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# Trace analysis of polar organic pollutants in aqueous samples Tools for the rapid prediction and optimisation of the solid-phase extraction parameters

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## Abstract

A method development is given for predicting the main solid-phase extraction parameters with emphasis to polar analytes which are poorly extracted using popular C<sub>18</sub> silicas. Recoveries and breakthrough curves have been modelled according to the sample volume. From the knowledge of the sample volume to be handled for the required detection level in the sample, the prediction of the necessary retention factor in water,  $\log k_w$ , can be done in order to have recoveries at least above 85%. The selection of the sorbents and amounts of sorbents allowing the predicted  $\log k_w$  values is discussed according to the knowledge of interactions between analyte, matrix and common reversed-phases sorbents (standard C<sub>18</sub> silicas, specifically designed C<sub>18</sub> silica for polar analytes, apolar copolymers, carbon-based sorbents). © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Liquid–liquid extraction (LLE) dramatically suffers from the obligatory reduction of the use of chlorinated solvents in analytical laboratories. Micro-LLE has been introduced in some US Environmental Protection Agency (EPA) methods, but does not allow trace detection at the low 0.1 µg/l level, as required for monitoring pesticides in drinking water in European countries [1]. Moreover, polar pollutants are often partly soluble in water and cannot be extracted with good recoveries whatever the organic solvent selected [2].

Solid-phase extraction (SPE) is a typical solvent-free approach requiring only 1 to 5 ml of non-chlorinated organic solvent to extract one litre of

water samples. But, SPE is not as straightforward as LLE. Many polar organic compounds are better analyzed and quantified by liquid chromatography (LC) which often requires the handling of sample volumes in the range 100–500 ml for quantification at the 0.1 µg/l level. The most popular C<sub>18</sub> silica extraction sorbent is always first tried, but rather unsuccessfully because low recoveries are obtained with polar organic pollutants [1,3–6]. Other sorbents are available, but, it appears that the selection of the appropriate sorbent is a difficult task. Many SPE methods are poorly developed with little consideration given to the chemistry involved in the process. It is certainly due in part to the fact that in analytical laboratories, the sample preparation is not recognized as an important step in the whole analytical scheme, and often given to the less trained chemist. But, it is also due to the fact that the literature is rather poor

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which provides the necessary knowledge and guidelines for the selection of the extraction sorbent and other SPE relevant parameters, according to the polarity of the solutes and to the sample volume required to meet the required concentration level.

However, the SPE area has been very active these last few years with regards to the automation of the SPE sequence and on-line coupling with chromatography [7–9]. Besides the classical cartridges, new formats have been introduced. Empore type disks became available with the sorbent in a glass fiber matrix. They are thicker and more rigid thus providing faster flow-rates than PTFE disks [10]. The most recent ones are laminar extraction disks engineered for very high throughput, since they allow the percolation of 1 l of surface water within 5 min without previous filtration [11]. New sorbents have also been commercialized, especially for the extraction of polar analytes: various  $C_{18}$  silicas, including those designed for polar compounds, several copolymers of the styrene–divinylbenzene (PS–DVB), graphitized carbons, mixed-mode sorbents and also cartridges packed with doubled layers beds.

The analogy which exists between the SPE process and classical elution LC allows prediction of the SPE parameters from data generated by LC [1,12–16]. But in many studies emphasis has been only given to the breakthrough volume which can be related to the retention factor of the analytes obtained with water as mobile phase,  $k_w$  [17–22]. These predictions based on  $k_w$  values in reversed-phase chromatography with  $C_{18}$  silicas use either approximate parameters such as octanol–water partition coefficients or more accurate solvatochromic parameters [23].

To understand the process, it is necessary to understand the interactions between sorbent, analyte and matrix, and not only for  $C_{18}$  silicas. The aim of this work is to provide rules for a rapid selection of the sorbent and other experimental parameters with emphasis given to the extraction of very polar analytes. A relevant parameter is to obtain a recovery in the range 85–100% with a sufficient sample volume for detection. The modelling of the curves recovery versus the sample volume for a set of  $k_w$  values indicates the combination of values to be selected that provides the required recovery. From the knowledge of the required trace-concentration level in the sample, of the detection limits of the

analytical systems used and of the polarity of the analytes, the SPE parameters are predicted. The necessary characteristics of various sorbents are also given in order to meet these predicted parameters.

## 2. Prediction of the SPE parameters

Processes involved in SPE are a frontal chromatography during the extraction step and a displacement chromatography during the desorption step. The breakthrough volume has received much attention because it represents the maximal sample volume which can be percolated with a theoretical 100% recovery.

### 2.1. Relation between breakthrough volumes, recoveries and LC data

Breakthrough occurs either when the analyte of interest is no longer retained by the sorbent or when the capacity of the sorbent has been overloaded [11]. In practical environmental analysis where concentrations are typically of the  $\mu\text{g/l}$  order, breakthrough is mostly caused by insufficient retention. When a solution spiked with traces of a solute,  $S$ , having an initial UV absorbance  $A_0$ , is percolated through a SPE cartridge, a frontal or breakthrough curve can be observed, beginning at a volume,  $V_b$ , usually defined at 1% of initial absorbance  $A_0$  up to a volume,  $V_m$ , defined at 99% of initial absorbance, where the effluent has the same composition as that of the spiked water sample. Under ideal conditions, this curve has a bilogarithmic shape, the inflection point of which is the retention volume,  $V_r$ , of the analyte. If the same SPE column is used in elution chromatography with water as mobile phase and with the same flow-rate, the injection of 10 or 20  $\mu\text{l}$  of a concentrated solution of the same analyte  $S$  will generate a peak detected at the same volume  $V_r$ . The recovery, defined as the ratio between the amount extracted to the amount percolated depends on the sample volume percolated and is theoretically 100% recovery only for a sample volume equal or lower than  $V_b$ .

### 2.2. Prediction of breakthrough volumes and recoveries from LC data

The breakthrough volume can be estimated using

$V_r$ , which is related to chromatographic data and cartridge or pre-column characteristics by the relation:

$$V_r = V_0(1 + k_w) \quad (1)$$

where  $V_0$  is the void volume of the pre-column or the cartridge and  $k_w$  is the retention factor of the solute eluted by water.  $V_0$  can be calculated from the porosity of the sorbent ( $\varepsilon$ ) and the geometric volume ( $V_c$ ) of the pre-column or sorbent bed in the cartridge or disk ( $V_0 = \varepsilon V_c$ ). Most of the reversed-phase sorbents used in cartridges have an average porosity between 0.65–0.70. With an average density of 0.6 g/ml for the  $C_{18}$  silica used in cartridges,  $V_0$  is estimated as 0.12 ml/100 mg of sorbent.

The  $V_b$  values read at 1% of the initial absorbance can be also calculated from the  $k_w$  values as developed below, because  $V_r$  is linked to  $V_b$  by the relation:

$$V_b = V_r - 2.3\sigma_v \quad (2)$$

where  $\sigma_v$  is the standard deviation depending on the axial dispersion along the bed of particles in the pre-column or cartridge.  $V_b$  is therefore controlled by retention and kinetic parameters [1,12,14,16,23]. The  $\sigma_v$  term can be calculated if the number of theoretical plates,  $N$ , of the pre-column or cartridge is known by the relation:

$$\sigma_v = (V_0/\sqrt{N})(1 + k_w) \quad (3)$$

$N$  can be directly measured with pre-columns because the on-line set-up can allow the recording of breakthrough curve or of the elution peaks by direct injection onto a pre-column [13]. It is much more difficult to measure the efficiency of a SPE cartridge or that of an extraction disk, so that  $N$  has to be estimated. Miller and Poole [16] have studied the kinetic and retention properties of an SPE cartridge packed with 500 mg of  $C_{18}$  silica and they measured an average of 20 theoretical plates for a flow-rate of 5 ml/min.

The breakthrough curves have been modelled according to the relations described above and the mathematical representation of the breakthrough curves as function of the percolated volume which was described in Ref. [13]. In order to compare with experimental curves, the effect of  $\log k_w$  on the shape of the curves has been modelled for a sorbent

having a void volume of 0.54 ml (which corresponds to an extraction disk containing 450 mg of sorbent) and with 20 plates. The Fig. 1 reports the general shape of the breakthrough curves depending on the  $\log k_w$  values of the analytes, varying in the range 1.5–3.7 which corresponds to a range of relatively polar to non-polar compounds when reversed-phase sorbents are used.

The corresponding theoretical recovery curves are represented in Fig. 2. First, the more polar the analytes are, the sharper the fronts are. These curves are much more relevant from a practical point of view than breakthrough curves. On one hand, they show that breakthrough can be overloaded to a great extent, with small losses in recoveries, for compounds with high  $\log k_w$  values. For example, a compound characterized by a  $\log k_w$  of 2.9 (calculated  $V_r$  value of 430 ml), has a breakthrough volume of 210 ml, but, the theoretical recovery value obtained with a sample volume of 500 ml is still around 85%. Only compounds with  $\log k_w$  lower than 2.5 will be extracted with recoveries lower than 50% with a 500-ml sample volume. On the other hand, when  $\log k_w$  is lower than 2, the recovery decreases rapidly as soon as overloading of  $V_b$  occurs.

Since it is difficult to estimate  $N$ , especially in cartridges, it appeared necessary to evaluate the effect of this parameter on recovery curves. Fig. 3 shows the predicted recovery curves for a compound characterised by a  $\log k_w$  value of 2.7 using a sorbent containing 10 and 20 plates and having a  $V_0$  value of 0.54 ml. With 10 plates the  $V_b$  value is 100 ml. If  $N$  is underestimated and equal to 20 then  $V_b$  is 150 ml. However, with a sample volume of 150 ml and 10 plates, the recovery is still 98%. Therefore, the error is of the order of the experimental ones.

Depending on the sample volume required, these theoretical curves indicate the necessary  $k_w$  for obtaining a recovery in the range 90–100%, so that  $k_w$  is the most relevant parameter to be known for prediction. The practical problem is then to select a sorbent able to provide the required  $k_w$  value.

### 3. Experimental

#### 3.1. Apparatus

A Model 9012 LC system equipped with a Model

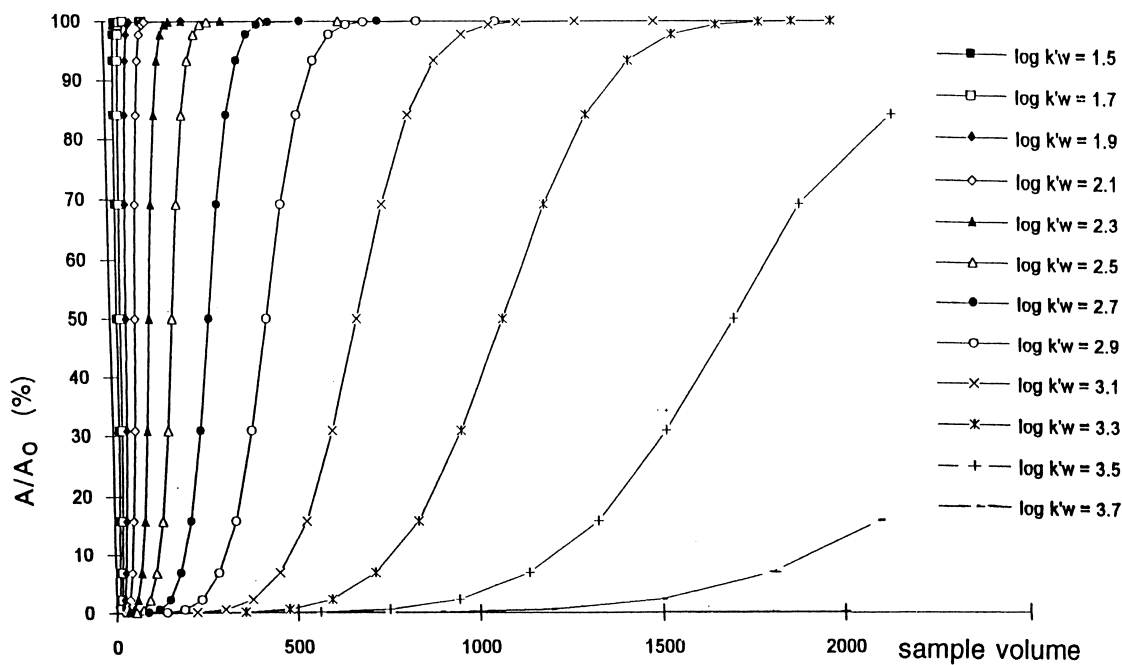


Fig. 1. Effect of the  $\log k'_w$  values of the analyte on theoretical breakthrough curves versus sample volume in ml (prediction assuming 20 plates in the cartridge or disk, and calculated with 450 mg of sorbent).

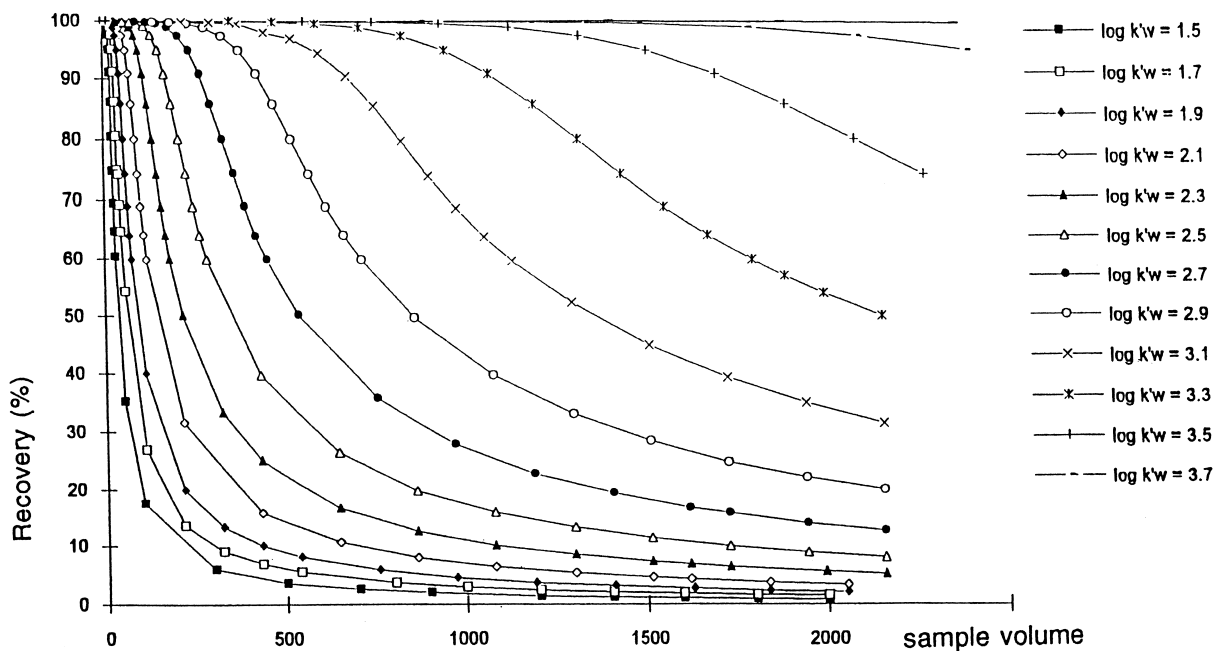


Fig. 2. Effect of the  $\log k'_w$  values of the analyte on theoretical recovery curves versus sample volume in ml (prediction assuming 20 plates in the cartridge or disk, and calculated with 450 mg of sorbent).

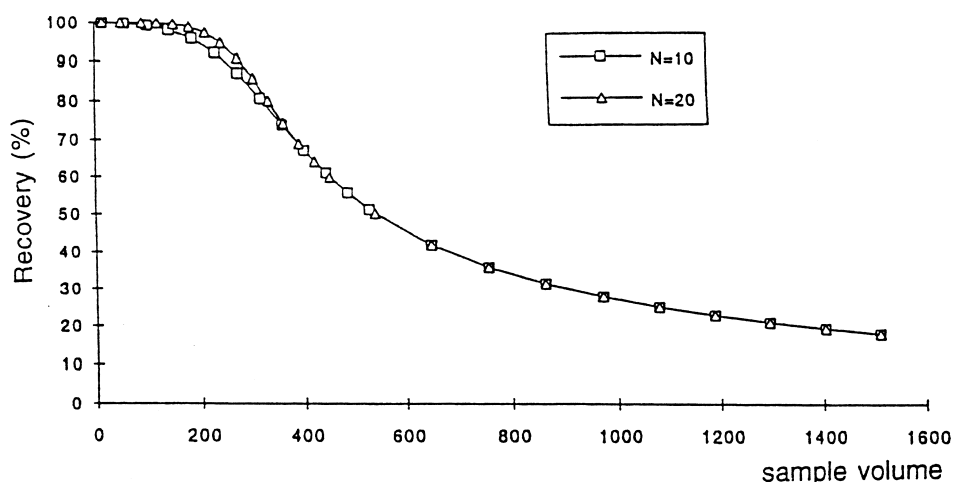


Fig. 3. Effect of the number of plates ( $N=10$ ) on the recovery curves (constructed for  $\log k_w=2.7$  and calculated with 450 mg of sorbent).

9065 Polychrom diode array detector (Varian, Palo Alto, CA, USA) was used for direct injection of standard solutions and extracts obtained with off-line preconcentration. On-line percolations of samples were performed with manually packed cartridges or with disposable cartridges using the Prospekt system (Spark Holland, Emmen, Netherlands). The pre-column and analytical columns switching was achieved by connection with Rheodyne (Cotati CA, USA) valves. The off-line simultaneous extraction of six samples was performed using a 12-port vacuum manifold Spe-12, (Mallinckrodt–J.T. Baker France, Noisy-le-Sec, France). The extraction using Empore disks was performed using a Baker Separex apparatus.

### 3.2. Stationary phases and columns

Various commercially available columns (5 to 25 cm  $\times$  4.6 mm I.D.) prepacked with octadecylsilicas were used for retention factor measurements: Bakerbond Narrow Pore 5  $\mu$ m (Mallinckrodt–J.T. Baker), LiChrosorb RP-18 5  $\mu$ m (Merck, Darmstadt, Germany) and Sepralyte (Colochrom, Montgeron, France). A 10 cm  $\times$  4.6 mm I.D. Hypercarb porous graphitic carbon of 5- $\mu$ m particles (Hypersil, Runcorn, UK) and a PRP-1 copolymer, 10  $\mu$ m (Hamilton, Reno, NV, USA) were also used. Commercial pre-columns (10  $\times$  2 mm I.D.) used for on-line preconcentration were from Spark Holland and pre-

packed with Bakerbond  $C_{18}$  silica,  $C_{18}/OH$  and standard octadecylsilica from Analytichem. The disposable cartridges used for off-line extractions were 3-ml cartridges packed with 500 mg of  $C_{18}$  silicas Bakerbond  $C_{18}$  or Polar Plus  $C_{18}$  from J.T. Baker, 500 mg of  $C_{18}$  silica from Supelco, (Bellefonte, PA, USA) or with 200 mg of apolar copolymers such as PS–DVB from J.T. Baker, Isolute ENV+ from IST (Isolute International Sorbent Technology, Hengoed, UK), or Envichrom-P from Supelco. Empore disks containing  $C_{18}$  and PS–DVB were obtained from J.T. Baker.

### 3.3. Chemicals

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

The various pesticides were supplied by Riedel-de Haën (Seelze, Germany), Promochem (Wesel, Germany) or Cluzeau (Sainte-Foi La Grande, France). Stock solution of selected solutes were prepared by weighing and dissolving them in methanol and stored at 4°C. They were used for the preparation of diluted standard solutions and for spiking water samples.

The final spiked samples did not contain more than 0.5% methanol.

### 3.4. Procedure

Retention factor measurements were made using commercial analytical columns with water–methanol mobile phases. The void volume was determined in each mobile phase by injection of 2 M sodium nitrate. Measurements of  $k_w$  on  $C_{18}$  and PS–DVB disks were made by using a 5 cm×4.6 mm I.D. column prepared with a stack of small disks of alternatively 4- and 6-mm in diameter. This kind of stacking was chosen to limit the wall effect. For PS–DVB disks, a short column, 3 cm×4.6 mm I.D. was packed in the same way. The  $k$  measurements corresponding to sorbents contained in cartridges were made by emptying them for packing the 5 cm×4.6 mm I.D. column.

Off-line extraction steps using  $C_{18}$  cartridges were performed as follows: (1) conditioning the cartridge with 5 ml of methanol, (2) equilibrating with 10 ml of LC-grade water, (3) percolating the sample at 10 ml/min, (4) washing the cartridge with 5 ml of LC-grade water, (5) drying the cartridge with an air flow for 30 s, (6) desorption with 4 ml of methanol, (7) evaporation to dryness under a gentle stream of nitrogen, (8) reconstitution of the extract with an aliquot of the mobile phase used for the analysis in LC. A similar procedure was applied to the PS–DVB cartridge, except for desorption which was performed with 2 ml of methanol–acetonitrile (50:50, v/v)

Off-line extraction steps using  $C_{18}$  disks were performed as follows: (1) conditioning with 10 ml of a methanol–acetonitrile (50:50, v/v) mixture followed by 10 ml of methanol, (2) equilibrating with 20 ml of LC-grade water, (3) percolating the sample at 25 ml/min, (4) washing the cartridge with 5 ml of LC-grade water, (5) drying the cartridge with an air flow for 30 s, (6) desorption with twice 4 ml of methanol–acetonitrile (50:50, v/v) mixture at low flow-rate (7) evaporation to dryness under a gentle stream of nitrogen, (8) reconstitution of the extract with an aliquot of the mobile phase used for the analysis in LC. A similar procedure was applied to PS–DVB disks, except for desorption which was

performed by twice 6 ml of methanol–acetonitrile (50:50, v/v) mixture.

## 4. Results and discussion

### 4.1. Agreement between predicted and experimental curves

The agreement between experimental and theoretical recoveries curve has been obtained for a set of polar pesticides, using two types of extraction disks containing 450 mg of  $C_{18}$  silica and 450 mg of PS–DVB polymer, respectively. The  $\log k_w$  values were extrapolated from  $k$  values measured in methanol–water mixture using a short column in order to have experimental values with water rich mobile phases. Fig. 4 reports the experimental variations of the recoveries with the sample volume with the calculated curves for oxamyl and deethylatrazine using a  $C_{18}$  and a PS–DVB disk, respectively. Taking account of the fact that recoveries are obtained with average standard deviations of 10% due to the different steps of the SPE sequence, the agreement between calculated and experimental curves is very good. Breakthrough volumes have been also derived from the recovery curves and the good agreement between experimental and predicted values for a set of polar compounds can be seen in Table 1.

One should also mention the great difference in  $V_b$  values obtained using a  $C_{18}$  disk and a PS–DVB disk. The advantage of using a sorbent providing a larger retention factor in water is shown in Fig. 4 since for oxamyl, a recovery of 25% is observed for a 100-ml sample with a  $C_{18}$  disk and for a 1000-ml sample with a PS–DVB disk.

### 4.2. Recoveries obtained for sample volumes equal to $V_r$ values for polar analytes

Fig. 2 shows that when  $\log k_w$  is lower than 2, the recovery decreases rapidly as soon as overloading of  $V_b$  occurs. Calculation of  $V_b$  is rather time-consuming and its accurate experimental determination difficult. As in practice we just need a rapid approximation of  $V_b$  to appropriately select the sorbent and we have also looked at the approximation of  $V_b$  by  $V_r$  values,

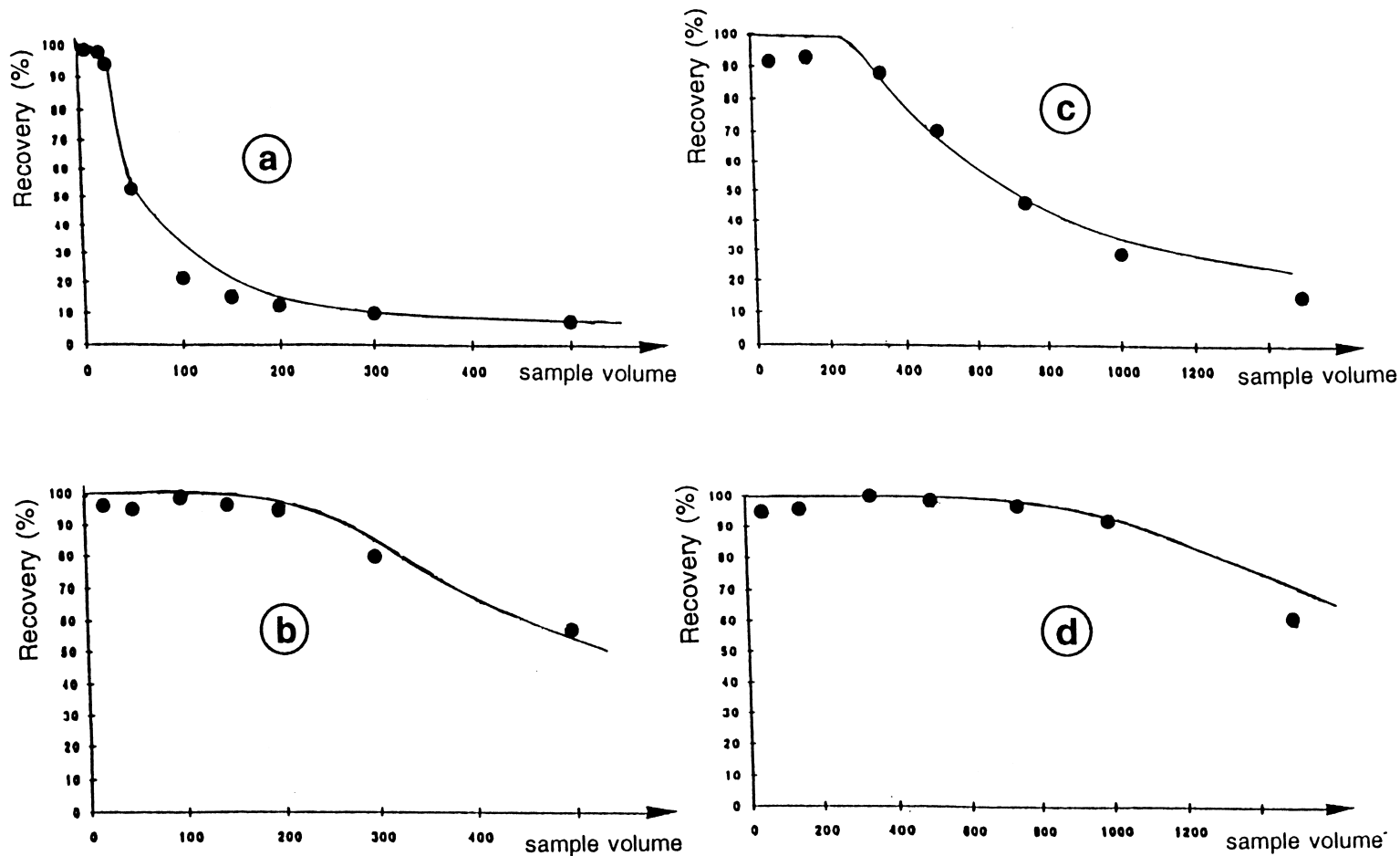


Fig. 4. Agreement between predicted recovery curves (plain line) and (●) experimental values obtained for oxamyl and deethylatrazine (DEA) when increasing the sample volume (ml). (a) Oxamyl and (b) deethylatrazine using a  $C_{18}$  Empore disk, (c) oxamyl and (d) deethylatrazine using a SDB Empore disk (J.T. Baker, diameter 47 mm). Experimental curves obtained using LC-grade water sample spiked with a constant amount (40  $\mu$ g) of analyte (see Section 3.4 for SPE sequences).

Table 1

Comparison between predicted and experimental breakthrough volume,  $V_b$ , retention volume calculated from  $\log k_w$  and recovery obtained for a percolated sample volume equal to  $V_r$  for polar pesticides and degradation products

Analyte	C <sub>18</sub> disk				
	Log $k_w$	Predicted $V_b$ (ml)	Experimental $V_b$ (ml)	Calculated $V_r$ (ml)	Recovery at $V_r$ (%)
Oxamyl	1.7±0.1	14±4	25±5	28±5	65–75
Deisopropyl-atrazine	2.3±0.1	60±15	80±10	108±20	70–80
Aldicarb	2.5±0.1	84±20	80±10	170±45	>80
Deethylatrazine	2.7±0.1	130±30	120±30	270±70	>85

Extrapolated  $\log k_w$  values obtained from experimental  $k'$  measurements using columns packed with the C<sub>18</sub> sorbent.

which are easily calculated from  $V_0$  and  $\log k_w$  values.  $V_r$  and  $V_b$  values have been reported in Table 1, as well as the recoveries obtained for  $V_r$  values. For low  $\log k_w$  value (<2.1), the difference between  $V_r$  and  $V_b$  is small because the front shape is sharp. The difference becomes important for  $\log k_w$  above 2.5 because the breakthrough curves spread ( $V_r$  value calculated to 170 ml,  $V_b$  calculated to 84 ml and experimental  $V_b$  observed at 80±10 ml). For higher  $\log k_w$  values, the fronts spread on more than 200 ml and the approximation is no more valid. However, for all these compounds, when percolating samples equal to  $V_r$ , Table 1 shows that corresponding recoveries are higher than 70%.

#### 4.3. Estimation of $k_w$ values with various *n*-alkyl silicas

##### 4.3.1. Prediction from measurements of retention factors in water–methanol mixtures

Values of  $k_w$  are often estimated from chromatographic measurement using C<sub>18</sub> analytical columns eluted with mobile phases composed of water–methanol mixtures. The advantage of this method is that experimental data are obtained rapidly by measuring the retention factor  $k$  of the analyte in methanol–water phases. Over a methanol content in the range 30–90%, the relationship is usually considered as linear. As shown in Fig. 5a, this has been observed for phenol using a C<sub>18</sub> silica and other reversed-phase sorbents. Then one can conclude that from rapid measurements with three or four mobile phases containing different methanol concentration,  $k_w$ , can be estimated by graphically extrapolating to zero methanol content. However, this relation is known not to be totally linear in water-rich mixture

and a better fit has been obtained with a quadratic relationship for some compounds [24]. We have investigated the shape of the curve  $\log k$ –methanol % for various polar pesticides having different structures and functionalities. Most of the curves have shown that when a wide range of mobile phase is studied polar compounds do not give raise to linear variations. Three typical representatives of the curves are given in the Fig. 5b where a very short analytical column has been used in order to obtain experimental data in water enriched mobile phases. When the  $\log k'$  values of simazine are only measured in the range 45–60% methanol, the curve can be considered as linear and the extrapolated value will be lower than 2 whereas this value is close to 3, using a quadratic extrapolation and experimental data in mobile phases containing a high proportion of water. Extrapolation have been made from the usual range 40–60% of methanol and from quadratic relations with water-rich mobile phases. Results are reported on Table 2 and indicate that extrapolation from the usual range 40–60% of methanol are always lower than real values or those extrapolated from water-rich values.

##### 4.3.2. Relation with the octanol–water partition coefficient for polar analytes

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 octanol–water partition coefficient ( $K_{ow}$ ), which characterizes well the hydrophobicity of a compound and plays an important role in correlating phenomena of physical, chemical, bio-



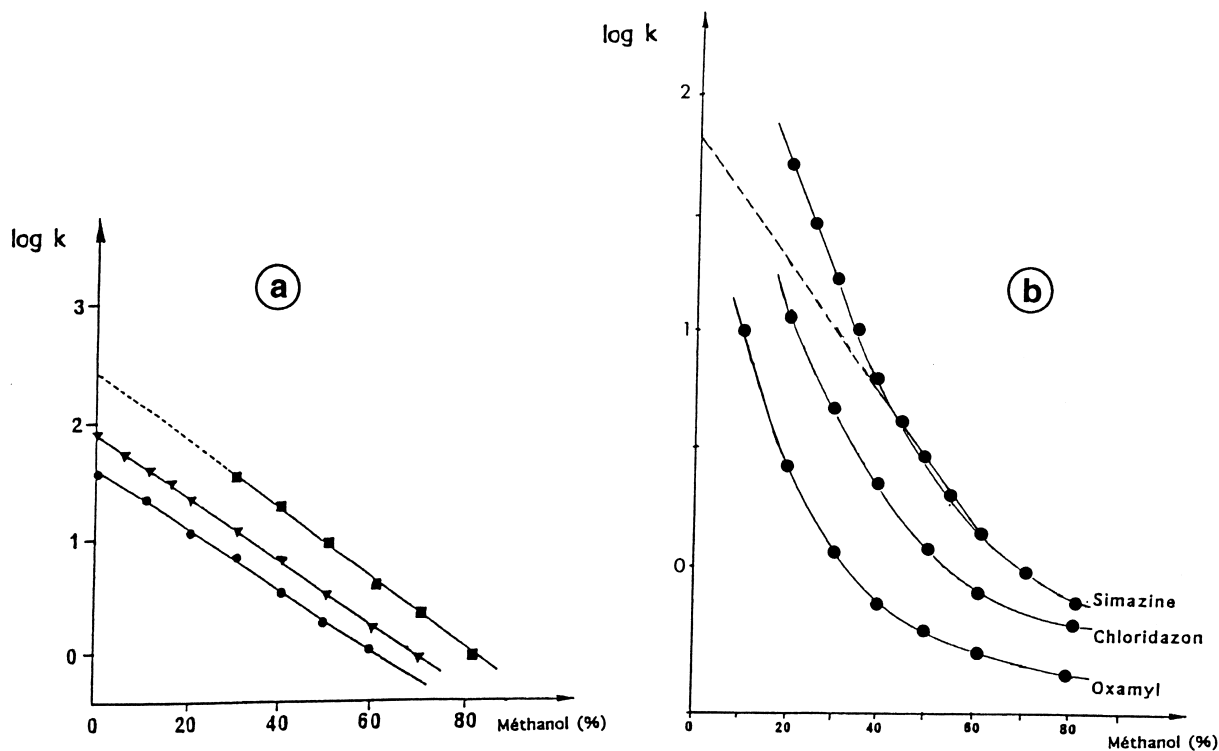


Fig. 5. (a) Variation of the retention factor of phenol with the percentage of methanol in the water–methanol mobile phase as measured with (●)  $C_{18}$  silica RP-18; (■) PRP-1 PS–DVB copolymer and (▼) Hypercarb PGC. (b) Variation of the retention factor of simazine, chloridazon and oxamyl with the percentage of methanol in the water–methanol mobile phase as measured with  $C_{18}$  silica RP-18 using a 5-cm long column to obtain experimental data in water enriched mobile phases.

logical and environmental interest [27–29]. Brauman [28] has gathered many  $\log k_w$  values obtained with different  $C_{18}$  silicas using methanol–water as mobile phases and 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. Therefore,  $k_w$  values can be approximated without any additional measurements when  $\log K_{ow}$  values are available. The  $\log K_{ow}$  values have been gathered by Noble [26] from the literature and one can see that different values have been found in a rather large range, sometimes more than one log unit. In the first column of Table 2 are given the  $\log K_{ow}$  values published in the last edition of the Pesticide Manual [25] and which have been provided for the first time by manufacturers. There is an acceptable agreement between  $\log K_{ow}$  values and extrapolated  $\log k_w$  values from measurement in the range 40–60%

methanol, using the linear relation. This simply indicates that among the different methods for determining  $K_{ow}$  values recently reviewed [30], one widely used is derived from the relation  $\log K_{ow}$  versus  $\log k_w$  values extrapolated from  $k$  values experimentally measured with mobile phases usually containing more than 50–60% methanol [31].

Few data have been published with regards to polar analytes. Our results indicate a large difference between  $\log K_{ow}$  and extrapolated  $\log k_w$  values as close as to real ones. Therefore,  $\log K_{ow}$  is of limited help for predicting the SPE recoveries, especially for very polar analytes with  $\log K_{ow}$  below 1.5. It can just serve as a first estimation, knowing that  $k_w$  thus predicted can be underestimated by a factor 10 to 50. For very polar analytes, a more rapid method is certainly to have in the laboratory a 10- or 5-cm long  $C_{18}$  column, and to extrapolate  $\log k_w$  from  $k$  measurement in a methanol–water mixture contain-

Table 2

Octanol–water partition coefficients of various polar pesticides and degradation products and comparison between  $\log k_w$  values extrapolated from the linear relation  $\log k$  versus methanol content of the mobile phase in the range 40–60% methanol, and from the quadratic relation constructed with  $\log k$  values up to 10 to 20% of methanol

Solute	Log $K_{ow}$		Log $k_w$	
	(a)	(b)	Linear extr. range 40–60%	Quadratic extr. water- rich mixtures
<i>Carbamate pesticides</i>				
Oxamyl		−0.47	0.2	1.9±0.1
Methomyl	1.24	0.1	0.8	1.7±0.1
Aldicarb		1.1–1.6	1.8	2.3±0.1
Carbendazim	1.5	1.4–1.6	1.95	2.2±0.1
Carbofuran		1.2–2.3		2.9±0.2
Aminocarb	1.52	1.7		3.0±0.2
Carbaryl	1.59	2.3–2.8	2.4	3.1±0.2
Captan	2.8	2.4–2.6	3.0	>3.5
Methiocarb	3.34	2.9	3.4	>4
<i>Phenylurea pesticides</i>				
Fenuron	nd	0.9–1	1.4	2.1±0.1
Metoxuron	1.6	1.6	2.1	2.6±0.1
Monuron	nd	1.5–2.1	2.2	2.7±0.1
Monolinuron	2.2	2.3	2.7	>3
Chlortoluron	2.5	2.3	2.7	>3
Isoproturon	2.5	2.25	3.0	>3
Diuron	2.85	2.8	3.0	>3
<i>Triazine and triazinone pesticides</i>				
Desethylatrazine		1.5	1.5	2.6±0.1
Hydroxyatrazine			1.5	2.5±0.1
Simazine	2.1	1.5–2.3	2.0	3.0±0.2
Cyanazine	2.1	1.6–2.3	2.1	2.9±0.2
Atrazine	2.5	2.2–2.8	2.5	3.4±0.2
Simetryne	nd	2.6–2.8	2.7	>3.5
Prometon	nd	3–3.1	3.0	>3.5
Propazine		2.9–3.0	3.0	>3.5
Terbutylazine	3.04	3.0–3.1	3.05	>3.5
Metamitron	0.83	0.8	1.4	2.1±0.1
Metribuzin	1.58	1.7	2.15	2.9±0.2
Hexazinone	1.05	1.7	1.5	>3

Water–octanol partition coefficients are (a) from Ref. [25] and (b) from Ref. [26].

ing as high as possible water content. This is rapid and can be easily performed with autosampler and HPLC devices.

#### 4.3.3. Differences between $C_{18}$ LC sorbents, standard $C_{18}$ SPE sorbents and $C_{18}$ SPE sorbents designed for polar analytes

Available cartridges are packed with  $C_{18}$  silicas having different characteristics and it is well established that in LC, retention differs from one to another  $C_{18}$  stationary phase, because retention

depends on the number of  $C_{18}$  chains bonded at the surface of the silica [32]. Extrapolated  $\log k_w$  values have been compared using analytical columns pre-packed with LiChrosorb RP-18, Bakerbond  $C_{18}$  and Sepralyte  $C_{18}$ . The standard deviation ranges between 0.05 and 0.12 for a set of analytes with mean values of  $\log k_w$  between 1.7 and 2.8. These results are in agreement with published works from Braumann et al. [28], when gathering values from different authors and using different  $C_{18}$  columns (mainly Nucleosil, Hypersil and LiChrosorb). The

values extrapolated have been also compared when using commercial prepacked analytical  $C_{18}$  columns and when packing columns with standard sorbents from  $C_{18}$  cartridges coming from three manufacturers. Slightly higher  $k_w$  values were obtained with sorbents in cartridges and this can be explained by the fact that extraction sorbents has been synthesised from silicas having large specific areas. In LC, in order to obtain a better efficiency and a totally apolar material, the trends are to minimize the number of residual silanol groups of the original silica, and for this purpose, a trifunctional silane is used for bonding the *n*-alkyl chains and an “end-capping” is carried out with trimethylsilane after bonding. Very often, the mobile phase contains an organic solvent which is adsorbed to the stationary phase and ensure a good contact between the solute and the solid. However, the purpose of an extraction is different from LC separations and it was observed that the contact between some polar analytes and a totally hydrophobic  $C_{18}$  silica during the SPE process was better when the  $C_{18}$  silica was prepared using a monofunctional silane and was not end-capped or contained some polar groups in addition to the alkyl chains. That are the characteristics of various  $C_{18}$  SPE cartridges specifically “designed” for trapping polar analytes (often named  $C_{18}/OH$  or polar plus  $C_{18}$ ). We have compared recoveries obtained for a set of polar carbamates with an on-line system using pre-columns of the same size but prepacked with two standard  $C_{18}$  sorbents and one  $C_{18}/OH$ . Results reported in Table 3 show that recoveries are slightly

Table 3  
Comparison of recoveries obtained for polar carbamates using different extraction sorbents in the pre-column (two standard  $C_{18}$  silicas, one specifically designed for polar compounds and a PS–DVB copolymer)

Compounds	Recoveries (%)			
	a	b	c	d
Aldicarb sulfone	9	18	16	29
Oxamyl	12	25	22	49
Methomyl	9	19	16	39
Aldicarb	50	102	97	89
Carbofuran	102	98	106	94

Sample volume: 25 ml; pre-column size:  $10 \times 2$  mm I.D., (a)  $C_{18}/OH$  from Analytichem, (b) standard  $C_{18}$  from J.T. Baker, (c) Standard  $C_{18}$  from Analytichem, (d) PLRP-S PS–DVB from Polymer Labs.

lower for the  $C_{18}/OH$  phase and comparable for the two standard  $C_{18}$  sorbents.

Using a monofunctional silane without end-capping provides the highest amount of residual silanol groups. A consequence is that secondary interactions such as hydrogen bonding between silanol groups and polar analytes can occur, thus facilitating their retention. A recent study has compared recoveries obtained for polar priority phenols using an on-line system, and recoveries were found higher with the monofunctional  $C_{18}/OH$  sorbents than standard  $C_{18}$  from IST [6]. As examples, using a 100-ml sample and  $10 \times 2$  mm I.D. pre-columns, recoveries were 25 and 33% for 4-methylphenol and 4-nitrophenol with the standard  $C_{18}$  and 54 and 56%, respectively using  $C_{18}/OH$ . Stronger secondary interactions can also occur also with basic analytes [22,23,33]. But, even if retention of polar analytes can be higher with such  $C_{18}$  silicas due to secondary interactions, one should realise that a two-fold retention induces only an increase of 0.3 units in the  $\log k_w$  value. The increase in retention using polymeric sorbents is far above, as explained below, and these specific silicas will never compete with the new polymers for extraction of polar analytes.

#### 4.4. Apolar PS–DVB copolymer sorbents

Resins with high specific surface areas, around  $1000 \text{ m}^2/\text{g}$ , are now available in disposable cartridges. However, these polymers are not available in analytical columns – they do not possess all the properties required – so that no chromatographic data have been reported up to now. LC data are available only for LC-grade PS–DVB. Retention behaviour of analytes on PRP-1 sorbent has been studied and compared to retention obtained with  $C_{18}$  silicas. First, it was shown that  $\log k_w$  could be also extrapolated from the relation  $\log k_w$ –methanol content [4,3]. For a set of many organic compounds, the results indicated that solutes are about 10- to 40-times higher retained by PRP-1 than by  $C_{18}$  silicas. The highest difference was for benzene derivatives substituted by nitro groups having a strong electron-withdrawing effect and the smallest for hydroxy group showing an electron-donating effect.

The effect of the specific surface area is important

Table 4

Comparison of log  $k_w$  values obtained with  $C_{18}$  silicas, various PS–DVB copolymers and porous graphitic carbons

Compounds	Log $K_{ow}$	Log $k_w$				
		$C_{18}$	PRP-1	PS–DVB (disk)	HSA/PS–DVB	PGC
Cyanuric acid	–0.2	<0.5	<0.5	nd	<0.5	2.6±0.1
Ammeline	–1.2	<0.5	<0.5	nd	<0.5	2.4±0.2
Ammelide	–0.7	<0.5	<0.5	nd	<0.5	2.5±0.2
Hydroxy-DIA	–0.1	1.0±0.1	1.0±0.1	nd	1.8±0.1	3.0±0.2
Hydroxy-DEA	0.2	1.5±0.1	1.8±0.1	nd	2.3±0.2	2.8±0.2
DEDIA	0	1.3±0.1	1.2±0.1	nd	nd	2.8±0.1
Deisopropylatrazine (DIA)	1.2	2.3±0.1	3.1±0.1	3.2±0.2	4.4±0.3	>3.5
Deethylatrazine(DEA)	1.4	2.7±0.1	3.5±0.3	3.5±0.2	4.8±0.3	3.2±0.2
Simazine	2.3	3.4±0.1	>4	4.1±0.2	5.9±0.3	>4
2-Chlorophenol	2.4	2.9±0.1	>4	3.6±0.2		>4
Oxamyl		1.7±0.1	nd	2.8±0.2	4.1±0.3	nd
Aldicarb	1.4	2.5±0.1	nd	4±0.2	5.3±0.3	nd
Carbendazim	1.5		nd	nd	5.7±0.3	>4
Chloridazon		2.3±0.1	nd	3.8±0.2		>4

Log  $k_w$  values extrapolated from the relationships log  $k$ –percentage of methanol.

Cyanuric acid: 2,4,6-trihydroxy-1,3,5-triazine, ammeline: 2,4-diamino-6-hydroxy-1,3,5-triazine; ammelide: 2-amino-4,6-dihydroxy-1,3,5-triazine.

as shown in Table 4. In order to estimate log  $k_w$  values in water-rich mobile phases, 5- and a 3-cm long columns were respectively, laboratory-packed with one of those high specific area PS–DVB (here named HSA/PS–DVB) polymer and with a stacking of PS–DVB polymer disks [34]. Data on  $C_{18}$  silica has also been reported for comparison. The retention factors are similar for PRP-1 and PS–DVB disk, but the specific surface area are not very different (415 and 350 m<sup>2</sup>/g, respectively) and are higher than those observed with  $C_{18}$  silica. With HSA/PS–DVB, there is a large increase in retention, since the difference is between 1.3 and 1.8 in log unit, indicating that this polymer has 20–60-fold more retention power towards polar pesticides than polymers with lower specific areas have. Comparison

with  $C_{18}$  silica is higher than 100-fold. Similar values of  $k_w$  for deisopropylatrazine and deethylatrazine have been extrapolated using PS–DVB, EnviChom P and Isolute ENV+. A study also reported similar recoveries for the extraction of some polar organophosphorus pesticides using LiChrolut EN or PS–DVB [35]. Recoveries have been compared using either LiChrolut EN or Isolute ENV+ 200-mg cartridges for the extraction of polar phenolics and slightly higher recoveries have been obtained using Lichrolut EN, certainly due to the slightly higher specific area [36].

Although they are not yet widely used, these HSA/PS–DVB are the sorbents to be selected for the extraction of very polar analytes when large sample volumes are required [1,6,11,33–40]. Table 5

Table 5

Recoveries (%) of extraction obtained for polar pesticides in water samples spiked at 0.1 µg/l on 47-mm  $C_{18}$  disk (450 mg of sorbent, J.T. Baker, sample 500 ml), 47-mm PS–DVB disk (PS–DVB, J.T. Baker, 450 mg of sorbent, sample 11) and on a 200-mg HSA/PS–DVB cartridge (J.T. Baker, sample 11)

Solute	Log $K_{ow}$	$C_{18}$ disk	PS–DVB disk	HSA/PS–DVB cartridge
Oxamyl	–0.47	<3	27	82
Deisopropylatrazine	1.1	21	53	92
Deethylatrazine	1.5	58	93	100
Carbendazim	1.56	62	84	88
Aldicarb	1.1–1.5	69	72	90
Simazine	1.96	95	90	94

Log  $K_{ow}$  from Ref. [26].

shows examples of high recoveries obtained from 1-l samples. The retention order is similar to that obtained with C<sub>18</sub> silica and the higher the hydrophobicity of the molecule is, the higher retention. But, there is a limit in polarity for extraction of compound. In Table 4, one can see that log  $k_w$  values are lower than 2 for the highly polar degradation products of atrazine. Using a 200-mg PS–DVB cartridge, the recovery for deethyldeisopropylatrazine (2,4-diamino-6-chloro-1,3,5-triazine) was measured to 20±8% with a 500 ml sample volume.

Recent works have also shown that ionic organic compounds are well retained by these HSA/PS–DVB owing to interactions between the PS–DVB matrix and the organic part of the compounds [34]. This is of high interest for the analysis of acidic pesticides (ionisation constants in the range 3–6) which can be extracted under their ionic form from surface waters at pH 7–8 with good recoveries using 500-ml samples. Using C<sub>18</sub> silicas, the extraction of acidic compounds required the acidification of the samples in order to have these acids in their neutral form, because low recoveries are obtained for ionic compounds. But, then, most of the polar compounds cannot be determined due to a large matrix peak obtained at the beginning of the chromatogram when surface water samples are analyzed. This matrix peak is due to fulvic and humic acids which are co-extracted and co-eluted. Using HSA/PS–DVB, humic and fulvic acids are not recovered from the HSA. Therefore, polar analytes can be determined at trace level samples can be analysed at pH 7 because there is a clear baseline at the beginning of the chromatogram.

#### 4.5. Carbon-based sorbents

Carbon-based sorbents are more and more used for the extraction of polar compounds and several carbon-based sorbents are now available for SPE in water [41]. The most common ones are graphitized carbon blacks (GCBs) obtained by heating carbon blacks at high temperature (2700–3000°C) and characterised by an homogeneous structure and a low specific around 100 m<sup>2</sup>/g. Their higher efficiency over C<sub>18</sub> silica for trapping polar pesticides have been extensively shown by the group of Di Corcia and co-workers [5,42–44]. GCBs are not enough pressure resistant to be used in LC so that no data

indicating the LC behaviour of solutes are available. Porous graphitic carbon (PGC) is available in SPE cartridges and is similar to the LC-grade Hypercarb, which appeared at the end of the 1980s [45]. It is characterized by a highly homogeneous and ordered structure and by a specific area around 120 m<sup>2</sup>/g. PGC shows a reversed-phase behaviour in the sense that retention decreases when the methanol content of the mobile phases increases. Owing to its crystalline structure made of large graphitic sheets held together by weak Van der Waals forces, it is often presented as a more retentive reversed-phase sorbent than C<sub>18</sub> silica [46]. But the retention mechanism was shown to be very different from that observed on C<sub>18</sub> silicas or PS–DVB polymers. Compounds are retained by both hydrophobic and electronic interactions, so that non-polar analytes, but also very polar and water-soluble analytes were shown to be retained in water [3,47–50]. As an example, the retention factor in water of the very polar 1,3,5-trihydroxybenzene (phloroglucinol) is about 1000 with PGC whereas it was found 3 with PRP-1 [48]. This compound is not retained by C<sub>18</sub> silica and it was even proposed as an experimental probe for determining the void volume of C<sub>18</sub> columns.

Because the retention mechanism is different, log  $k_w$  cannot be predicted and there is no relation between log  $k'_w$  and log  $K_{ow}$  except for alkylbenzenes. There is even no link at all between the retention order and the hydrophobicity and polarity of the molecule [51]. From a qualitative point of view, it was found that high retention are obtained for planar molecules containing several polar groups with delocalized electronic charges via  $\pi$ -bonds and lone pairs of electrons. The potential of PGC for extracting very polar compounds is shown in Table 4 for dealkylated and hydroxylated degradation products of atrazine down to cyanuric acid [50]. Most of them have log  $K_{ow}$  values lower than 1 indicating that these solutes are more soluble in water than in organic solvents. The limitation of both C<sub>18</sub> silica and PRP-1 polymer is clearly shown for the very polar ammeline, ammeline and cyanuric acid with log  $k_w$  values lower than 0.5 whereas they are higher than 2 with PGC. Using a 200-mg PGC cartridge, recoveries were above 90% with the handling of 250 ml of water sample for all the metabolites except the three more polar ones for which a 500-mg cartridge was required to obtain similar recoveries.

Since no guide can be given for  $\log k_w$  prediction, The only rapid and easy mean is to inject the polar analyte of interest onto an available analytical column of PGC with a methanol–water mobile phase and to estimate  $\log k_w$  values via the relation  $\log k$ –methanol content. As an example, using 200 mg of Hypercarb, deethyldeisopropylatrazine (2,4-diamino-6-chloro-1,3,5-triazine) is completely recovered from a 500 ml water sample, whereas it was at 20% using PS–DVB sorbents. For the extraction of the more polar and cyanuric acid, it was necessary to increase the amount of carbon in the cartridge to 500 mg for complete recovery from 500 ml samples.

One has to take care of the prediction of the desorption conditions, which also are not similar to those observed on  $C_{18}$  silicas or PS–DVB polymers. Methanol and acetonitrile can be inefficient and it is preferable to use methylene chloride or tetrahydrofuran, or to perform desorption in the backflush way compared to the percolation way [51]. Cartridge allowing percolation and desorption in opposite way are now available.

## 5. Conclusions

The selection of the sorbents for the extraction of polar analytes is based on  $\log k_w$  values, provided these data should be available or predicted. We have shown the high potential of PS–DVB and carbonaceous sorbents for the extraction of polar compounds. Thanks to this knowledge, fractionation can be optimised in a polarity base, and recently bilayers cartridges have appeared on the market.

The selectivity of the SPE step is an important characteristic. New trends in SPE development should be to integrate as possible the clean-up step in the SPE step for complex samples. Highly retentive PS–DVB sorbents can trap very polar analytes, but also many other analytes and chromatograms can be very complex. Thanks to the higher retention of analytes by HSA/PS–DVB, addition of an organic solvent can be added in the samples, with good recoveries, although the addition of organic solvent usually dramatically reduce the retention factor [11]. We have mentioned that the elimination of co-interfering humic and fulvic acids can be performed by a better selection of the pH samples. Another area of

development is sorbents based on immunoaffinity chromatography. Their high selectivity has been already demonstrated [51–53]. They will be certainly the sorbents able to extract so polar compounds that cannot not retained by the sorbents presented in this study, because the antigen–antibodies interactions are not based on hydrophobicity.

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