Multiresidue solid-phase extraction for trace-analysis of pesticides and their metabolites in environmental water

V. Pichon

École Supérieure de Physique et Chimie Industrielles de Paris, Laboratoire Environnement et Chimie Analytique (ERS CNRS 657), 10 rue Vauquelin, 75231 Paris Cedex 05, France

Despite the advances in separation and quantification techniques, the sample preparation is still the weakest link and the time determining step in the whole procedure for trace-analysis of pesticides. In order to reduce the price and time of environmental monitoring, it is relevant to perform multiresidue analysis which includes modern polar pesticides and their degradation products. Multiresidue solid-phase extraction is described taking into account the diversity of chemical functional groups of pesticides with varying polarity and physico-chemical properties.

Recent research on the fate and transformation of pesticides in the environment has pointed out the need for including more and more polar analytes in multiresidue analysis. Liquid chromatography have been shown to be suitable for multiresidue separation of many compounds over a wide range of polarity without previous derivatization. Examples can be found in the literature, the most impressive one being the multiresidue separation of 72 pesticides in one run published by Di Corcia and Marchetti some time ago [1]. However, despite the advances in separation and quantification techniques, no sample can be directly analyzed and a multiresidue extraction is a compulsory step in the analytical procedure.

In recent years, enrichment of trace compounds on suitable sorbents has been shown to be an interesting alternative to LLE, and has now become a reliable and useful tool for sample handling. In addition, many modern pesticides and identified degradation products are fairly soluble in water and are therefore less amenable to solvent extraction.

Automation and new trends in SPE

The solid-phase extraction (SPE) area has been very active these past years, certainly due to the now well-recognized trends for using solvent-free methods in environmental analytical laboratories and for its suitability to automation [2]. The four individual steps of a typical SPE sequence-i) conditioning of the sorbent, ii) application of the sample, iii) rinsing and cleaning of the sample, and iv) desorption and recovery of the analytes to be separated- can be performed sequentially for up to 24 cartridges at the same time using extraction units working under positive or negative pressure. The whole sequence can also be easily automated with devices now available by several companies using any commercial cartridges or extraction disks. Examples are the ASPEC from Gilson, Microlab from Hamilton, AutoTrace and RapidTrace from Zymark. Possibility exists for some of these devices for automatic injection of an aliquot of the final extract into the chromatographic system. The complete automation also exists which couples SPE with direct on-line LC analysis (ASPEC XL from Gilson, Prospekt from Spark Holland, OSP-2 from Merck). These last two apparatus improved productivity since the next sample is automatically prepared while the previous sample is being analyzed. Therefore, method development can easily be automated with various degrees of automation.

Off-line SPE materials are mainly disposable cartridges and disk membranes. Besides automation, two other main SPE characteristics have been commercially developed. The first one tends to increase the sample thoughput and the second one to broaden the polarity range of analytes to extract.

Restricted flow rates and clogging are often observed when handling water containing suspended solids such as surface water. Various approaches have been developed to solve this problem. One consists in depth filters which can be placed above the cartridge or membrane extraction disk, or which are now integrated in some SPE cartridges providing fast flow rates. Empore disks became recently available with sorbent trapped in a glass fiber matrix. They are thicker and more rigid thus providing faster flow-rate than teflon disks. These disks are also included in cartridges, known as disk cartridges. New laminar disks which consist in a thin bed of microparticles supported in a laminar structure allow the percolation of one litre of surface water without any previous filtration in less than five minutes.

Many sorbents are now specified as specially made for broadening the polarity range of analytes. These include not end-capped C_{18} silicas and monofunctional C_{18} silicas, the aim being to increase the number of non modified silanol groups at the bonded silica surface in order to provide secondary polar interactions with basic polar solutes. Cross-linked styrene-divinylbenzene (SDB) copolymers with high specific areas in the range 500 – 1200 m^2/g are now available by all manufacturers in cartridges and/or in disks. Typical amount of sorbent is 100 to 200 mg and the cartridge designs have been optimized for processing rapidly large volumes of water samples. Carbonaceous sorbents have also been shown to extract very polar analytes.

Article available at http://analusis.edpsciences.org or http://dx.doi.org/10.1051/analusis:199826060091

Selection of the extraction sorbent for multiresidue extraction

Processes involved in SPE are a frontal chromatographic process during the extraction step and a displacement chromatography during the desorption step. The same sorbents as those used in reversed-phase LC are utilized. The analogy which exists between the SPE processes and classical elution chromatography has been shown to allow prediction and optimization of the main SPE parameters from data generated by LC [2-7]. Among the various tools for selecting the sorbent and predicting the recovery according to the percolated sample volume, the most important is the retention factor of the analyte in water, k_w. Therefore, developing a SPE method requires to understand the interactions between the analytes and the sorbents and to know the retention behaviour of the analytes with the extraction sorbent in LC with water as mobile phase, as measured by k_w. The analogy between LC and SPE allowed to model both breakthrough curves and recovery curves according to the sample volume [8].

The extraction of analytes from water requires to select an extraction sorbent which will provide a 90 – 100% recovery with the sample volume required for the necessary quantification. In pesticide analysis, it is necessary to have detection limits in drinking water as low as 0.01 – 0.03 µg/L in order to be able to quantify them at the 0.1 µg/L according to the EEC regulations. In surface water, detection limits of 0.1 µg/L are wished for transport and fate studies. Therefore, according to the detection limits obtained with conventional LC-UV diode arrays detectors or MS interfaces, typical sample volumes using off-line extraction procedures are around 500 mL. With an amount of sorbent of 500 mg, a recovery in the range 90 – 100% will required a sorbent providing log $k_w > 3$ for the analytes.

N-alkyl silicas

C_{18} silicas and to a less extent C_8 silicas have been the universal extraction sorbents for many years [9]. In reversed-phase chromatography, it is well known that hydrophobic compounds are well retained by these sorbents in water as mobile phase and that their separation requires a mobile phase containing an organic solvent whereas polar analytes are difficult to be retained and separated with an aqueous mobile phase. The limitation of using *n*-alkyl silicas will therefore occur for the more polar pesticides and degradation products [1,2,7–11]. For very apolar analytes, one has just to take care of avoiding losses by adsorption on flasks and connection tubes which can be solved by the addition of some organic solvent before the percolation of samples through the extraction device [12,13]. The desorption step may require a strong eluting solvent and a higher volume than 2 or three times the void volume, as usually done for moderately polar analytes.

Limitation for the extraction of polar analytes

The problem in using C_{18} silicas is in the extraction of polar analytes, which can be defined by compounds with water-octanol partition coefficient, log K_{ow}, below 2. To give an example, recoveries of deisopropylatrazine and phenol (receptively log K_{ow} values of 1.2 and 1.5) are lower than 20% with a sample volume of 500 mL and using an extraction disks containing 450 mg of C_{18} silica. By increasing the amount of sorbent to 1 g in the cartridge, the recovery of deisopropylatrazine could be increased to 52 and 44% from a sample volume of 1 L using respectively C_{18} Polar Plus from J.T. Baker and LiChrolut RP18 from Merck.

Since the retention mechanism is primarily governed by hydrophobic interactions between the analyte and the carbonaceous moieties of the alkyl chains grafted at the silica surface, a relation has been observed between the retention factors of the analytes and their water-octanol partition coefficient (K_{ow}). A linear relation was found between the average log k_w values and log K_{ow} for closely related compounds and even for compounds having different polarities and chemical properties [14]. For example, 60 compounds covering a wide range of structure from polar aniline (log K_{ow} = 0.91) to the very hydrophobic *p,p'*-DDT (log K_{ow} = 6.2) are related by log k_w = 0.988 (± 0.051) log K_{ow} + 0.020 (± 0.060). Therefore, k_w values can be approximated without any additional measurements when log K_{ow} values are available. These values have been considered confidential for many years and some of them can be found in a review from Noble [15]. They have been recently given by many manufacturers and have been reported in the last edition of the Pesticide Manual for most pesticides [16].

Therefore, if the more polar of the mixture to be analyzed have log $K_{ow} > 2.5 – 3$, SPE C_{18} silicas are in general appropriate for multiresidue extraction.

The trends in LC alkyl silicas is to reduced at maximum the number of residual silanols. Therefore, trifunctionnal silanes are preferred over monochloro silanes for the bonding synthesis because a layer or multiple carbon-siloxane covalent bonds on the silica surface is formed. The objective in SPE is to increase at maximum hydrophobic interactions and the surface coverage so that porous silica is usually selected, with an average surface areas above 500 m^2/g and with average carbon content of 17 – 18% for *n*-alkyl-silicas. These C_{18} silicas will provide the highest retention for the more polar analytes. Similarly to LC phase, the SPE alkyl silicas were first endcapped. But, in order to enhance secondary interactions, it was interesting to increase the number of residual silanol groups by eliminating endcapping procedures or applying slight ones, or by using monofunctional silane and no endcapping. Hydrogen bonding interactions and especially, ionic interactions with polar basic after pH adjustment can be increased and that is the reason of the broader range of polarity with can be achieved by these silicas specially designed for polar analytes analytes. However, even if an increase of recoveries for some polar basic analytes have been observed, the increase in log k_w values is small, 0.2 – 0.5 in log units, as compared to that obtained when comparing any C_{18} silica to any SDB sorbent as shown below.

Application to drinking water samples

The potential for determining many pesticides over a wide range of polarity in drinking water at the low 0.1 µg/L is shown in figure 1 [17].

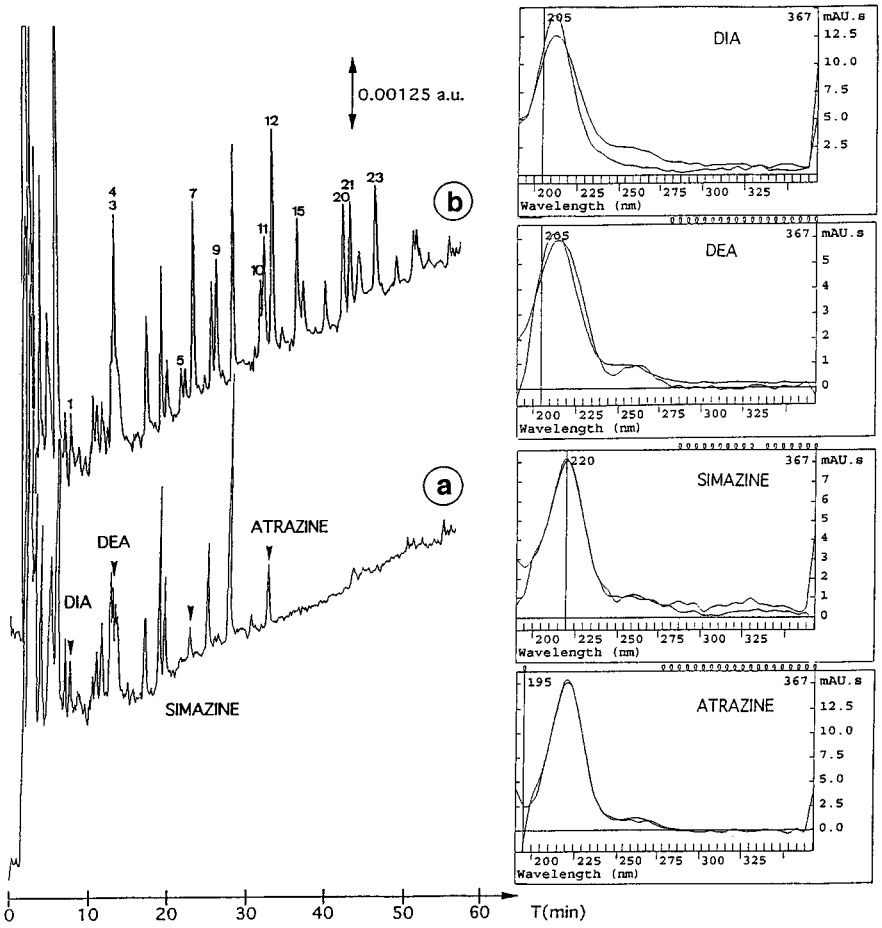

Figure 1. Chromatograms corresponding to a 50 µL extract from 500 mL of drinking water a) non-spiked and b) spiked with 0.1 µg/L of each analyte (adapted from Ref. [17]). Preconcentration using 500 mg C_{18} silica cartridge, desorption with 4 mL of methanol, evaporation to dryness, and addition of 500 µL of an acetonitrile/water mixture (20/80, v/v). Analytical column: Supelcosil LC-18-DB 25 cm × 4.6 mm I.D.; acetonitrile gradient with 0.005 M phosphate buffer at pH 7; UV detection at 220 nm. Peaks: 1, DIA; 2, fenuron; 3, OHA; 4, DEA; 5, hexazinone; 6, metoxuron; 7, simazine; 8, monuron; 9, cyanazine; 10, metabenzthiazuron; 11, simetryne; 12, atrazine; 13, chlortoluron; 14, fluometuron; 15, prometon; 16, monolinuron; 17, isoproturon; 18, diuron; 19, difenoxuron; 20, sebutylazine; 21, propazine; 22, buturon; 23, terbutylazine; 24, linuron; 25, chlorbromuron; 26, chlorooxuron; 27, difluzbenzuron; 28, neburon.

The group of triazines and phenylureas have been selected because they include some polar analytes such as the degradation products of atrazine, i.e. deisopropylatrazine, hydroxyatrazine and deethylatrazine, and fenuron or metoxuron (with log k_w lower or around 2.5), many moderately polar ones and rather apolar pesticides such as neburon (log K_{ow} = 4.3). The analytical separation was carried out by reversed-phase chromatography using a C_{18} analytical column and an acetonitrile gradient in phosphate buffer at pH 7. The separation was not optimised because the occurrence of each compound in the same sample is unlikely. Only some target compounds have to be well separated on the basis of their amount of usage. In addition, co-eluted analytes do not belong to the same group and can easily be differentiated by the UV diode array detector (DAD). The chromatogram figure 1b represents the chromatograms at 220 nm obtained for an extract from 500 mL of drinking water spiked with 0.1 µg/L of each pesticide, after dissolving the dry extract in 500 µL of mobile phase and when injecting a 50-µL aliquot into the analytical column. Recoveries were above 85 – 90% for each analyte, except the early eluted peaks 1 to 4 for which recoveries were respectively 26, 51, 68 and 68%. Recoveries of peak 7 and 12 were even higher, due the presence of these compounds in the sample, as shown in figure 1a where a non-spiked sample was analysed with the same experimental conditions. The occurrence of simazine (peak 7) and atrazine (peak 12) were confirmed by 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 retention times and the two UV spectra was excellent so that no further confirmation was required. The peaks which showed up at 7.9 and at 13.3 min can be deisopropylatrazine and deethylatrazine, but the match was not excellent and another mean should required for confirmation.

Multiresidue extraction including acidic pesticides: Matrix effects and pH of samples

Acidic herbicides are not (or slightly) retained by C_{18} silica in their ionic form so that they can be extracted using a C_{18}

Table I. Recoveries (%) of acidic herbicides after the preconcentration of samples (500 mL) of drinking water adjusted at different pH and spiked with 0.5 µg/L of each analyte using a 500-mg C_{18} cartridge.

Compound	*pK_A*	*pH 2*	*pH 3*	*PH 7*
Dicamba	1.94	89	46	2
Bentazone	3.2	100	100	6
Ioxynil	3.96	98	83	31
MCPP	3.07	104	108	27
2,4 DB	4.8	98	92	38
2,4,5 TP		100	78	10
Dinoterb	5.0	72	49	30

silica cartridge provided the sample has been previously acidified before the percolation. Table I shows the recoveries of extraction measured for some acidic herbicides when percolating 500 mL of drinking water at pH 7 or acidified at pH 2 or 3 with perchloric acid and spiked at 0.5 µg/L.

At pH 7, recoveries are low and for very acidic ones, it is necessary to acidify the samples at pH 2. When natural water samples are acidified at pH 2 and 3, there is an interfering peak due to the co-extraction of humic and fulvic acids as shown in the chromatograms in figure 2 [18].

In recent studies, it was shown that the strong-acid characteristic of those interfering compounds (pK_A 3.0 or less) was due half to keto acids and aromatic carboxylic-group structure, and half to aliphatic carboxyl groups in unusual and/or complex configuration [18,19]. This strong acidity explains why interferences are only detected at acidic pH and are more important at pH 2 than at pH 3. If one takes into account this co-extraction of humic and fulvic acids and optimize the mobile phase gradient in order to elute the first compounds after the interfering peak, most of the pesticides can still be determined at the 0.1 µg/L level in drinking water samples. As shown in figure 2 corresponding to pH 2, only the very polar ones will show up in the interfering peak if the mobile phase gradient was adjusted in order that most of the peaks should be eluted after 20 min. Surface water contains higher amounts of humic and fulvic acids and determination of pesticides at the 0.1 µg/L level become impossible, as shown in figure 3.

Detection limits could be improved with an additional clean-up step using a Florisil cartridge as shown in figure 4 [17].

However setting-up the analytical conditions for this step is laborious and at the origin of additional losses in recoveries. The removal of these interferences by handling the samples at pH 7 and with complete recoveries for acidic analytes can be easily integrated in the extraction using SBD copolymers which is a more straightforward solution.

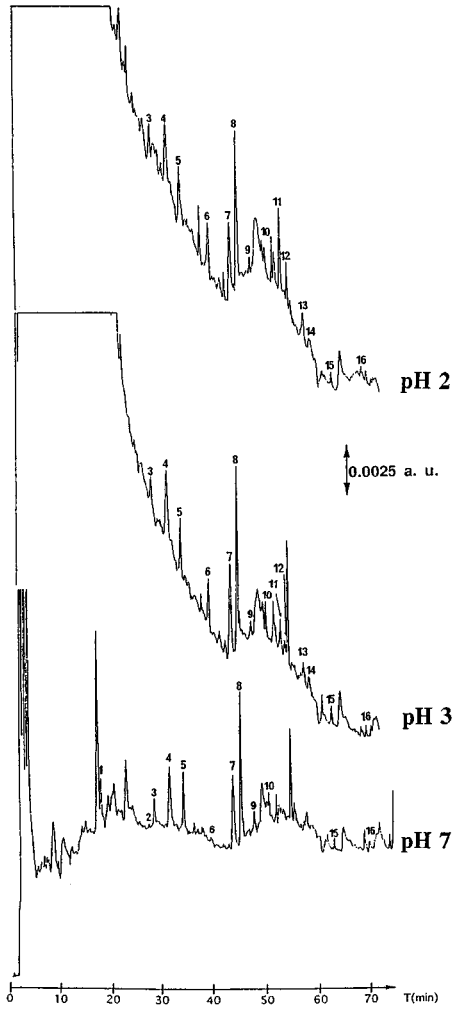

Figure 2. Effect of the pH of the sample on the preconcentration of 500 mL of drinking water spiked at 0.1 µg/L (from Ref. [17]). Preconcentration through a 500 mg C_{18} silica cartridge, desorption with 4 mL of methanol, addition of 50 µL of a mixture containing MeOH/NH_3 (4/1, v/v), evaporation to dryness, and addition of 200 µL of an acetonitrile/water mixture (20/80, v/v) and injection of 50 µL. Analytical column: Bakerbond Narrow Pore C18 silica, 25 cm × 4.6 mm I.D.; acetonitrile gradient with 0.005 M phosphate buffer at pH 3. UV detection at 220 nm. Peaks: 1, chloridazon; 2, aldicarb; 3, metoxuron; 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.

Apolar highly cross-linked styrene-divinylbenzene (SDB) copolymers

LC-grade apolar styrene divinylbenzene polymers (PLRP-S and PRP–1) were only available in prepacked precolumns used in on-line techniques [11,20]. The first disposable devices containing SDB polymers were Empore extraction membranes. These recent years, ultra-clean highly cross-linked SDB polymers with relatively high specific surface areas have been introduced by almost each manufacturer in disposable cartridges and have shown high capabilities to extract polar analytes [21-24]. This is demonstrated by 100% recoveries for phenol and de-isopropylatrazine from a sample volume of 1 L and using 200 mg of SDB sorbents. The retention factors in water have been measured or estimated for a C_{18} silica and SDB with different specific surface areas (see Tab. II).

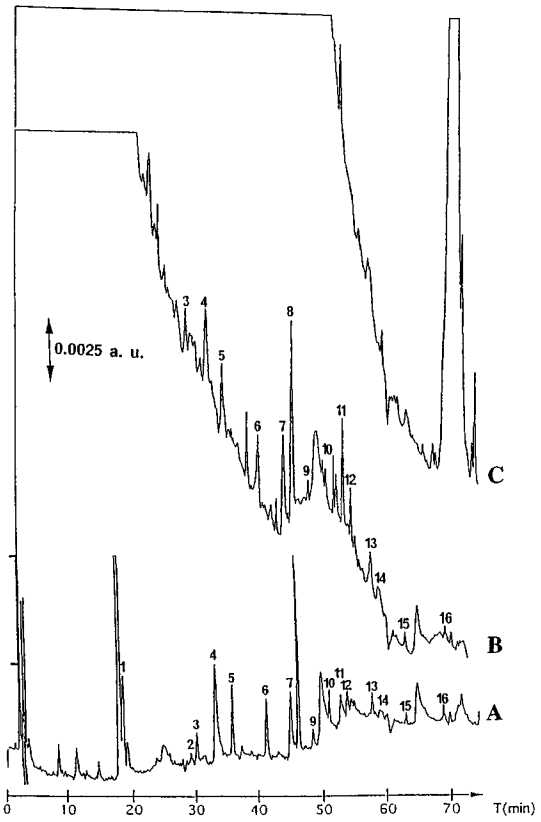

Figure 3. Preconcentration of 500 mL of (A) LC-grade water, (B) ground water, (C) river Seine water spiked with 0.1 µg/L of each analyte and acidified at pH 2 (from Ref. [17]). Other conditions as in figure 2.

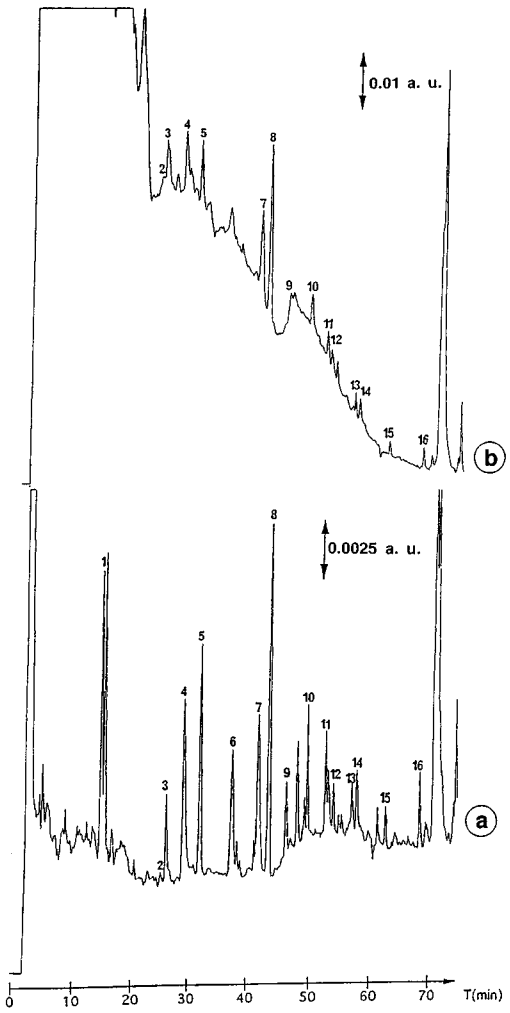

Figure 4. Preconcentration of 500 mL of River Seine spiked with 0.5 µg/L of each analytes, acidified at pH 2 with (a) and without (b) clean-up (from Ref. [17]). Other conditions as in figure 2.

The higher retention of SDB sorbents over C_{18} silicas is due to strong π – π interaction types between analytes and the SDB matrix in addition to common hydrophobic interactions. An increase in retention by a factor 20 to 50 was shown to exist between C_{18} silicas and PRP–1 [2,7,11]. The effect of the surface area is very important and an increase

Table II. Comparison of log k_w obtained on various sorbents for polar analytes and measured or estimated from LC data.

Analytes	*log K_{ow}*	*log k_w*			
		C_{18} silica[a]	*PRP–1 (415 m^2/g)*	*SDB (350 m^2/g)*	*SDB (1060 m^2/g)*
Oxamyl	0.3	1.7 + 0.1	nd	2.8 ± 0.1	4.1 ± 0.2
Chloridazon	1.2	2.3 ± 0.1	nd	3.8 ± 0.2	nd
De-isopropylatrazine	1.2	2.3 ± 0.1	3.1 ± 0.1	3.2 ± 0.2	4.4 ± 0.2
Phenol	1.5	1.9 ± 0.1	nd	3.0 ± 0.1	nd
Aldicarb	1.4	2.5 ± 0.1	nd	4.0 ± 0.2	5.3 ± 0.2
De-ethylatrazine	1.5	2.7 ± 0.1	3.5 ± 0.3	3.5 ± 0.2	4.8 ± 0.3
Simazine	2.3	3.4 ± 0.1	>4	4.1 ± 0.2	5.9 ± 0.3
2-Chlorophenol	2.4	2.9 ± 0.1	>4	3.6 ± 0.2	nd

[a] C_{18} silica in Empore disk from J.T. Baker, specific surface area 510 m^2/g, carbon loading 17 – 18% C, end-capped; nd for not determined.

in retention by a factor 20 to 100 is observed when the specific area of the SDB sorbent increases from 400 to 1 000 m^2/g [24].

Therefore, high cross-linked SDB are the sorbents of choice for multiresidue extraction of a mixture containing highly polar analytes.

Multiresidue extraction including acidic pesticides: Removal of humic and fulvic interferences by percolation of samples at neutral pH

Since new polymeric sorbents provide higher retention for moderately polar pesticides, the retention of acidic pesticides was studied at pH > 3 in order to decrease the amount of co-extracted humic and fulvic acids in surface waters [24]. The recoveries of the acidic pesticides which have been reported in table II using a C_{18} silica cartridge were also measured using a 200-mg SDB cartridge and a sample volume of 500 mL of drinking water spiked with 0.1 µg/L of the acidic analytes and adjusted to pH 7. The recoveries of dicamba which was lower than 3% on a 500-mg C_{18} silica cartridge under the same extraction conditions was measured to 78% and the recoveries of all other acidic compounds was found higher than 85 – 90%. As on C_{18} silicas, humic and fulvic interferences were shown to be co-extracted at pH 3 whereas they are not at pH 7 as shown by figure 5.

The fact they are still not retained at pH 7 is due to their high polarity because of the numerous ionized groups and/or to their different configuration at pH 7 and their possible occurrence in the colloidal fraction [19,20]. However, the consequence of a high retention of acidic pesticides in their ionic form together with the absence of retention of humic and fulvic interferences is the remarkable possibility of determining acidic and neutral pesticides in surface water samples without any clean-up at the low 0.1 µg/L as shown in figure 6 [24].

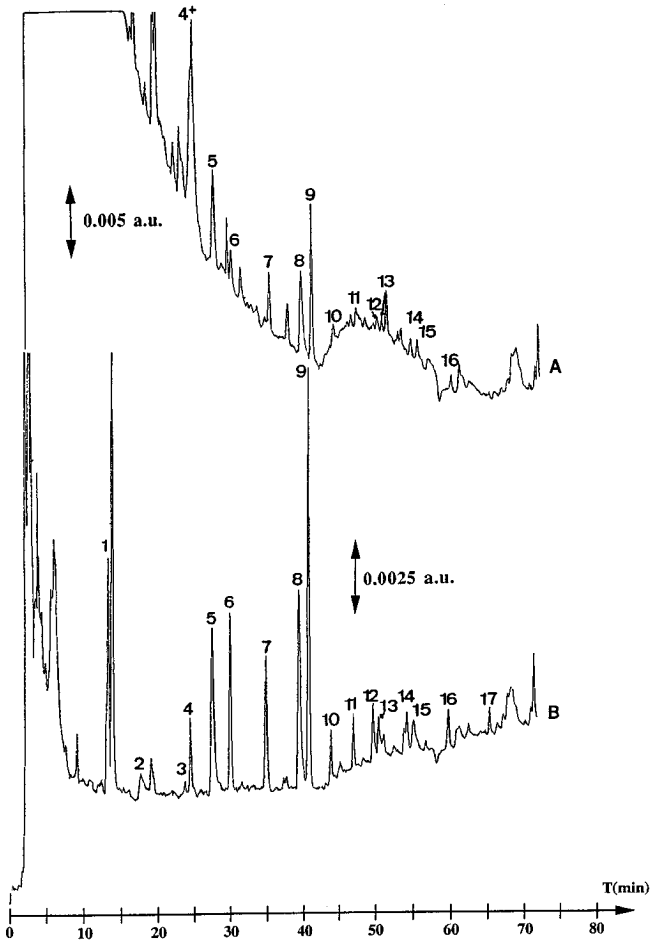

Figure 5. Effect of the pH of the sample on the preconcentration of 500 mL of drinking water spiked with 0. 1 µg/L. Sample (A) adjusted to pH 3 with perchloric acid and (B) not adjusted (pH 7) (from Ref. 24). Preconcentration through a 200-mg SDB cartridge and following the same procedure as in figure 2. Analytical condition similar to figure 2 except numbering of peaks: Peaks: 1, chloridazon; 2, dicamba 3, aldicarb; 4, metoxuron; 5, simazine; 6 cyanazine; 7, bentazone; 8, atrazine; 9, carbaryl; 10, isoproturon; 11,ioxynil; 12, MCPP; 13, difenoxuron, 14, 2,4-DB; 15, 2,4,5 TP; 16, metolachlor; 17, dinoterb.

Carbonaceous sorbents

The most common ones are graphitized carbon blacks (GCB) with a low specific surface area around 100 m^2/g, so that they are often described as non-porous sorbents. Their higher efficiency over C_{18} silica for trapping polar pesticides have been extensively shown by the group of Di Corcia et al. [1,25-28]. GCB are not enough pressure resistant to be used in LC so that no data indicating the LC behaviour of solutes are available. These recent years, a porous graphitic carbon (PGC) has been available in SPE cartridges which

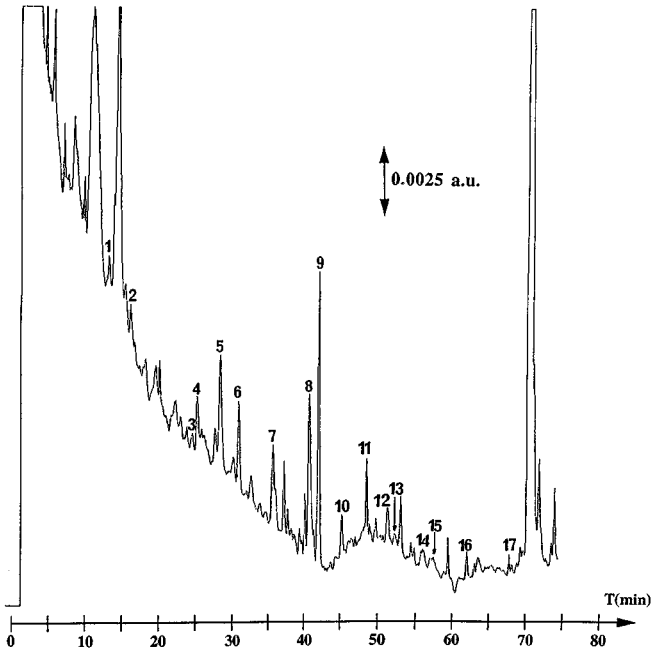

Figure 6. Preconcentration of 500 mL of river Seine water at pH 7 and spiked with 0.1 µg/L of each pesticide (from Ref. [24]). Experimental conditions as in figure 5.

has been derived from that made for LC [29] under the trade mark Hypercarb. It is characterized by a highly homogeneous and ordered structure and by a specific surface area around 120 m^2/g. PGC has been shown to be particularly efficient for the extraction of some polar analytes which cannot be extracted by the SDB polymers such as for instance di- and tri-hydroxyphenols, aminophenols, and other aromatic derivatives containing several polar functional substituents [30-32]. They were also shown to extract the highly polar degradation products of atrazine including cyanuric acid [33,34]. The retention mechanism is based on both hydrophobic and strong electronic interactions, so there is no straight relation between log k_w and log K_{ow} so that prediction from LC data is difficult [35]. Since the primary retention mechanism is not based on hydrophobicity, the desorption can be very difficult since some compounds can still be strongly retained with pure methanol or acetonitrile [32]. Desorption procedures with THF or methylene chloride or backflush desorption with THF were recommended. More details on the potential of carbons can be found in reference [2].

Practical and theoretical problems encountered with multiextraction of compounds over a wide range of polarity and solution

The problem of highly polar analytes can be solved by using SDB polymers with high surface areas. But, non polar pesticides with water solubilities lower than 1 or 2 mg/L such some organochlorine insecticides, trifluraline, chlorpyrifos are poorly recovered. It was verified that this loss was not due to an incomplete desorption of analytes from the cartridge and losses were attributed to an adsorption of these "highly" non polar analytes on vessels and tubings. Increasing the recovery of these compounds was easy by addition of 10% of methanol in the sample before percolation to prevent from these losses. Several studies in the literature show good recoveries for these analytes without adding any organic solvent, but very often, experiments are made with as high spiked concentration as 50 µg/L, so that the part lost by adsorption is negligible. But it is not when samples are spiked at the low µg/L level.

However, the addition of 10% methanol in the sample has the drawback of decreasing the log *k'* values and consequently the breakthrough of analytes and to introduced losses in recoveries of the more polar analytes. In addition, the total solubilization of the extract requires a mixture of water and organic solvent for the more polar ones, but this is often accompanied with an incomplete solubilization of the non polar ones. This result shows that, depending on the respective properties of the more polar and of the less polar analytes in the mixture, multiextraction can be performed with the alone SDB sorbent or not. When the range of polarity contains compounds with extreme polarities, two separated procedures are recommended, one optimized for the polar and moderately polar ones and a second one made for the non polar ones. The procedure for non-polar analytes is better optimized using C_{18} silica because the desorption required a lower volume than SDB. Moreover, the addition of 10% in the samples before percolation has the advantage of including an additional clean-up by limiting the co-extraction of polar interfering compounds. Figures 7A and 7B show the analysis of pesticides included in the French priority list, the polar and moderately polar ones being extracted on a SDB laminar disk and the non-polar ones

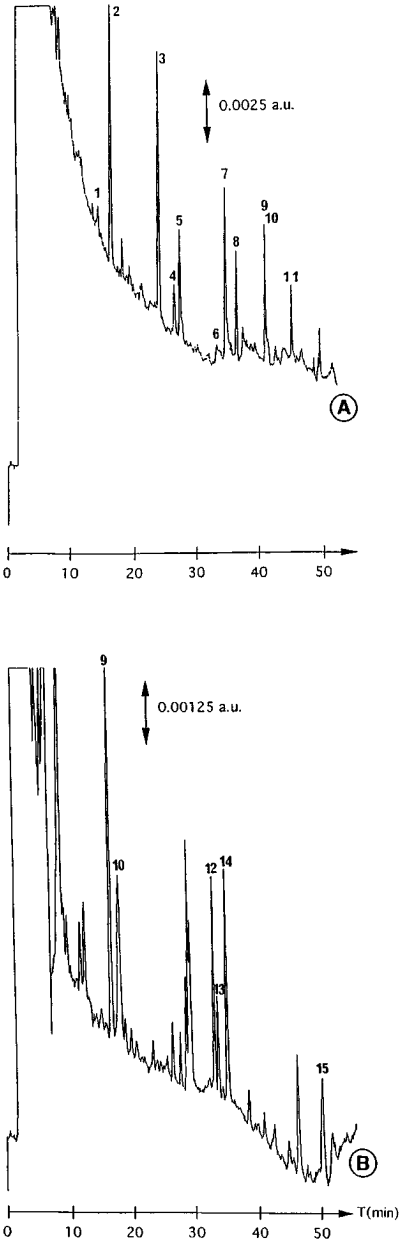

Figure 7. Preconcentration of 250 mL of River Seine water spiked with 0.5 µg/L of each pesticide (A) using the procedure for the polar and moderately polar pesticides and (B) using the procedure for non polar pesticides. (A): Sample adjusted to pH 6, preconcentration using a SDB Speedisk, desorption with acetonitrile. (B): Sample adjusted to pH 6, addition of 25 mL methanol. Preconcentration using a C_{18} Speedisk, desorption with a mixture of methylene chloride and methanol (4/1, v/v) (from Ref. [36]). Analytical conditions : Analytical column: Bakerbond Narrow Pore C_{18} silica, 25 cm × 4.6 mm I.D.; acetonitrile gradient with 0.005 M phosphate buffer at pH 3. UV detection at 220 nm. Peaks: 1, aldicarb; 2, simazine; 3, atrazine; 4, isoproturon; metoxuron; 5, diuron; 6 ioxynil; 7, terbutylazine; 8, linuron; 9, fluzilazole; 10, alachlor; 11, dinoterb; 12, chlorpyriphos; 13, trifluraline; 14, triallate; 15, fenpropimorphe.

using a C_{18} laminar disks with previous addition of 10% methanol in the sample [36]. Detection limits are lower than 0.1 µg/L for most of the pesticides in 250 mL of surface water.

Conclusion

Research in new techniques for sample preparation is a very active area at that moment, partly explained by the need for reducing as much as possible the use, disposal and release in the environment of toxic solvents, together with a reduction of the total analysis cost. This is certainly the near end of the basic liquid-liquid extraction and Florisil clean-up tandem for sample preparation that many laboratories still use.

In Europe, chemists are faced to the drastic drinking water regulatory level of 0.1 µg/L for each pesticide. Therefore, trends are for setting up multiresidue analysis. Trends are also for simplifying the sample preparation labour, increasing its reliability and eliminating the clean-up step of aqueous samples by decreasing as much as possible the amount of interfering components in complex matrices. Regarding these last two aspects, the new polymeric extraction sorbents have a remarkable potential.

References

1. Di Corcia, A.; Marchetti, M. *Environ. Sci. Technol.* **1992**, *26*, 66.
2. Barceló, D.; Hennion, M. C. Sample handling techniques (extraction and clean-up of samples) In: Trace determination of pesticides and their degradation products in water, Elsevier, Amsterdam, NL, 1997; pp 249-349.
3. Miller, K. G.; Poolen C. F. *J. High Resolut. Chromatogr.* **1994**, *7*, 125.
4. Larrivee, M. L.; Poole, C. F. *Anal. Chem.* **1994**, *66*, 63.
5. Seibert, D.; Poole, C. F. *Chromatographia* **1995**, *41*, 51.
6. Mayer, M. L.; Poole, S. K.; Poole, C. F. *J. Chromatogr. A* **1995**, *697*, 89.
7. Hennion, M. C.; Pichon, V. *Environ. Sci. Technol.* **1994**, *28*, 576 A.
8. Hennion, M. C.; Cau-Dit-Coumes, C.; Pichon, V. *J. Chromatogr. A* (in press).
9. Liska, I. *J. Chromatogr.* **1993**, *665*, 163.
10. Font, G.; Manes, J.; Molto, J. C.; Pico, Y. *J. Chromatogr.* **1993**, *642*, 135.
11. Hennion, M. C.; Coquart, V. *J. Chromatrogr.* **1993**, *642*, 211.
12. House, W. A.; Ziqing, O. *Chemosphere* **1992**, *24*, 819.
13. Van der Hoff, G. R.; Pelusio, F.; Brinkman, U. A. Th.; Baumann, R. A.; Van Zoonen, P. *J. Chromatogr. A* **1995**, *719*, 59.
14. Braumann, T. *J. Chromatogr.* **1986**, *373*, 91.
15. Noble, A. *J. Chromatogr*. **1993**, *642*, 3.
16. The Pesticide Manual, 10th edition, Worthing, C. R.; Hance, J. Eds., British Crop Protection Counc, 1995.
17. Pichon, V.; Cau Dit Coumes, C.; Chen, L.; Hennion, M. C. *Intern. J. Environ. Anal. Chem.* **1996**, *65*, 11-25.
18. Leennheer, J. A.; Wershaw, R. L.; Reddy, M. L. *Environ. Sci. Technol.* **1995**, *29*, 393.
19. Leennheer, J. A.; Wershaw, R. L.; Reddy, M. L. *Environ. Sci. Technol.* **1995**, *29*, 399.
20. Hennion, M. C.; Barceló, D. *Anal. Chim. Acta* **1996**, *318*, 1.
21. Guenu, S.; Hennion, M. C. *J. Chromatogr. A* **1996**, *737*, 15.
22. Junker-Buchleit, A.; Witzenbacher, M. *J. Chromatogr. A* **1996**, *737*, 67.
23. Puig, D.; Barceló, D. *Chromatographia* **1995**, *40*, 435.
24. Pichon, V.; Cau Dit Coumes, C.; Chen, L.; Hennion, M. C. *J. Chromatogr. A* **1996**, *737*, 25.
25. Di Corcia, A.; Samperi, M. *Anal. Chem.* **1990**, *62*, 1490.
26. Di Corcia, A.; Marchese, S.; Samperi, R. *J. Chromatogr.* **1993**, *642*, 175.
27. Di Corcia, A.; Marchese, S.; Samperi, R. *J. Chromatogr.* **1993**, *642*, 163.
28. Di Corcia, A.; Samperi, R.; Marcomini, A.; Stelluto, S. *Anal. Chem.* **1993**, *65*, 907.
29. Knox, J. H.; Kaur, B.; Millward, G. R. *J. Chromatogr.* **1986**, *352*, 3.
30. Coquart, V.; Hennion, M. C. *J. Chromatogr*. **1992**, *600*, 195.
31. Guenu, S.; Hennion, M. C. *J. Chromatogr. A* **1994**, *665*, 243.
32. Guenu, S.; Hennion, M. C. *J. Chromatogr. A* **1996**, *725*, 57.
33. Pichon, V.; Chen, L.; Guenu, S.; Hennion, M. C. *J. Chromatogr. A* **1995**, *711*, 257.
34. Crescenzi, C.; Di Corcia, A.; Guerriero, E.; Samperi, R. *Environ. Sci. Technol*. **1997**, *31*, 479.
34. Hennion, M. C.; Coquart, V.; Guenu, S.; Sella, C. *J. Chromatrogr*. *A* **1995**, *712*, 287.
36. Pichon, V.; Charpak, M.; Hennion, M. C. *J. Chromatogr*. *A* **1998**, *795*, 83.