handled on the basis of a 100%-recovery and of a required limit of concentration of 0.02 µg/l for a possible quantification at the 0.1 µg/l level in drinking water samples. With a LOD of 2 ng obtained by injection of 100 µl of the extract (maximum volume that can be injected in a 25-cm long analytical column without any loss of efficiency), and taking into account of the fact that the extract cannot usually be dissolved in a volume lower than 200–500 µl, depending on the sample matrix, a simple calculation indicates that the sample volume to be handled should be in the range 300–500 ml. Figure 1b represents the chromatograms at 220 nm and 244 nm obtained from an extract from 500 ml of drinking water which was spiked with 0.1 µg/l of each pesticide, after dissolving the dry extract in 500 µl of mobile phase and when injecting 50 µl into the analytical column. If recoveries are 100%, the amounts in the injected extract are the same as those injected in Figure 1a. Except the early eluted peaks 1 and 2 for which recoveries are lower than 100%, the peak heights which correspond to the spiked pesticides are similar in Figure 1a and 1b. Peaks 7 and 12 are even higher, which is due to the occurrence of these compounds in the sample. Figure 2 represents the analysis of the non-spiked sample. The occurrence of simazine (peak 7) and atrazine (peak 12) is confirmed by the simultaneous comparison of retention times and of UV spectra from the library of the DAD at respective concentrations of 0.016 ± 0.003 µg/l and 0.12 ± 0.02 µg/l. The match between the two retention times and UV spectra is excellent so that no further confirmation is required. The peaks which show up at 7.9 and 13.3 min can be DIA and DEA, but the match is not excellent as can been observed in Figure 2 and another mean is required for confirmation.

The chromatograms in Figure 1b clearly show that the limits of concentration are in the range 0.01–0.05 µg/l for all the analytes with the handling of a 500-ml sample extracted with a-500 mg C_{18} silica cartridge.

Recoveries. Table 1 reports the recoveries obtained when handling a sample volume of 500 ml of drinking water through a 500-mg C_{18} silica cartridge. They are close to 100% for all the pesticides except for the more polar ones, namely DIA, fenuron, OHA and DEA, for which the percolated volume is higher than the breakthrough volume. However, the recoveries of DEA and OHA are 68%, so that these compounds can still be analyzed at the 0.1 µg/l. If these recoveries should be increased, their breakthrough volumes can be increased by selecting a cartridge packed with a higher amount of C_{18} silica, or packed with another sorbent showing a higher retention for analytes such as polymeric sorbents[6]. From Table 1, one can conclude that in practice, the measurements of recoveries are important for polar pesticides characterized by log P_{ow} values lower than 2.

Quantification methods. The pesticides are characterized by their retention time, their spectrum and the injected amount which are stocked in a library. The library was built from a direct injection of the mixture by using the same injection loop as for the extracts. This method of quantification has been compared in a previous work with the standard addition method and with the use of calibration curves constructed in LC-grade and drinking waters. Similar results were obtained by those different methods and the MCA one has the advantage to give results in shorter times[11].

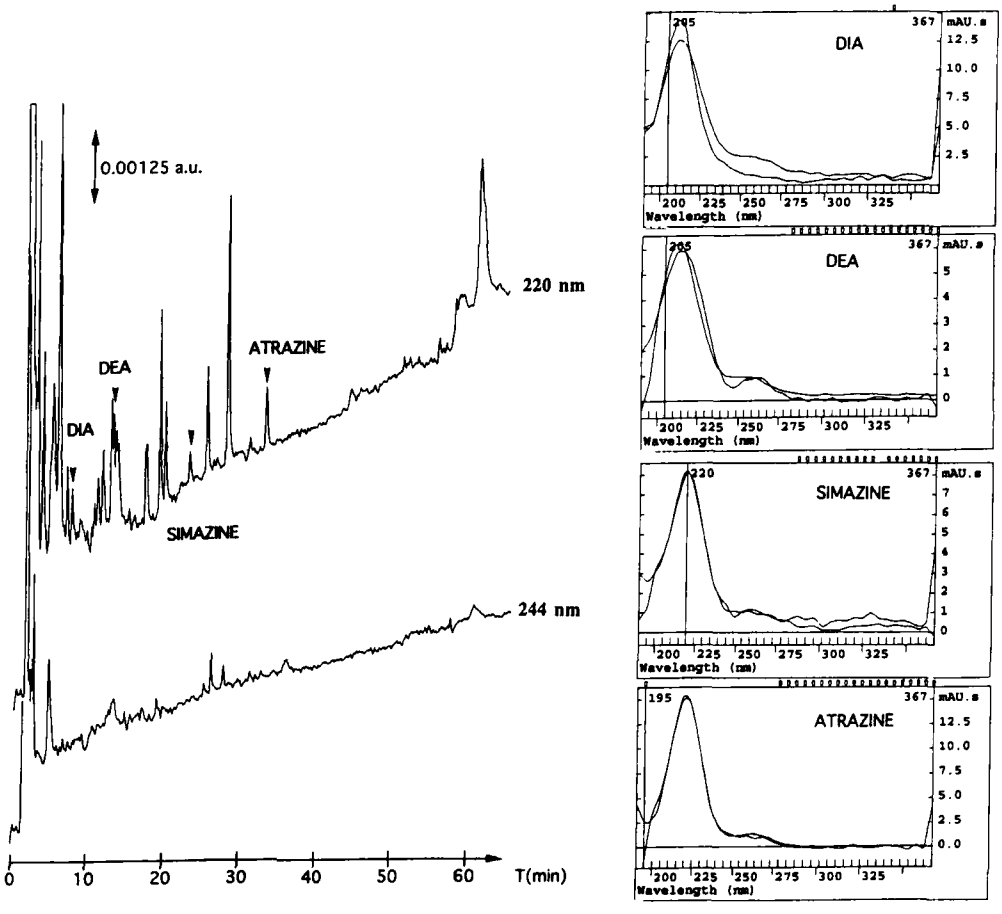

Figure 2 Preconcentration of 500 ml of drinking water and spectra of the peak identified with the MCA method (comparison between the spectrum of the unknown compound with the spectrum of the standard). Analytical conditions: see figure 1.

Multiresidue analysis in drinking water including neutral and acidic compounds

The possibility to extract simultaneously neutral and acidic pesticides was investigated using C_{18} sorbent with similar sample volumes. The pesticides reported in Table 2 have been selected because they are the most applied in European countries and may migrate in ground water[1,17]. Bentazone, dicamba, ioxynil, MCPP, 2,4-DB, 2,4,5-TP, and dinoterb are under their ionized form at neutral pH because their pKa values are between 3 and 5. They are not or just slightly retained by C_{18} silica in their ionic form so that their analytical separation requires an acidified mobile phase. For the same reason, they can be extracted using a C_{18} silica cartridge provided the sample has been previously

Table 2 Influence of the pH of the sample on the recoveries of extraction (%) of neutral and acidic compounds. Preconcentration of 500 ml of drinking water spiked at 0.5 µg/l.

Compounds	*pH 2*	*pH 3*	*pH 7*
Chloridazon	100	98	100
Dicamba	89	46	0
Aldicarb	93	92	96
Methoxuron	106	101	102
Simazine	100	100	100
Cyanazine	98	86	105
Bentazone	100	100	6
Atrazine	97	97	100
Carbaryl	101	98	95
Isoproturon	103	87	94
Ioxynil	98	83	31
MCPP	104	108	27
Difenoxuron	96	108	81
2,4 DB	98	92	38
2,4,5 TP	100	78	10
Metolachlor	102	104	102
Dinoterb	72	49	30

acidified before the percolation. Table 2 shows the recoveries of extraction measured for the compounds when percolating 500 ml of drinking water at pH 7 or acidified with perchloric acid at pH 2 or 3 and spiked at 0.5 µg/l. The solubility of the silica does not allow to use lower pH values than 2. As expected, if the recoveries of the neutral compounds are not pH dependent, recoveries of the acidic one decrease when the pH values increase. Figure 3 shows the chromatograms obtained when 500-ml of drinking water sample have been adjusted to pH 2, 3 and 7 after spiking at the 0.1 µg/l for each pesticide. At pH 7, the acidic compounds (peaks N° 6, 11–15 and 16) cannot be quantified owing to the low recoveries but the base line is flat. At pH 2 and 3, the acidic compounds are extracted, but one can see a large interfering peak due to co-extracted humic and fulvic acids. At pH 7, these humic materials which contain many phenolic groups are ionized and not retained whereas their co-extraction increase from pH 3 to pH 2.

The co-extraction of humic and fulvic acids should be taken into account for setting up the conditions of the separation, since the first eluted peak should not show up in the interfering peak. In Figure 3, one can see that the mobile phase gradient was adjusted in order that most of the peak should be eluted after 20 min. Note that the shape of this interfering peak depends on the shape of the gradient applied and it can appear in the middle of the chromatogram as a large hump[11]. However, one important point is that provided an appropriate gradient, the procedure as applied to the sample in Figure 3 – acidification to pH 3 and handling of a 500-ml sample through a 500-mg C_{18} cartridge – allows a limit of concentration in the range 0.02–0.1 µg/l for all the analytes in drinking water.

The repeatability of the measurements in peak areas and peak heights which was obtained by direct loop injections into the analytical column was as shown by the RSD values reported in Table 3. With four repeated direct injections of 12.5 ng of each of the 5 compounds, the RSD was measured between 2.0 and 5.4%. The RSD values were lower with three direct injections of 75 ng. The repeatability of the preconcentration step was also studied when preconcentrating 500 ml of drinking water samples spiked

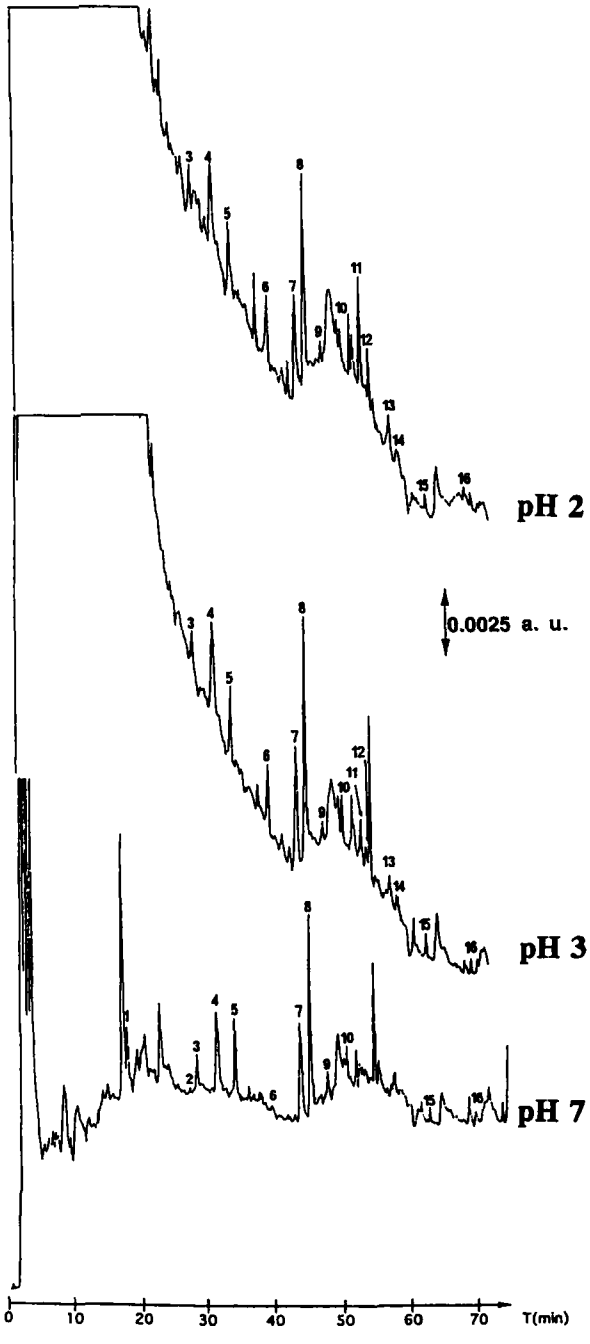

Figure 3 Effect of the pH of the sample on the preconcentration of 500 ml of drinking water spiked at 0.1 µg/l. Analytical column: Bakerbond Narrow Pore 25 cm × 4.6 mm I.D.; flow rate: 1 ml/min; loop: 50 µl; mobile phase: acetonitrile gradient with 0.005 M phosphate buffer acidified at pH 3 ($HClO_4$); gradient: 10% to 30% acetonitrile from 0 to 40 min and 30 to 77% from 40 to 80 min. Compounds: (1) chloridazon, (2) aldicarb, (3) methoxuron, (4) simazine, (5) cyanazine, (6) bentazone, (7) atrazine, (8) carbaryl, (9) isoproturon, (10) difenoxuron, (11) ioxynil, (12) MCPP, (13) 2,4-DB, (14) 2,4,5-TP, (15) metolachlor, (16) dinoterb.

Table 3 Repeatability of the method tested by different direct injections of 12,5 ng (a) and 75 ng (b) of the standard solution and recoveries of the preconcentration of 500 ml of drinking water spiked at 0.1 µg/l (measurements from 4 replicates, in peak heights).

Compounds	*Standard solution*		*Drinking water*
	R.S.D.		*R.S.D.*
	(a)	*(b)*	
Simazine	2.1	0.4	2.1
Atrazine	2.0	1.9	2.0
Isoproturon	5.4	1.0	5.4
MCPP	5.0	1.2	5.9
Metolachlor	2.4	4.2	10.6

at 0.1 µg/l with the same compounds. As can be seen in Table 3, the RSD is between 2.0 and 5.9% for four compounds and 10.6 for metolachlor. Its trace-level analysis is difficult owing to its poor UV detection.

Calibration plots for those five compounds were drawn by seven direct injections of a 50-µl volume in the range of 0.1–1.5 mg/l. The correlation coefficients were all satisfactory ($0.998 \leq R^2 \leq 1$) except for metolachlor ($R^2 = 0.990$).

In conclusion, this solid-phase extraction procedure using acidified samples is an easy and reliable method to reach the limit of detection of 0.1 µg/l required in drinking water for neutral and acidic compounds in one run.

Application to surface water: additional clean-up step

When applied to surface water samples, the procedures described above give higher limits of concentration than in drinking water samples owing to the numerous co-extracted analytes in addition to a much higher amount of humic and fulvic substances. The effect of the sample matrix is shown in Figure 4 with chromatograms corresponding to the extraction of 500 ml of LC-grade water (A), drinking water (B) and surface water samples (C) spiked at the 0.1 µg/l level and represented at the same attenuation range of the UV DAD. It is impossible to detect these analytes at this level in river samples owing to humic and fulvic substances. Figure 5A represents the chromatogram of a 500-ml Seine River sample spiked at the 0.5 µg/l level, showing that for acidic pesticides, the limits of concentration are in the 0.1–0.5 µg/l range.

To remove this interfering peak, a clean-up procedure with Florisil was carried out. In this procedure, the dry extract is dissolved in a non-polar solvent and clean-up occurs on the basis of a polarity fractionation scheme, as in adsorption chromatography with silica[6]. Non-polar analytes are the less retained whereas the polar ones can be strongly retained and one can expect to quantitavely desorb the pesticides of interest whereas the polar humic and fulvic substances would remain trapped on the sorbent. Automation of such a clean-up sequence was described for the determination of pyrethroid pesticides in water[18]. As mentioned above, one has to take care of dissolving the dry extract in a non-polar solvent in order to avoid loss of the non-polar analytes, but, the main practical problem encountered was that it was impossible to dissolve the extract from Seine River

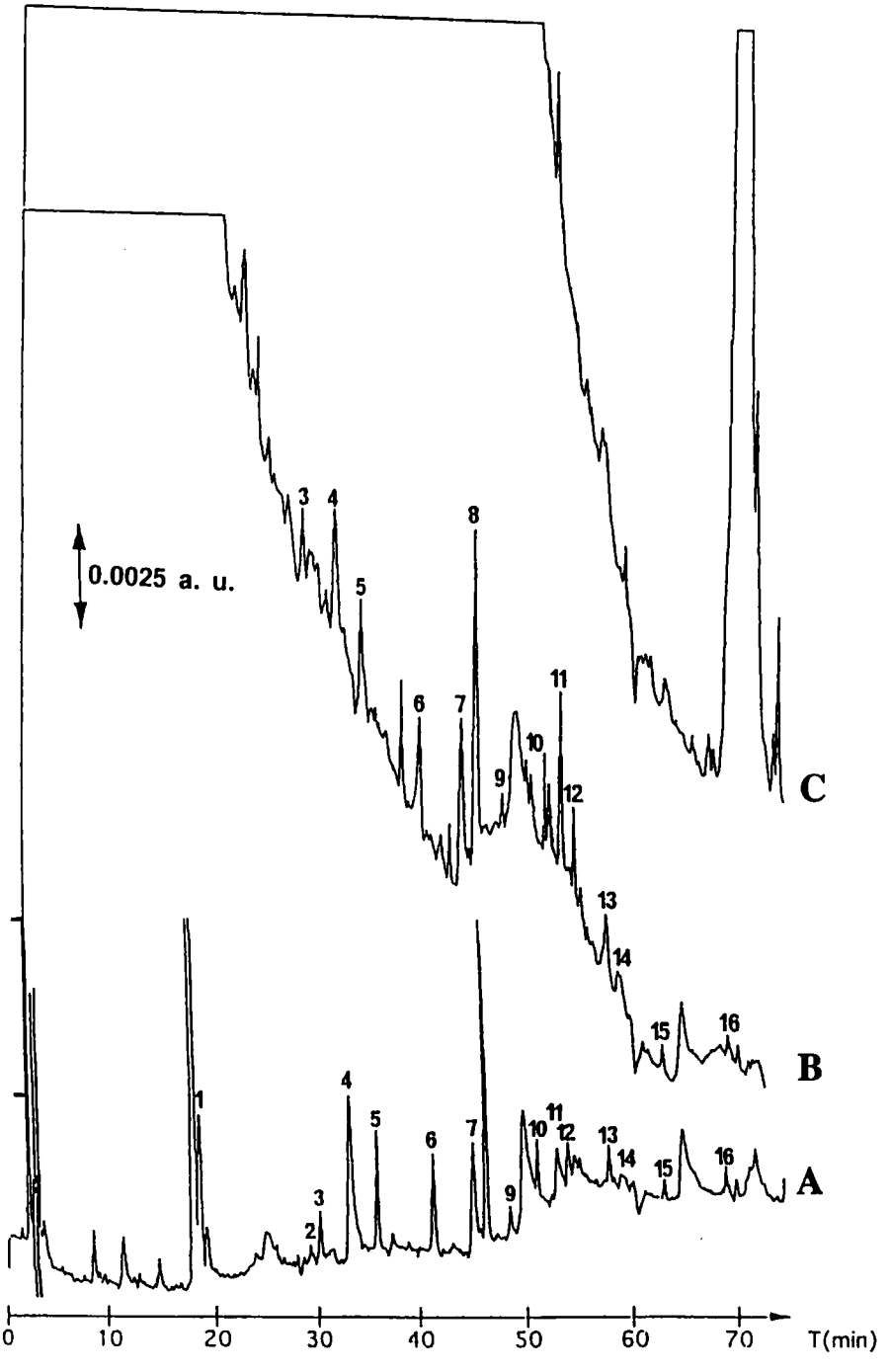

Figure 4 Preconcentration of 500 ml of LC-grade water (A), drinking water (B) and Seine River water (C) spiked at 0.1 µg/l and acidified at pH 2. Analytical conditions and peak names: see figure 3.

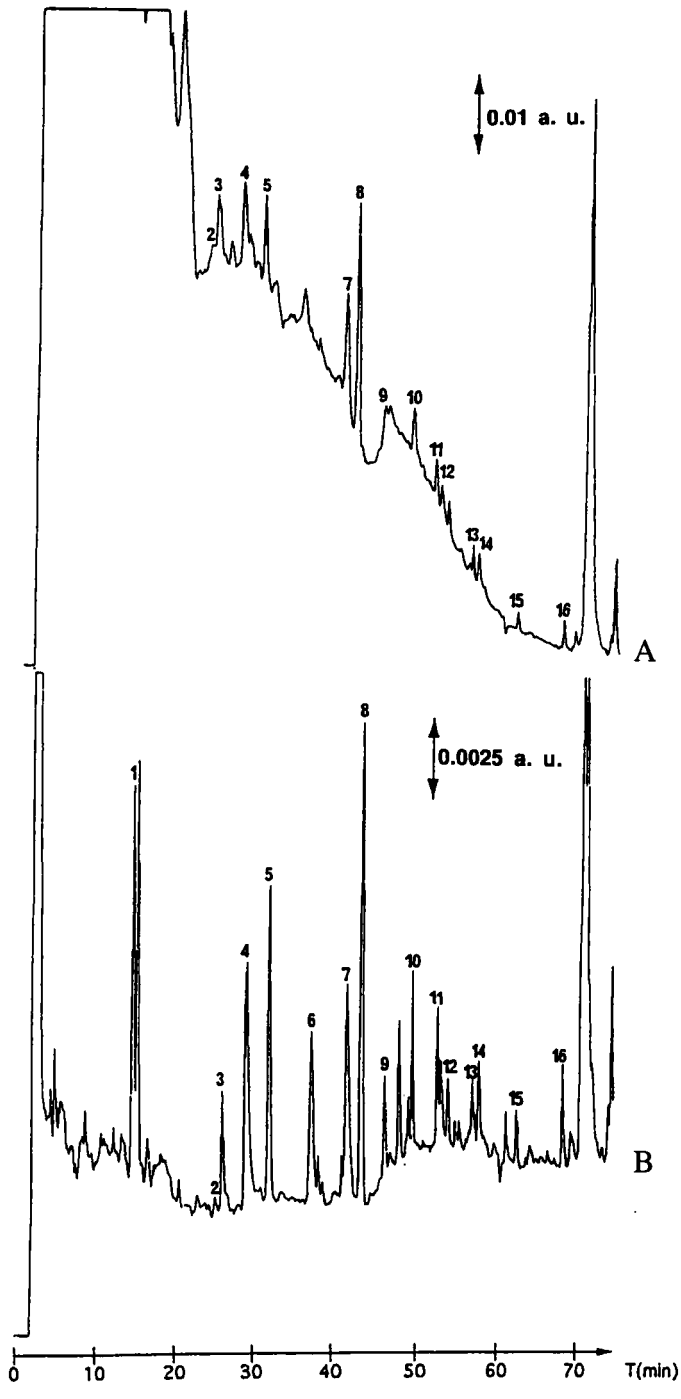

Figure 5 Preconcentration of 500 ml of Seine River water spiked at 0.5 µg/l and acidified at pH 2 with (B) and without (A) a clean-up step on Florisil. Analytical conditions and peak names: see figure 3.

water in hexane, even when increasing the volume to 20 ml. A moderately polar solvent should be added and a compromise has to be done between the volume and the added amount of polar solvent in order to avoid breakthrough for the apolar pesticides of the mixture. Different solvents were investigated and a solution of 12 ml of hexane and 120 µl of isopropanol was selected that permits a good dissolution of the extract without the loss of the more apolar pesticides of the mixture. Once the extract dissolved in the hexane-isopropanol mixture, it was percolated through the Florisil cartridge and the desorption was performed with 12 ml of a methanol-ethyl acetate solution (50/50, V/V). The polar interfering humic and fulvic acids were not eluted by this solution and remained on Florisil. Figure 5B shows the chromatogram corresponding to the preconcentration of 500 ml of the Seine River water acidified at pH 2, spiked at 0.5 µg/l, after extraction on C_{18} silica and subsequent clean-up on Florisil. When comparing with the chromatogram in Figure 5A corresponding to a simple extraction on C_{18} silica, the efficiency of the clean-up is clearly shown. The base-line is flat and lower attenuation range of the DAD can be used. The limit of quantification are therefore lower, in the range 0.05–0.3 µg/l.

Table 4 shows recoveries of extraction obtained for drinking water spiked at 0.1 µg/l and acidified at pH 2 with or without a clean-up step on Florisil. This procedure results in a decrease of recoveries for the more apolar compounds (from difenoxuron to dinoterb) that were certainly eluted during the percolation step on Florisil. The lower recovery for aldicarb is explained by loss during the evaporation step to dryness and for this compound, any method involving dry extract is not appropriate because such a loss cannot be reproducible. The low recoveries obtained for atrazine and carbaryl are certainly due to incomplete solubility in the mixture of isopropanol and hexane. But,

Table 4 Effect of the clean-up step on the recoveries for the preconcentration of 500 ml of drinking spiked at 0.1 µg/l (measurements from 3 replicates, R.S.D. between 0.5 and 5.5%); n.d.: not determined.

Compounds	*Recoveries (%)*	
	Without clean-up	*With clean-up*
Chloridazon	n.d.	80
Dicamba	n.d.	71
Aldicarb	88	55
Methoxuron	144	91
Simazine	102	90
Cyanazine	104	94
Bentazone	98	86
Atrazine	89	62
Carbaryl	100	53
Isoproturon	92	98
Ioxynil	100	94
MCPP	101	86
Difenoxuron	97	73
2,4 DB	94	53
2,4,5 TP	100	82
Metolachlor	104	83
Dinoterb	97	72

although some of the recoveries decreased because of this clean-up step, they allow to reach limits of detection lower than 0.5 µg/l in surface water and good reproducibilities as shown in Table 4.

However, despite its performance and reproducibility, setting-up the experimental conditions of the clean-up step is laborious and time-consuming, especially when compounds over a wide range of polarity are to be recovered. This step has to be studied with real surface water samples, because one problem comes from the dissolution of the extracts. One should also be aware of the conditioning of the Florisil cartridges, which can be a cause for non-reproducible results from one cartridge to another one. The use of automated device is recommended for reproducibility of the whole SPE sequence.

CONCLUSION

Solid-phase extraction associated to the LC analysis is a simple technique for the determination of many pesticides in drinking or surface waters. In drinking water, quantification limits in the low 0.1 µg/l range can be obtained for the simultaneous determination of acidic and neutral herbicides after acidification of the samples using a single C_{18} cartridge. In surface water, interferences due to co-extracted and co-eluted humic and fulvic acids occur and detection limits are around 0.5 µg/l. Lower detection limits require the addition of a clean-up step using solid-phase extraction on Florisil.

There is a real need for developing more selective sorbents. In this direction, immunoaffinity sorbents are being developed which are able to selectively extract a class of pesticide and involve interactions that are not based on the polarity of the analytes. New apolar copolymers have been also recently available which retain the analytes to a more extent. Work is under study for investigating their potential for providing better recoveries of acidic pesticides at higher pH, thus decreasing the effect of the humic and fulvic substances.

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