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Review

Solid-phase extraction for multiresidue analysis of organic contaminants in water

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Abstract

To overcome the limitations of the detection systems associated with gas or liquid chromatography, a sample pretreatment is required with the objective to provide a sample fraction enriched with all the target analytes and as free as possible from other matrix components. There is now no doubt that solid-phase extraction (SPE) has now become the method of choice for carrying out simultaneously the extraction and concentration of many compounds in aqueous samples. Many recent applications of SPE to multiresidue analysis are reviewed with an emphasis on the importance of the choice of the sorbent and of the sample volume. SPE is particularly well adapted to multiresidue analysis including compounds from a wide range of polarity or characterized by various physico–chemical properties. However, SPE is not completely free from practical problems inherent to the nature of the compounds or to the coupling to the chromatographic systems. Many examples are reported to illustrate these problems which can in most cases be circumvented. New developments in SPE are also reviewed.

Keywords: Reviews; Solid-phase extraction; Multiresidue analysis; Organic contaminants

Contents

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1. Introduction

Many organic contaminants are present in waters in trace amounts at the μg/l level and often below. As a result, very low detection limits are required for directly monitoring waters or studying the fate and transport of contaminants in the environment. Recent research has pointed out the need to add more and more analytes in multiresidue analysis, among them especially polar and ionisable compounds. In recent years, there has been a growing interest in trace enrichment techniques that use solid-phase extraction (SPE) as an alternative to the laborious and time-consuming liquid–liquid extraction (LLE). This is also due to the high consumption of organic solvents in LLE. In addition, recoveries of many polar analytes obtained using LLE are low because of their relatively high partial solubility in water. SPE has widely developed during the last 5 or 6 years with many improvements in format, automation and also with the introduction of new sorbents with the capability for new ones of trapping polar analytes.

The problems associated with the extraction of compounds with a wide range of physico–chemical properties are numerous and can appear at the different steps of the SPE sequence. As an example, polar compounds are easily lost during the sample percolation due to their low affinity for the sorbent emphasizing the need of a careful selection of the sorbent. Non polar compounds are efficiently trapped on common C_{18} sorbents but they have a tendency to adsorb on the flask walls and the connecting tubes. Moreover, their desorption may be difficult due to their high retention on hydrophobic sorbents. The extraction of ionisable compounds can require an adjustment of the sample pH in order to enhance their retention. Problems can also result from the loss of volatile compounds during the evaporation step or from the reconstitution of dry extracts containing compounds with large differences in water solubility. In addition to the problems related to the analyte properties, interfering compounds in sample matrices can be co-extracted. For instance, humic and fulvic acids are often seen as large interfering peaks co-eluted with the polar analytes that prevent their trace determination.

Obtaining extracts free from matrix interferences in a few steps – a single one when possible – has been recognized as an important goal and selectivity is now included in the development of the SPE procedure. It is clear that the more selective the SPE step is, the more sensitivity is obtained. Hence the recent introduction of new types of sorbents such as the emerging selective immunosorbents or molecular imprinted polymers have recently been introduced in that way.

In this overview are reported recent papers dealing with new developments in SPE for multiresidue analysis of water samples and showing the advantages and limitations of this technique hyphenated to analytical separations in LC or GC. The on-line coupling of SPE with these analytical methods is also discussed.

2. Basic principles of solid-phase extraction

The key of the problem when applying SPE remains the method development and the primary decision for the analysts is the choice of the sorbent that is able to solve their trace-analysis problem. Method development being related to the properties of the analytes of interest, many aspects due to the various physico–chemical properties of compounds included in a multiresidue analysis have to be considered. A first approach for the method development is the process which occurs during the extraction. To a first approximation, this process can be considered as a simple liquid chromatographic process. The sorbent is the stationary phase and the mobile phase is the water constituting the aqueous sample during the extraction step and the organic solvent during the elution step. Compounds that do not elute with the water constituting the matrix of the sample are trapped on the sorbent during the percolation step. High enrichment factors are obtained when analytes are strongly retained by the sorbent in the presence of water, allowing the percolation of a large volume of sample and when there is a low retention when eluting by organic solvents. This enrichment factor is also linked to the method of coupling of SPE to the analytical system: SPE can be used off-line, i.e., the sample treatment is completely separated from the subsequent chromatographic analysis, or on-line, i.e., it is directly integrated to the analytical system.

3. Off-line versus on-line solid-phase extraction sequence

A typical SPE sequence consists of several steps: (i) conditioning the sorbent, (ii) percolating the sample, (iii) rinsing and – when possible – cleaning to remove interfering compounds, (iv) desorption and recovery of the analytes to be separated. In the off-line procedure, the extraction is carried out on a sorbent packed in a cartridge or enmeshed in the inert matrix of a membrane-based extraction disk. The different steps of the SPE procedure can be performed sequentially using up to 24 cartridges at the same time with extraction units working under positive or negative pressure. The whole sequence can also be automated using commercially available devices for cartridges or disks. Such automation has contributed to the SPE development. However, the off-line procedure has the inherent disadvantage of possible losses during the evaporation of the extract and losses of enrichment factors resulting from the injection of only an aliquot of the extract.

On-line coupling of SPE with LC or GC has largely been used. The coupling with LC is easy to perform and was applied to the monitoring of pesticides in spring or surface waters [1–7]. In this system, the sorbent is packed in a pre-column inserted at the loop position of a six-port switching valve connected to a solvent delivery unit that provides the solvent necessary to purge, wash and activate the pre-column and applies the required volume of sample. For the desorption, trapped compounds are directly eluted from the pre-column into the analytical column by a suitable mobile phase used for the analytical separation. More accurate results can be expected because there is no sample manipulation between the extraction and the analytical steps. The sample volume can be lower than in off-line SPE because all the compounds trapped on the sorbent during the sample percolation are transferred and analyzed. On-line automatic devices are also commercially available.

Hogenboom and co-workers have also developed an on-line device based on the use of a single short column (10–20 mm) for both trace enrichment and separation [8–11]. This technique is particularly dedicated to the rapid screening of organic contaminants. It sacrifices the selectivity due to the low efficiency of the short column but takes advantage of the high resolving power of the MS instrument always associated with this technique. With this method, only small volumes are preconcentrated, typically 4–15 ml, thus rendering difficult the detection of very low levels of concentration but allowing to reach concentration levels of 0.5–1 μg/l that are sufficient for the monitoring of surface waters [8]. Two short columns can also be used in tandem to improve the separation of compounds without affecting too much the time of the analytical procedure [12,13].

The on-line coupling of SPE with GC in the case of water analysis is more complicated because it is necessary to remove even the last traces of water before desorption of the compounds into the GC part of the system. Different systems based on N_2 drying of the sorbent before elution [14] or the introduction of a short cartridge containing drying reagents, such as anhydrous sodium sulfate or silica, inserted between the pre-column and the retention gap [15] have been used. Other sophisticated systems have also been used for the coupling of SPE–GC with particular detection systems such as AED [16] or IR [17]. The on-line combination of aqueous-sample preparation with capillary GC was recently reviewed [18,19] and this coupling associated with a mass detector has proven to be very effective for monitoring purposes in association with SPE–LC–DAD [3–5]. As an example, 500 microcontaminants were monitored and identified by MS in the Nitra river (Slovak Republic) [5]. Moreover, sensitivity of the detector associated with GC allows sample volumes as small as 2–20 ml [14,17,18], instead of 100–150 ml in SPE–LC, which can be interesting for the extraction of compounds having low breakthrough volume such as polar phenols [14]. For instance, Fig. 1 corresponds to an on-line SPE–GC–MS procedure applied to the analysis of 10 ml of river Rhine water spiked at the 0.5 μg/l level with about 80 microcontaminants covering a wide range of volatility [20].

Derived from the SPE technique and recently developed by Pawliszyn, solid-phase microextraction (SPME) is a new fast and simple analytical technique based on the partition equilibrium of the analyte between a sorbent, i.e., a solid-phase coated on a silica fiber support and the sample. This

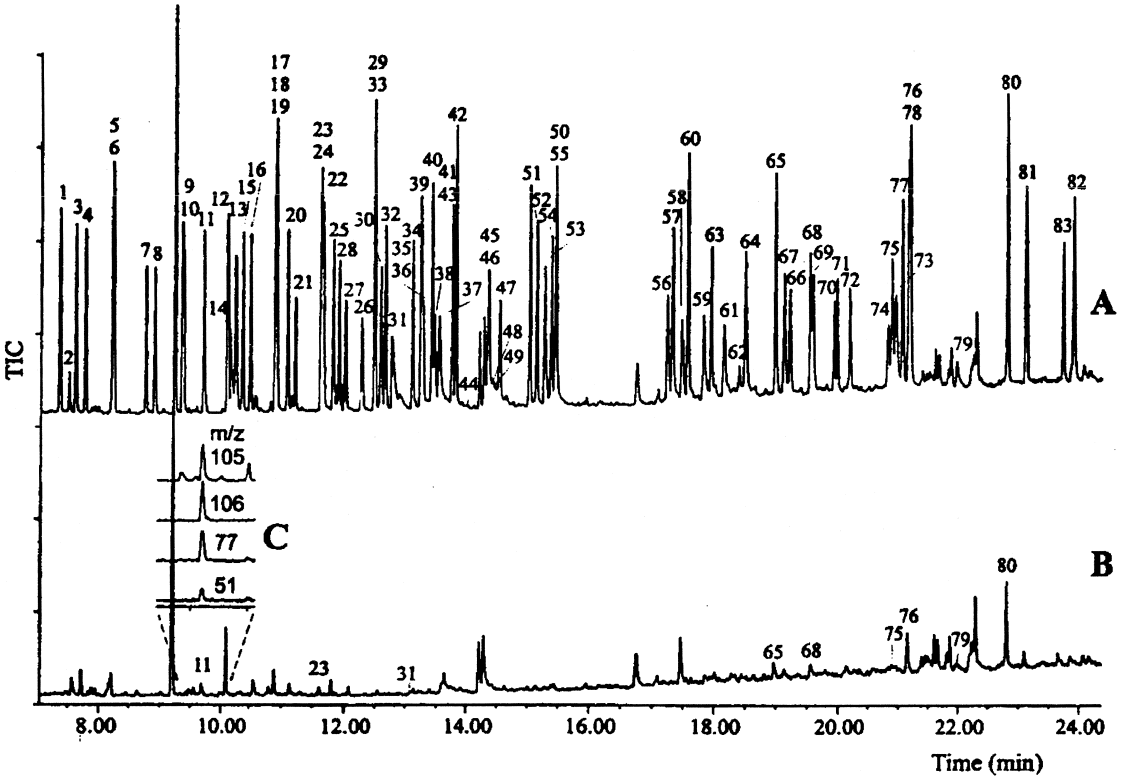

Fig. 1. TIC chromatogram for SPE–GC–MS of 10 ml of river Rhine water (B) non-spiked and (A) spiked at 0.5 μg/l level with 86 microcontaminants including chlorobenzenes, substituted aromatic compounds, anilines and phenolic compounds and organonitrogen and organophosphorus pesticides. The insert (C) shows the mass chromatograms of four characteristic masses of benzaldehyde (*m*/*z* 51, 77, 105 and 106). From Ref. [20].

technique has largely been applied to the trace determination of volatile compounds such as BTEX or chlorinated hydrocarbons. However, the availability of new fibers has also allowed its application to the extraction of various environmental pollutants from water. An automated system of SPME directly coupled to GC is commercially available [21,22]. The coupling between SPME and LC is more difficult. The first application concerned the study of PAHs in water [23] while recent works dealt with the development of specially designed interfaces for the coupling with LC although most applications are still based on the use of GC [24].

4. Choice of the sorbent for the extraction of neutral compounds

The analogy between LC and SPE has largely been described and has shown the possibility to predict and optimize the main SPE parameters from data generated by LC [25–30]. Among the various tools for selecting the sorbent and predicting recoveries according to the percolated sample volume, the most important factor 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 behavior of the analytes with the extraction sorbent in LC. Both breakthrough curves and recovery curves have been modeled according to the sample volume [31] and it was demonstrated that, with an amount of sorbent of 500 mg, a recovery in the range 90–100% for a percolated volume of 500 ml requires a sorbent providing log $k_w > 3$ for the analyte. This guide value is the basis of the choice of the sorbent [25].

The choice of the sorbent is guided first by the

aqueous nature of the samples. The best sorbents are reversed stationary phases, mainly alkyl-modified silica, apolar copolymers and carbonaceous sorbents.

4.1. n-Alkyl bonded silicas

Octadecyl and octyl bonded silicas have been the universal extraction sorbents for many years. Since the retention mechanism is primarily governed by hydrophobic interactions between the analyte and the carbonaceous moieties of the alkyl chain, a relation has been observed between the retention factor of the analyte and its octanol–water partition coefficient (K_{ow}). Therefore, k_w values can be approximated without any additional measurements from K_{ow} values that can be found in the literature or calculated. It has been shown that the use of C_{18} silica is well appropriate for the trace enrichment of compounds characterized by log K_{ow} values higher than 2 [32,33]. As an example, recoveries of deisopropylatrazine and phenol (log K_{ow} of 1.2 and 1.5, respectively) are lower than 20% for a sample volume of 500 ml on a C_{18} silica (disk format, 450 mg). Applications of C_{18} silica to the multiresidue extraction of moderately polar to non-polar analytes has largely been described and used for monitoring purposes [6,7]. Most of these applications concerns the on-line coupling of this sorbent to reversed-phase LC. Recent studies deal with the analysis of organophosphorus pesticides in LC–MS [34], triazine and phenylurea pesticides in LC coupled to FT-IR [35] or a mixture of pesticides including chlorophenoxyacids that require an acidification of the sample to pH 3 to enhance their retention before the on-line SPE–LC–MS [36].

Similarly to LC phases, the SPE alkyl silica phases were first endcapped. But in order to enhance secondary interactions, it was interesting to increase the number of residual silanol groups. Hydrogen bonding interactions and especially, ionic interactions with polar basic compounds after pH adjustment can be increased and that is the reason for the broader range of polarity which can be achieved with these silicas (often named C_{18}-OH or polar plus C_{18}) specially designed for polar analytes. However, if an increase in retention for polar basic compounds has been observed for carbamates [37], phenols [38], metabolites of triazines [39] or basic compounds [28,30], this increase is much lower than that obtained by using any apolar copolymer of polystyrene–divinylbenzene (PS–DVB) and particularly the highly cross-linked copolymers recently commercially available as shown below.

4.2. Apolar copolymers

The higher potential of PS–DVB resins, such as Amberlite XAD-type, over C_{18} silicas for trapping polar compounds was largely demonstrated but these sorbents were not available in prepacked cartridges because they required laborious purification steps before use. The first commercially available PS–DVB copolymers were the LC-grade PRP-1 and PLRP-S in disposable pre-columns designed for on-line set-up. One of the advantages offered by this sorbent over C_{18} silica is its stability when percolating samples in the 1–14 pH range. The good quality of coupling of this polymeric sorbent with C_{18} analytical column has allowed its application to multiresidue extraction including polar compounds that are not extracted on C_{18} silica such as, recently reported, for mixtures of organic contaminants including metabolites of triazines [1,40], phenolic compounds [38] and anilines [41] and for monitoring purposes [1,3–5]. For off-line use, the first PS–DVB sorbent was available in disk format and was used to extract polar compounds with higher recoveries than on C_{18} silicas [38,42–46] and applied to the monitoring of micropollutants from a wide range of polarity (including polar atrazine metabolites and apolar organochloride insecticides) in surface and ground water [47]. PS–DVB disks have also been used on-line using a stainless steel membrane disk holder [43,44]. However, with these polymeric sorbents, recoveries are still low for polar metabolites such as deisopropylatrazine or for compounds such as phenol, aniline when applying sample volumes of 50–150 ml required for the detection after LC analysis [1,38,41,48]. Polar compounds can only be extracted when low sample volumes are percolated, hence the need for detectors as sensitive or specific as those used with GC. For instance, sample volumes of 2 ml were used for the analysis of derivatized phenols and chlorophenols with FID [14], 10–20 ml for the extraction of compounds from different groups detected with MS [15] or IR using a cryotrapping interface [17], and 10 ml for the extraction of organophosphorus compounds detected with AED

[16]. Low sample volumes may also be sufficient in LC analysis associated with DAD for the monitoring of compounds in surface water at the μg/l level. As an example, a 5-ml sample was enough for the monitoring of surface water and the quantification of compounds including polar pesticides such as metamitron and apolar ones such as trifluraline at 1 μg/l [2]. The very polar glyphosate and its degradation product AMPA were also extracted on PLRP-S after a derivatization in the sample with FMOC to improve its retention on the polymeric sorbent and in LC; in this case, a sample volume of 4 ml was enough to reach 0.03 μg/l in LC–ESI-MS [49]. Using a post-column derivatization and fluorescence detection – thus achieving a high sensitivity for the LC analysis – a volume of 5 ml was also sufficient and high recoveries were obtained for the extraction of the polar *N*-methylcarbamates [37]. In this case, recoveries were satisfactory on both PLRP-S and C_{18}-OH but the latter was finally preferred for a better coupling with the C_{18} analytical column. This was also the case for the extraction of phenols [38].

Over the last years, resins with high specific surface areas (in the range 700–1200 m^2/g instead of 350–500 m^2/g) have become commercially available in disposable cartridges. Some studies have shown the high potential of these highly cross-linked polymeric sorbents for the extraction of very polar compounds from water [31,42,47,50–61]. However, these polymers are not available in analytical columns because they do not possess all the properties required for a LC stationary phase. Therefore very few chromatographic data have been reported up to now. These data have been obtained by measurements using laboratory-made analytical columns packed with polymeric sorbent retrieved from commercially available cartridges [31]. With these highly cross-linked polymers, a large increase in the retention was reported, thus indicating that these polymers have 20–60-fold more retention power for polar analytes than the previous PRP-1 or PLRP-S. As an illustration, log k_w values obtained by chromatographic measurements on the different sorbents are reported in Table 1. These results show an increase of the retention by a factor 20–50 for the PS–DVB polymers with a specific surface area of 400 m^2/g when compared with C_{18} silica; this is due to strong additional π–π interaction types generated between analytes and the polymeric matrix. The effect of the specific surface area is important and an increase in the retention by a factor 20–70 is observed when the specific surface area is doubled. Table 2 reports the recoveries of extraction for catechol, phenol, chloro-, nitro- and methylphenols obtained after the percolation of 500, 1000, 1500 ml of water on various PS–DVB sorbents. For a sample volume of 1000 ml, most of the compounds were extracted with recoveries higher than 80% and 60% on the two highly cross-linked polymeric sorbents, i.e., LiChrolut EN and IsolutENV+, respectively and with recoveries between 25 and 55% for the polymeric sorbent with a specific surface area of 550

Table 1
Comparison of log k_w values obtained on various sorbents for polar analytes and measured or estimated from LC data[a]

Analyte	Log K_{ow}	Log k_w				
		C_{18} silica, 510 m^2/g	PRP-1, 415 m^2/g	PS–DVB		PGC, 120 m^2/g
				350 m^2/g	1060 m^2/g	
Oxamyl	−0.47	1.7±0.1	nd	2.8±0.1	4.1±0.2	2.3±0.1
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
Chloridazon	1.19	2.3 ±0.1	nd	3.8 ±0.2	nd	>5
DIA	1.12	2.3±0.1	3.1±0.1	3.2±0.2	4.4±0.2	>3.5
Phenol	1.5	1.9±0.1	nd	3.0±0.1	nd	nd
Aldicarb	0.85–1.6	2.5±0.1	nd	4.0±0.2	5.3±0.2	2.3±0.1
DEA	1.5	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	nd	>4

[a] DIA: Disopropylatrazine, DEA: deethylatrazine. Adapted from Refs. [54] and [31].

Table 2
Mean recoveries (%) obtained on loading different sample volumes spiked to 5 μg/l with each phenolic compound on LiChrolut EN, Isolut ENV+ and Porapack RDX[a]

Compound	Sample volume (ml)								
	Isolut ENV+, 1000 m^2/g			LiChrolut EN, 1200 m^2/g			Porapak RDX, 550 m^2/g		
	500	1000	1500	500	1000	1500	500	1000	1500
Catechol	28	0	0	28	0	0	17	0	0
Phenol	64	59	33	79	79	37	51	40	14
4-Nitrophenol	75	74	68	89	87	45	55	35	25
4-Methylphenol	65	60	50	93	91	38	40	26	18
2,4-Dinitrophenol	72	73	29	79	82	42	48	41	22
2-Chlorophenol	79	60	54	84	84	41	38	29	21
2,4-Dimethylphenol	64	55	53	76	81	37	36	34	19
4-Chloro-3-methylphenol	72	65	61	86	86	42	50	37	27
2,4-Dichlorophenol	67	62	59	80	86	42	53	44	25
2,4,6-Trichlorophenol	85	84	68	104	92	51	60	55	50
Pentachlorophenol	81	65	24	89	87	46	47	40	23

[a] RSD values in the range 4–15% (n=5). Adapted from Ref. [59].

m^2/g. These results show that the similar specific surface areas of LiChrolut EN and IsolutENV+ lead to similar recoveries of extraction. Although an increase in the retention of polar compounds due to the increase in specific surface area was observed, these polymers do not allow the extraction of very polar compounds such as catechol if high sample volume are required. Poor recoveries were obtained for this compound that requires another type of sorbent or the use of volumes lower than 500 ml [59]. Fig. 2a–c correspond to an application of these highly cross-linked PS–DVB sorbents to the off-line extraction of polar compounds (log K_{ow} in the range −0.5 to 1.7) from 1 l of LC-grade or drinking water. Detection limits below 0.05 μg/l were obtained in the case of drinking water samples for each polar pesticide including the very polar carbamates. For river water (Fig. 2d and e), the sample volume was lowered to 200 ml in order to decrease the effect of interfering compounds and the average detection limits were between 0.1 and 0.3 μg/l without any clean-up [52].

Functionalized resins were then produced to increase the retention of polar compounds such as phenols, alcohols, aldehydes, esters and ketones by the introduction of a carboxylic function [62] or using sulfonated resins [63,64]. In those cases, sorbents can develop hydrogen bonding with analytes and can also act as cation exchangers. Recently, Masqué et al. have chemically modified a PS–DVB resin by introducing a carboxy-nitrobenzoyl moiety for the on-line extraction of polar pesticides and phenolic compounds. This sorbent has shown a higher potential than the same non-modified sorbent for the extraction of phenols [65]. However, for very polar compounds, i.e., resorcinol and catechol, the recoveries are still very low for a percolated volume of 100 ml.

4.3. Carbonaceous sorbents

The most widely used carbon-based sorbents for SPE are graphitized carbon blacks (GCBs). This material is characterized by a highly homogeneous and ordered structure and by a specific surface area around 120 m^2/g. In spite of this low surface area, its potential for trapping polar compounds with a higher efficiency than C_{18} silica has largely been demonstrated [66–70]. Several applications concerned the simultaneous extraction of acidic, neutral and basic compounds followed by two elution steps, one for neutral and basic compounds and a second for acidic ones retained by the positive residual charges on the surface of the sorbent [71–73]. Another carbon-based sorbent characterized by a

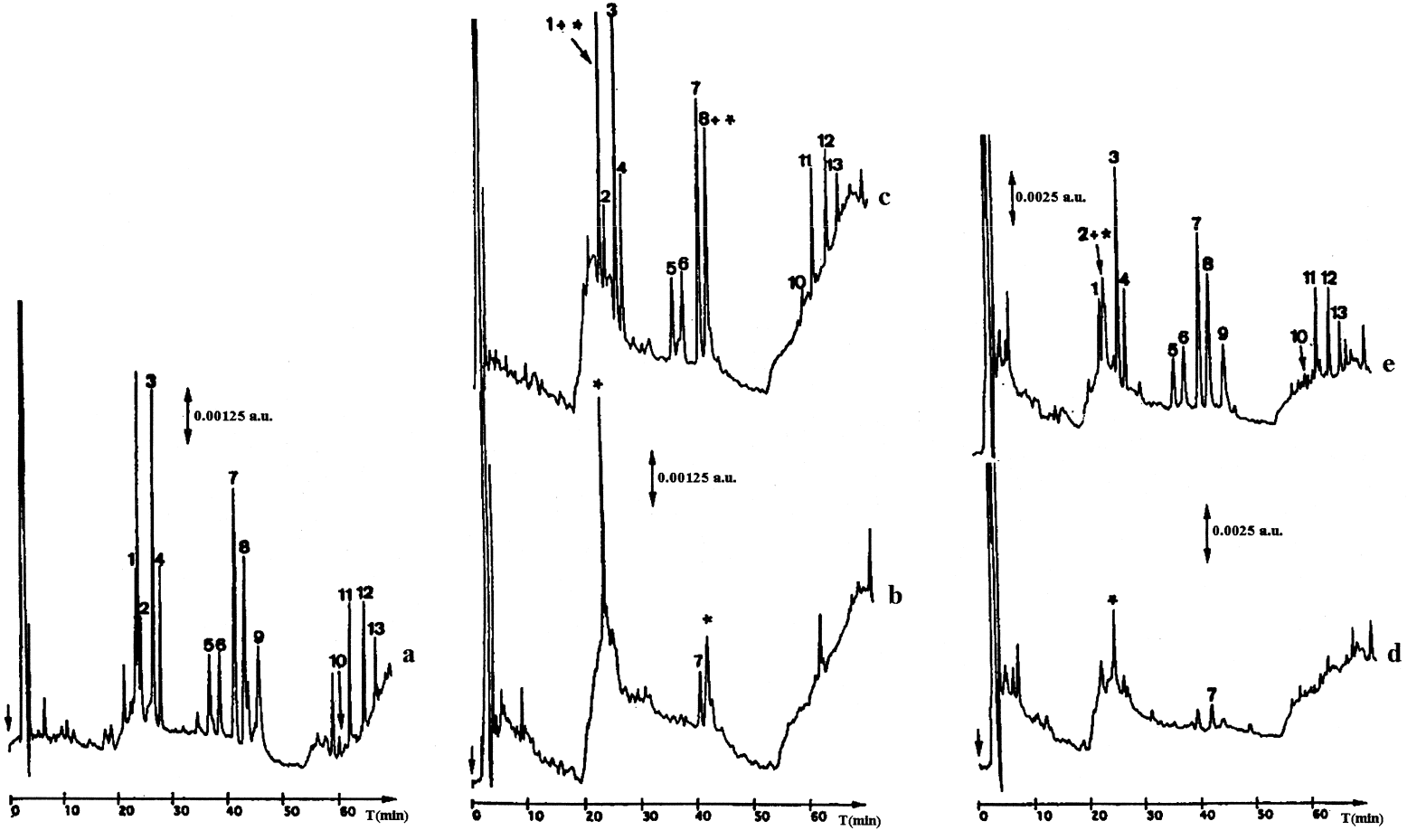

Fig. 2. Multiresidue analysis of water by SPE–LC–DAD. Preconcentration of different aqueous matrices using a 200 mg PS–DVB cartridge (around 1000 m^2/g): (a) 1 l of LC grade water spiked at 0.1 μg/l; 1 l of drinking water (b) non-spiked and (c) spiked at 0.1 μg/l; 200 ml of river Seine water (d) non-spiked and (e) spiked at 1 μg/l. Detection at 220 nm. Compounds: 1, oxamyl; 2, methomyl; 3, deisopropylatrazine; 4, monocrotophos; 5, fenuron; 6, metamitron; 7, deethylatrazine; 8, chloridazon; 9, carbendazim; 10, aldicarb; 11, aminocarb; 12, metribuzin; 13, metoxuron. LC conditions: C_{18} analytical column (25×0.46 cm I.D.), mobile phase acetonitrile–water gradient from 5% ACN to 30% at 60 min. Adapted from Ref. [52].

crystalline structure made of large graphitic sheets held together by weak Van der Waals forces, porous graphitic carbon (PGC), has also widely been used for the extraction of polar pollutants from water [1,31,54,74–78]. The retention mechanism differs from the one observed on C_{18} silicas [74,77,79]. Compounds are retained by both hydrophobic and electronic interactions so that non-polar but also very polar and water-soluble analytes can be extracted from water with higher recoveries than on C_{18} or PS–DVB polymers. The potential of this sorbent is illustrated by log k_w values reported in Table 1, that are equivalent or higher for PGC than for highly cross-linked polymeric sorbent. Most applications using carbonaceous sorbents have been carried out following an off-line procedure. The on-line coupling with classical reversed-phase C_{18} silica analytical column is difficult because polar analytes may be so strongly retained on PGC that the high water content of the mobile phase required for the separation of these polar compounds on C_{18} silica is incompatible with the elution of the analytes from PGC, and that a large band broadening appears [78]. This problem can also be encountered when using polymers of high specific surface areas in a pre-column [52]. A solution is to couple these sorbents with an analytical PGC column because in this case, a higher amount of organic solvent can be used in the mobile phase for the separation of polar compounds [52,78]. Fig. 3 corresponds to the on-line coupling of PS–DVB sorbent (1000 m^2/g) to a PGC column for the analysis of polar pesticides from LC-grade (Fig. 3a and b) and drinking water (Fig. 3c and d). No band broadening was observed when comparing these chromatograms to the chromatogram of a direct injection of these compounds [52]. With this system, the direct determination of the polar compounds at 0.1 μg/l can be achieved. The PGC/PGC coupling was automated and used for the monitoring of polar metabolites of atrazine in ground waters [1]. Another solution consists in percolating only the organic solvent constituting the mobile phase through the pre-column to elute compounds and to mix it with water before the analytical column. This system was used for the study of polar compounds trapped on a sulfonated resin [65]. A special review is dedicated to these carbonaceous sorbents in this issue.

5. Extraction of analytes over a wide range of polarity in one run

For the extraction of compounds from a wide range of polarity, the analyst usually focuses on the low retention of polar analytes which can be lost during the extraction step. The potential of the highly cross-linked polymers for the extraction of polar compounds was previously demonstrated. However, for this type of analysis, difficulties other than those related to the low retention of polar compounds can be expected. Compounds with low water solubility cannot be recovered. This can be due to adsorption of these compounds on tubings and vessels [32,62,80] or to an incomplete desorption of strongly retained compounds on the sorbents. The difficulty to simultaneously extract compounds from a broad range of polarity was well described by Norberg et al. in the case of the study of organophosphorus compounds [80]. When plotting the recoveries vs. the sample volume, three types of behavior were observed as exemplified by the plots shown in Fig. 4. For the most polar compound (monocrotophos), a quantitative recovery was found for low sample volumes only (early breakthrough). For the moderately polar compounds (as paraoxon), recoveries were quantitative over the whole 10–100 ml range. For the most hydrophobic analytes, recoveries slowly increased with the sample volumes because a fraction of the analytes was adsorbed in the preconcentration system. To eliminate adsorption phenomena, a low percentage of organic solvent or a low amount of surfactant can be added directly to the sample. However, the presence of these modifiers decreases the retention of polar compounds on the sorbent during the percolation and causes loss of these compounds. Therefore, the amount of modifier has to be carefully optimized and a compromise has to be found between adsorption of the low water-soluble compounds and the retention of the highly polar ones.

Concerning the problem of incomplete desorption, it can be difficult to find the solvent that will allow a complete desorption in a small volume in order to obtain a high enrichment factor. This volume can be reduced by evaporation of the residue but this step needs to be well controlled because of the risk of loss of high vapor pressure compounds, i.e., phenols

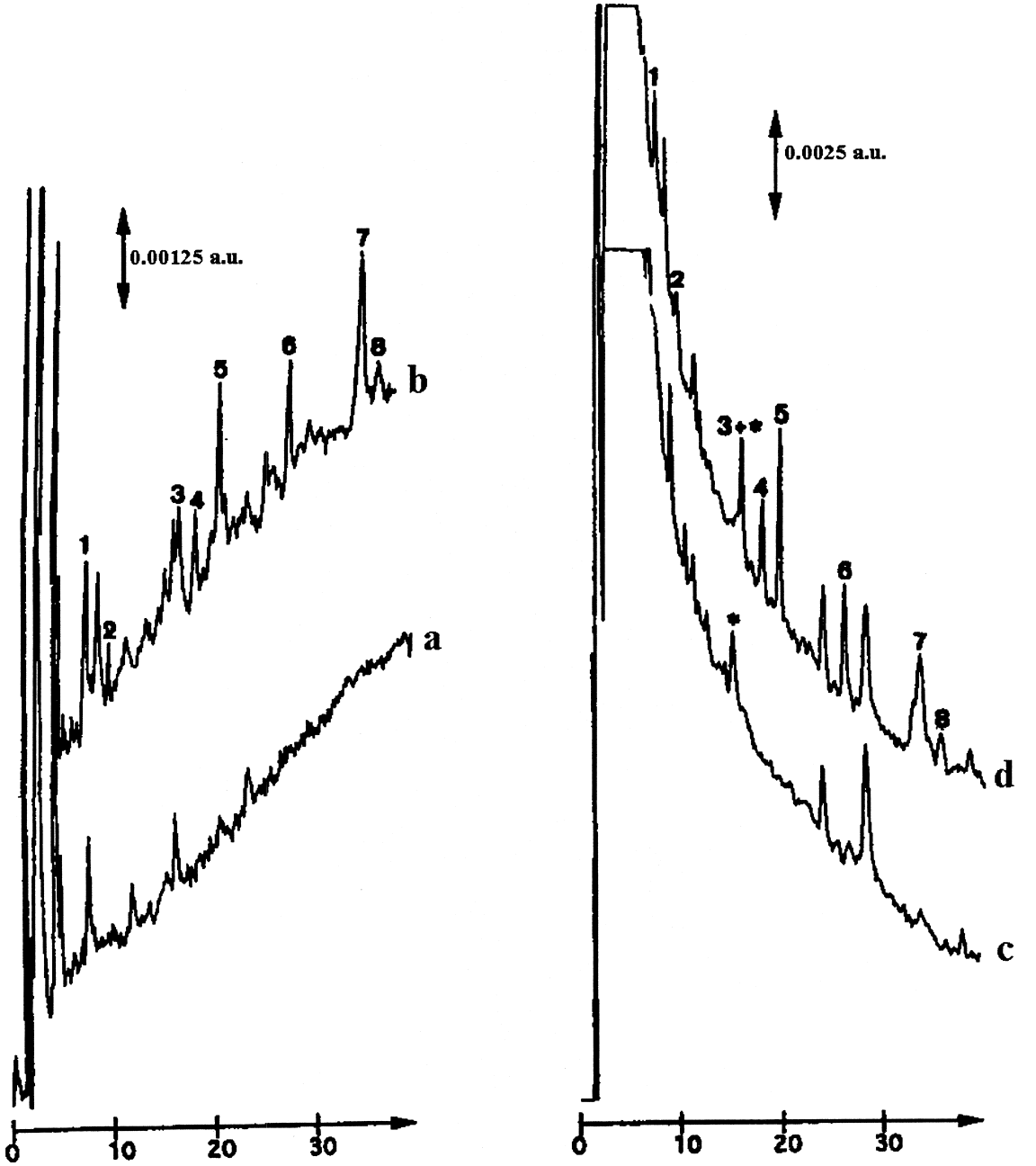

Fig. 3. On-line preconcentration of 100 ml of different aqueous samples acidified to pH 2 on a highly cross linked PS–DVB pre-column coupled with a PGC analytical column (10×0.46 cm I.D.). LC-grade water (a) non-spiked and (b) spiked at 0.1 μg/l; drinking water (c) non-spiked and (d) spiked at 0.2 μg/l. Acetonitrile gradient with a $5 \cdot 10^{-3}$ *M* phosphate buffer at pH 7, from 10 to 15% ACN from 0 to 5 min and up to 40% at 40 min. Detection at 220 nm. Compounds: (1) chlorpyralide, (2) oxamyl, (3) dicamba, (4) monocrotophos, (5) pichloram, (6) bentazone, (7) deisopropylatrazine, (8) fenuron. Adapted from Ref. [52].

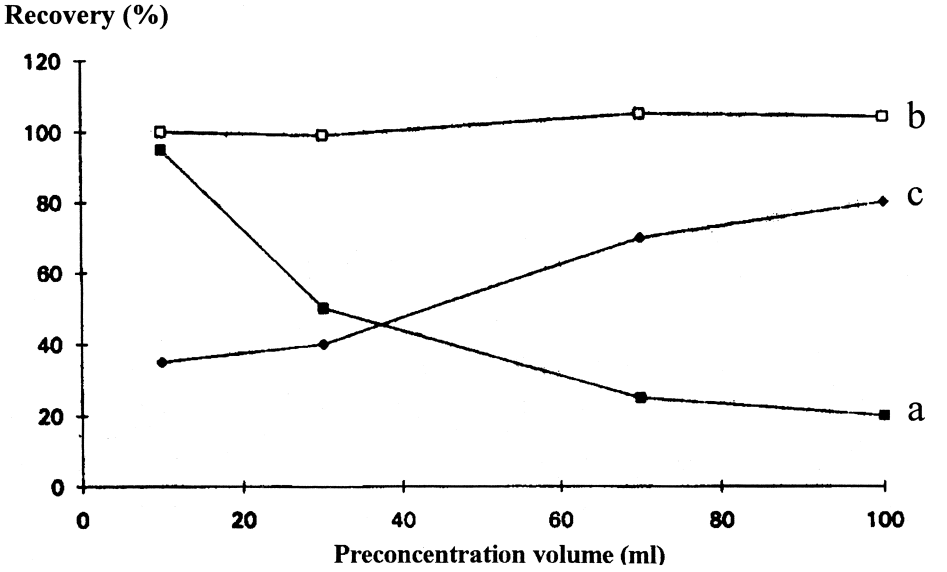

Fig. 4. Percent recovery versus preconcentration volume plots recorded for (a) monocrotophos, (b) paraoxon and (c) bromophos-ethyl. Adapted from Ref. [80].

[59] or organophosphorus compounds [32,60]. Moreover, a degradation of compounds in contact with some solvents can occur during this step as it was mentioned for organophosphorus compounds [32] or aryloxyphenoxypropionic acids [68]. In an off-line procedure, the choice of the eluting solvent is easier than in the case of an a on-line system because this solvent has not to be compatible with the analytical system. In case of incompatibility, the solvent used for the desorption can be removed by evaporation and another one can be used to solubilize the extract before its analysis. However the elution strength has to be adapted to all the trapped compounds. Many studies reported the difficulty to select this solvent [53,55,59]. As an example, a recent work has shown that it can sometimes be difficult to elute the more polar compounds that are still supposed to be slightly retained on hydrophobic PS–DVB sorbent: methanol was preferred to acetonitrile for the desorption of catechol from PS–DVB sorbent (LiChrolut EN) owing to a better solubilization of this compound with methanol, all the other polar compounds (but less polar than catechol) being completely eluted with acetonitrile [59]. For moderately polar to apolar compounds a mixture of methylene chloride and methanol is often used as eluting solution according to their eluting strength on reversed-phase sorbent. For the on-line coupling of SPE with LC, desorption conditions are determined by the conditions of the analytical separation, thus rendering difficult the development of analyses for compounds from a wide range of polarity.

In most cases, in order to limit the loss of volatile compounds, the evaporation step is carried out under mild conditions, i.e., under a stream of nitrogen instead of the use of a rotary evaporator until a final volume of 50–500 μl and a fraction of this extract is injected for analysis. When dry extracts are obtained, it is sometimes difficult to solubilize the residue. For LC analysis, it is recommended to use a solvent corresponding to the composition of the mobile phase at the beginning of the gradient. However, when very polar and non-polar analytes are present together, a complete solubilization of the extract can be impossible: an addition of water is required for the more polar ones, whereas very hydrophobic analytes can only be dissolved using non-polar organic solvents.

Sometimes, when the range of polarity of the compounds is too broad, two separate procedures are

recommended, one optimized for the polar and moderately polar ones, and a second one suited to the non-polar ones. In one instance, the on-line extraction of PAHs on PS–DVB disks required 15% of acetonitrile to be added in order in the aqueous samples to solubilize and to extract the low molecular mass PAHs and 20% of isopropanol for the more hydrophobic PAHs [44]. When two procedures are required, it can also be interesting to use two different sorbents to facilitate the desorption. As an example, two off-line procedures were defined: (i) the polar and moderately polar pesticides were extracted on a PS–DVB disk and subsequently eluted with acetonitrile, (ii) after the addition of 10% of methanol to the sample, the apolar pesticides were extracted on a C_{18} disk and eluted with a mixture of methylene chloride–methanol (4:1) [45].

The effect of the addition of an organic solvent to solubilize hydrophobic compounds in water and the difficulty to desorb these compounds from reversed-phase sorbent is illustrated, in Table 3, by recoveries obtained for compounds from a broad range of polarity extracted on a PS–DVB sorbent. A 500-ml volume of water spiked with each compound and containing 0 or 10% methanol were percolated on the sorbent that was eluted with a mixture of acetonitrile–methanol or methylene chloride–methanol. When the sample is free of methanol, recoveries for the less hydrophobic compounds are quantitative but are lower than 60% for the more hydrophobic compounds. Some of them, i.e., chlorpyriphos and trifluraline, are not recovered at all. By adding 10% of methanol to the sample, recoveries are higher than 70% for all the hydrophobic compounds. The low recoveries obtained when methanol is not added to the sample cannot be explained by an insufficient elution strength of the acetonitrile–methanol mixture because the substitution of acetonitrile by methylene chloride without a preliminary addition of methanol to the sample only yields a slight increase in the recovery of chlorpyriphos. This second example illustrates the difficulty to extract simultaneously

Table 3
Recoveries ($n=3$) obtained after the percolation of 500 ml of water without or with 10% methanol and spiked at 0.4 μg/l with each compound on PS–DVB sorbent (200 mg)[a]

Compounds	Log K_{ow}	Solubility (mg/l)	Recovery (%)		
			0% Methanol		10% Methanol
			CH_3CN–CH_3OH	CH_2Cl_2–CH_3OH	CH_2Cl_2–CH_3OH
Aldicarb	1.15	4930	91±8	–	–
Simazine	2.1	6.2	96±9	–	–
Atrazine	2.5	33	93±12	–	–
Isoproturon	2.5	65	97±7	–	–
Diuron	2.85	42	87±5	–	–
Ioxynil		50	84±14	–	–
Terbutylazine	3.05	8.5	91±8	–	–
Linuron	3.0	81	77±7	–	–
Alachlor	2.8	242	99±5	–	96±13
Cyproconazole β	2.9	140	–	68±10	83±12
Folpel	3.1	1	–	23±8	80±9
Fluzilazole	3.7	45	18±4	–	91±8
Endosulfan β	4.79	0.33	54±21	–	93±3
Chlorpyriphos	4.7	1.4	nd	15±10	99±4
Pendimethaline	5.18	0.3	–	<10	90±4
Trifluraline	5.3	0.2	nd	<10	71±4
Triallate		4	51±17	–	97±8
Fenpropimorphe	4.1	4.3	51±34	–	95±5

[a] Elution with 4 ml of a mixture of CH_3CN–CH_3OH (1:1) or CH_2Cl_2–CH_3OH (4:1). Solubility values (measured at 20 or 25°C) and log K_{ow} values were from The Pesticide Manual, 10th Edition. nd: Not detected.

polar and hydrophobic compounds and the necessity to use, as in this case, two separate procedures, one for the polar to moderately polar compounds and another one for the more hydrophobic compounds that necessitates the addition of a solubilizer and also well adapted desorption conditions.

For hydrophobic compounds, a C_{18} disk is usually preferred to a PS–DVB sorbent since recoveries are good for a sample volume of 500 ml even after the addition of methanol before the extraction step [45]. The advantage of using C_{18} sorbent instead of PS–DVB is an easier desorption. Moreover, the addition of methanol in the sample prevents the extraction of other polar interfering compounds that usually produce a large peak at the beginning of the chromatogram. This is illustrated by the chromatogram in Fig. 5 that corresponds to the preconcentration of 1 l of drinking water spiked at 0.1 μg/l of each apolar

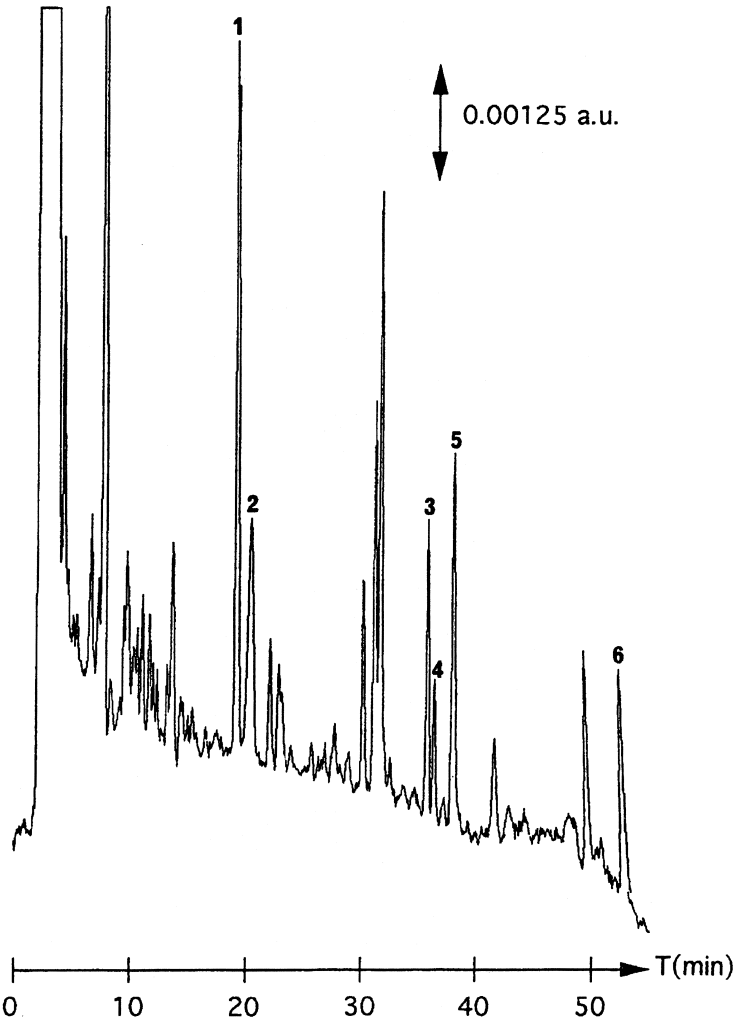

Fig. 5. Preconcentration of 1 l of drinking water adjusted at pH 6, containing 10% methanol and spiked at 0.1 μg/l of each compound on a C_{18} silica cartridge (750 mg). Detection at 220 nm. Compounds: (1) fluzilazole, (2) alachlor, (3) chlorpyriphos, (4) trifluraline, (5) triallate, (6) fenpropimorphe. LC conditions: acetonitrile gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer (pH 7) from 40 to 70% ACN from 0 to 30 min, 75% ACN at 45 min and 100% at 60 min. Adapted from Ref. [45].

pesticide. Detection limits are in the 5–50 ng/l range.

When applying SPE to the analysis of natural waters, the risk of co-extraction of interfering compounds using sorbents developing non-specific hydrophobic interactions is important, therefore, clean-up procedures are sometimes required. To limit the co-extraction of the polar humic and fulvic substances a washing step using a few milliliters of pure water or water containing a low amount of organic solvent or surfactant can be added to the procedure before the elution step but the risk is to loose slightly retained compounds, i.e., the most polar compounds. This technique is often used for on-line applications but is particularly difficult to apply when compounds belonging to a wide range of polarity are studied [80]. The second possibility used for off-line applications consists in cleaning-up the extract by using a second sorbent that can be a polar sorbent, i.e., silica, alumina, Florisil, or ion exchangers. As an example, for the analysis of glyphosate and AMPA, ionic humic and fulvic acids were removed from the extract, obtained after SPE on a highly cross-linked polymeric sorbent, by ionic interactions using a SAX [61]. A SAX sorbent was also used in association with a C_{18} silica sorbent in a double disk SPE device: humic and fulvic substances were trapped under their ionized form on the ion exchanger during the percolation of the sample and were still retained during the elution of the herbicides from C_{18} silica with methanol [81]. The positive residual charges of GCB were also used for the removal of ionized humic and fulvic compounds: these contaminants were trapped and remained on the sorbent during the elution of neutral surfactants, i.e., aliphatic ethoxylate alcohols and nonylphenol polyethoxylates, that were further analyzed by LC. Limit of detections (signal-to-noise ratio=3) were estimated to be about 0.002 and 0.0002 μg/l for each analyte in surface and drinking waters, respectively [70].

6. Multiresidue extraction including neutral and ionic compounds

Ionisable compounds can only be retained by C_{18} silica under their neutral form which implies a pH adjustment of the sample before the percolation, as in the case of the extraction of a mixture of acidic and neutral herbicides from drinking water [82]. However, the acidification of the sample at pH 2 or 3 – a pH lower than 2 being not recommended because of the solubility of silica – is the source of an interfering peak at the beginning of the chromatogram in LC. This is due to the occurrence of humic and fulvic acids in natural waters. Applied to the analysis of surface water, this method does not allow the trace detection of the more polar compounds co-eluted with the interfering peak [82]. To solve this problem, a clean-up step on a polar Florisil sorbent was added to the procedure, thus allowing the removal of the interfering compounds. An acidification of the sample results generally from a compromise between the increase in the retention of acidic compounds and the increase of the amount of co-extracted compounds [80,83,84]. It usually implies the necessity to introduce a clean-up step in the procedure. This acidification can also be a problem for some unstable compounds as reported for organophosphorus pesticides [32].

Some compounds such as aromatic sulfonates have strong acidic properties and are always ionized. When these ionic compounds are sufficiently hydrophobic, they can be retained on C_{18} silica as reported by Reemtsma for linear alkyl benzene sulfonates (LASs) [85]. However, for the more polar sulfonated compounds the addition of ion pairing reagents in the samples was necessary to improve their retention [86]. On-line coupling using an ion pairing reagent for the SPE and the LC separation was reported and showed a higher retention for interfering compounds that are extracted in a larger amount than they are without the addition of ion pairing reagents [85]. The large retention due to stronger hydrophobic interactions generated by highly cross-linked specific polymers allowed the extraction of benzene and naphthalene sulfonates without the addition of ion pairing reagents in the sample [87,88]. This possibility of using polymeric sorbents without any surfactant was particularly interesting for the study of sulfonates in CE as ion pair reagents interfere with CE separation [88]. However, this technique can only be applied to moderately polar sulfonated compounds: aminobenzene sulfonate or doubly negatively charged compounds are not sufficiently hydrophobic to be ex-

tracted with high recoveries without ion pairing reagents [88].

The use of the highly cross-linked PS–DVB polymers for the extraction at pH 7 of moderately polar acidic herbicides such as dicamba, bentazone, ioxynil, and some chlorophenoxyacid herbicides under their ionic form was reported. This study emphasizes the interest of working at pH 7 instead of acidic conditions thus limiting the co-extraction of humic substances that are better extracted at pH 2–3 [42,54]. The chromatograms in Fig. 6 correspond to the percolation on a PS–DVB sorbent of 250 ml of drinking water spiked at 0.5 μg/l and adjusted to pH 3 (Fig. 6b) and to pH 6 (Fig. 6a). Due to their high retention on the polymeric sorbent, acidic compounds can be extracted with recoveries of about

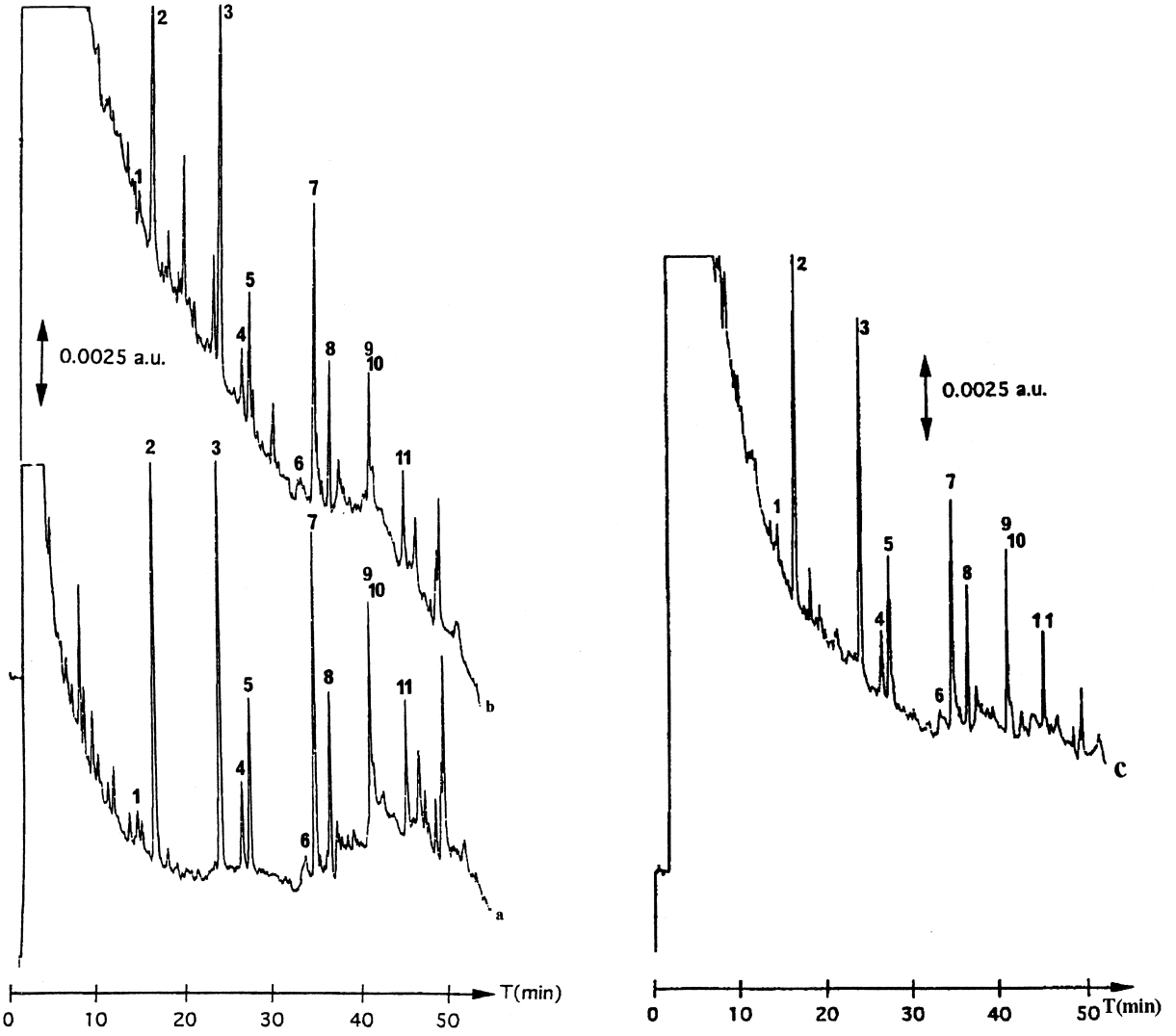

Fig. 6. Preconcentration of 250 ml on a PS–DVB sorbent (300 mg) of drinking water adjusted at pH 6 (a) and at pH 3 (b) and spiked at 0.5 μg/l with each compound and of river seine water adjusted at pH 6 and spiked at 0.5 μg/l (c). Detection at 220 nm. Compounds: (1) aldicarb, (2) simazine, (3) atrazine, (4) isoproturon, (5) diuron, (6) ioxynil, (7) terbuthylazine, (8) linuron, (9) fluzilazole, (10) alachlor, (11) dinoterb. LC conditions: acetonitrile gradient with $5 \cdot 10^{-3}$ *M* phosphate buffer acidified with $HClO_4$ (pH 3) from 20 to 43% ACN from 0 to 30 min, 77% ACN at 48 min and 100% ACN at 55 min. Adapted from Ref. [45].

100% without acidification thus limiting the extraction of humic and fulvic substances that are extracted in large quantities at pH 3 (Fig. 6b). Working at pH 6 allows the application of the same procedure to river Seine water with no clean-up step. The resulting chromatogram (Fig. 6c) presents a higher amount of co-extracted compounds than for drinking water but this amount is low enough to make the detection of the studied compounds in the range 0.1–0.5 μg/l possible without any clean-up. But for very polar compounds such as sulfonic acid degradates of chloroacetanilide and chloroacetamide herbicides, an acidification of the sample is required [89]. It is also the case when large sample volumes need to be percolated as described for aryloxyphenoxypropionic acid extracted from 1 to 2 l of water [68].

Studies also reported the fractionation of the extract by a stepwise elution for the analysis of acidic compounds on the one hand, and the sum of neutral and basic ones on the other. This approach was widely used for the extraction of a large number of pesticides using GCB as extraction sorbent [71,72,90]. These applications are based on the potential of this sorbent to extract polar compounds and on the ability of its residual positive charges to retain acidic ones according to an ion-exchange mechanism. However, some authors also reported an irreversible adsorption of compounds or a reduction of the capacity due to the presence of humic substances with these sorbents. A recent application concerns the extraction of polar, ionic and highly water-soluble organic pollutants from untreated industrial wastewaters. Two extraction procedures were used to obtain fractionated extracts. A PS–DVB sorbent (IsolutENV+) was used for the extraction of anionic analytes and a sequential SPE method using a C_{18} silica cartridge in series with a PS–DVB sorbent (LiChrolut EN). With this second procedure, four extracts were obtained by a stepwise elution of the sorbents. This method was applied to a pilot survey of textile and tannery wastewaters leading to the identification and quantification of 33 organic pollutants (phenolic compounds, benzothiazoles, non-ionic and anionic surfactants, sulfonates and related industrial compounds) [91]. The advantage of fractionation is that no clean-up step is required.

7. New selective solid-phase extraction sorbents for multiresidue analysis

The use of non-selective sorbents can be a problem when analytes of interest are present at very low concentration levels and interfering compounds at higher levels as in the case of humic and fulvic substances in natural waters. More selective sorbents involving antigen–antibody interactions have recently been produced. Antibodies produced against a target compound are immobilized on a support to form a so-called immunosorbent that is used just as a classical SPE sorbent. Due to the high affinity and to the high selectivity of these interactions, extraction and clean-up of complex aqueous matrices are achieved in the same step. Moreover, due to the cross-reactivity of the antibodies for analytes with chemical structures closely related to that of the analyte used for immunization, class-selective immunosorbents can be used for the selective trapping of a chemical group of analytes. This approach was applied to pesticides such as triazines and phenylureas [92–96], BTEX [97], polyaromatic hydrocarbons [98], benzidine and its congeners [99], nitroaniline and aromatic amines [100]. In most cases, the elution step was carried out off-line with a mixture of water and organic solvent or on-line with the mobile phase of the LC separation. The high selectivity of the immunosorbent is demonstrated by the comparison of the chromatograms resulting from the preconcentration of 50 ml of river Seine water spiked at 0.5 μg/l with phenylureas and triazines on a non-selective PLRP-S sorbent (Fig. 7a) and on a mixed-bed immunosorbent obtained by mixing anti-atrazine and anti-chlortoluron antibodies (Fig. 7b). The use of the mixed-bed immunosorbent allows the selective multiresidue extraction of triazines and phenylureas that are easily detected and quantified. This is particularly the case for the metabolite of atrazine, deethylatrazine, that is co-eluted with interfering polar compounds co-extracted on PLRP-S but easily detected when using the immunosorbent. The direct on-line coupling of the immunosorbents with LC is possible when antibodies are covalently immobilized on a sorbent that possesses chromatographic properties such as silica. If non-pressure resistant sorbents such as Sepharose, are used, a second pre-column is necessary in order to allow the

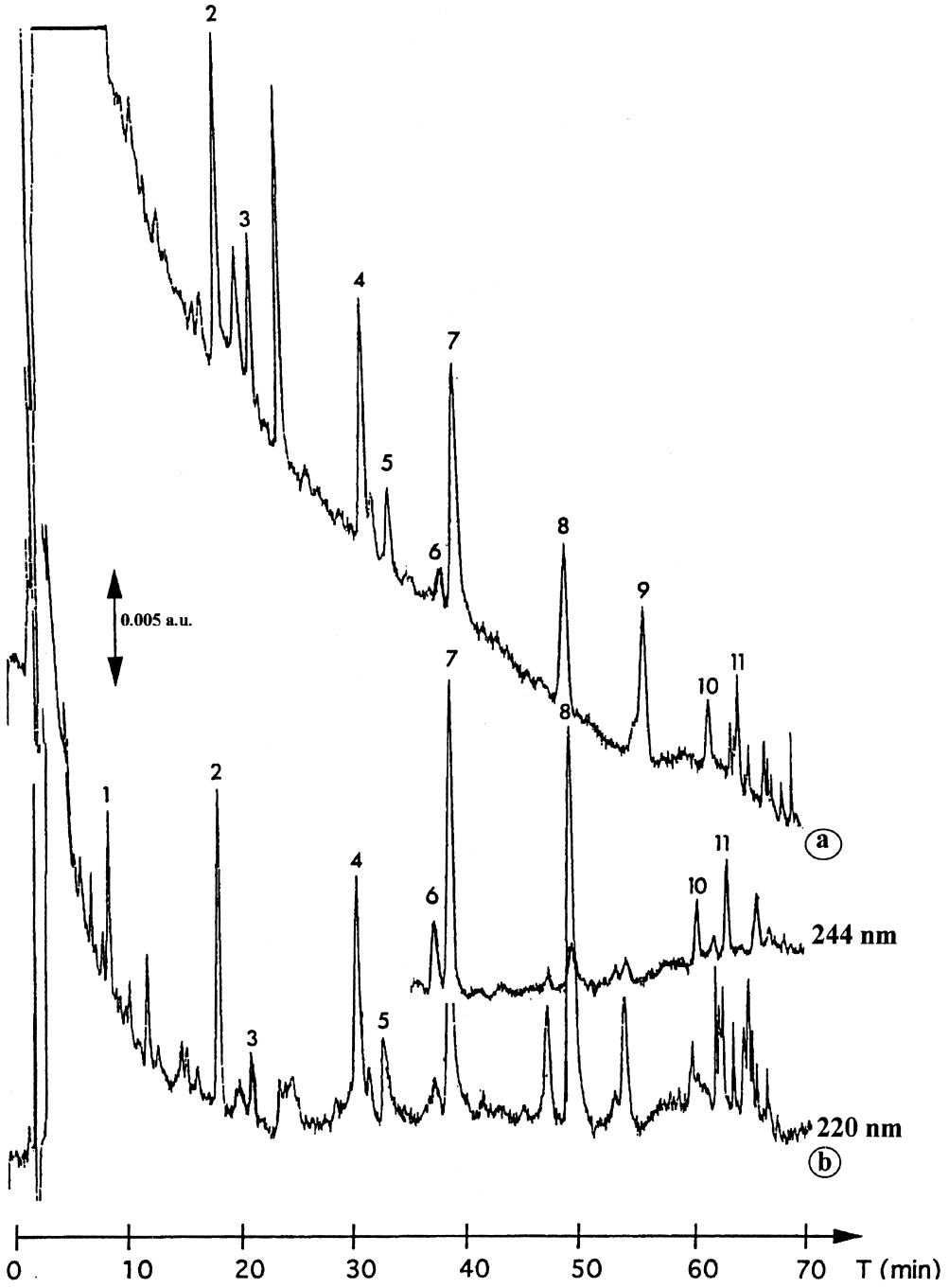

Fig. 7. Multiresidue analysis of two classes of herbicides using a mixed-bed immunosorbent (mix of anti-chlortoluron and anti-atrazine antibodies) (a) and using a non-selective PLRP-S extraction sorbent for the analysis of 50 ml of surface water spiked with 0.5 μg/l of each analyte. Compounds (1) deethylatrazine, (2) simazine, (3) monuron, (4) atrazine, (5) chlortoluron, (6) isoproturon, (7) diuron, (8) propazine, (9) terbuthylazine, (10) linuron, (11) chlorbromuron. Adapted from Ref. [93].

re-concentration of compounds eluted from the immunopre-column before their analysis in LC. This system based on the use of two pre-columns was recently employed for the on-line coupling of an immunosorbent with GC for the analysis of triazines from water [95].

The high selectivity provided by the immunosorbents has led to attempts to synthesize antibody mimics. One approach has been the development of molecular imprinted polymers (MIPs) that consists in the preparation of polymers with specific recognition sites for certain molecules: the synthesis is carried out by assembling monomers around a template molecule and subsequently initializing a polymerization in the presence of a cross-linker, thus providing a rigid material. The template molecules are then removed and the resulting polymer presents cavities, i.e., imprints, that are the recognition sites allowing the binding of template molecules. They have the advantages over the immunosorbents to be prepared more rapidly and easily and to be stable at high temperature and in a large pH range as well as in organic solvents. MIPs have found applications in LC as normal and chiral stationary phases. However, several studies have pointed out two specific problems associated with the use of MIPs in SPE. A first one is the difficulty to remove all the template analyte, even after extensive washings. This is a real problem when analytes are to be determined at the trace level because large amounts of templates are used for the synthesis and may remain in the MIP. A second problem is the difficulty in establishing quantitative and rapid desorption due to the high avidity of the MIP for the analyte [101]. This technique was recently applied to the purification of an extract obtained after SPE of triazines from waters on C_{18} silica [102]. The selectivity of the MIP is illustrated by the comparison of chromatograms corresponding to the direct analysis of the SPE extract and to the purification of the extract on the MIP (Fig. 8). Since MIPs are nowadays extensively studied by several groups one can expect many developments and improvements in the near future.

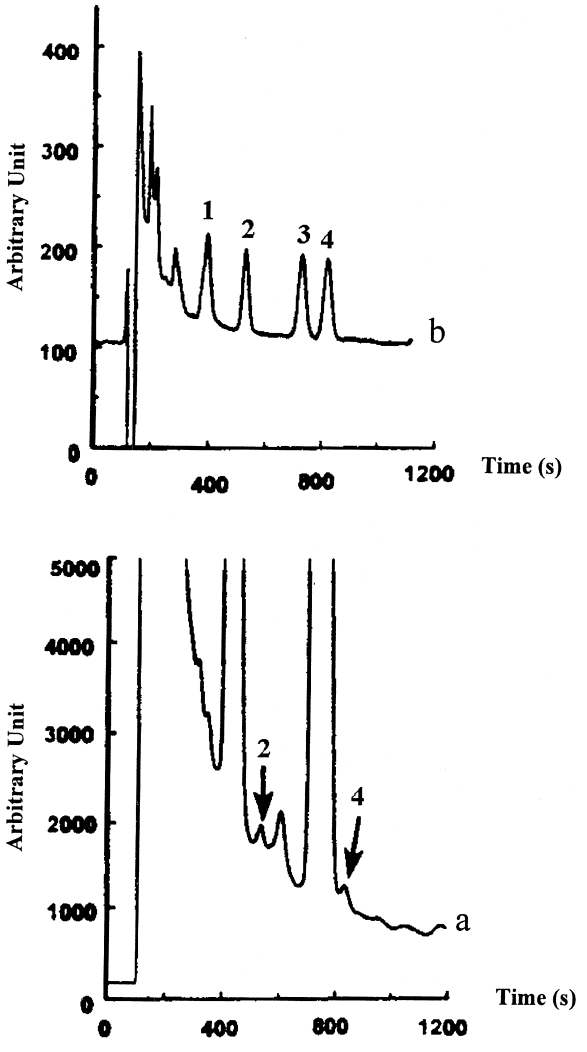

Fig. 8. Preconcentration of 200 ml of water containing 20 ppm of humic acids and spiked at 0.5 μg/l with each triazine on C_{18} silica without (a) and with a purification step on a MIP (b). Compounds: (1) simazine, (2) atrazine, (3) propazine, (4) terbuthylazine. Adapted from Ref. [102].

8. Conclusion

The potential of the SPE methods for the multiresidue extraction of compounds from waters is now admitted. The different sorbents were reviewed and it is clear that the development of the selective sorbents is now an active area of research. However, it was demonstrated that their application to the multiresidue analysis of compounds having very different characteristics can be difficult. Problems are likely to be essentially due to practical difficulties that can quite easily be overcome. They usually

concern the choice of the sorbent and of the sample volume as well as the necessity to adjust the pH of the sample. Losses due to the degradation of the compounds in organic solvents or to the evaporation step can be circumvented by the use of on-line coupling. However, some of them are inherent to the nature of the compounds and cannot be so easily solved. The simultaneous extraction of polar and hydrophobic compounds is difficult and can sometimes require the development of two separate procedures. Moreover, the addition of clean-up steps principally based on non-specific interactions such as hydrophobic and ionic interactions proves sometimes to be difficult and even impossible in the analysis of compounds having very broad physico–chemical characteristics.

9. Nomenclature

AED	Atomic emission detection
AMPA	Aminomethylphosphonic acid
BTEX	Benzene, toluene, ethylbenzene and xylene isomers
CE	Capillary electrophoresis
DAD	Diode array detection
ESI	Electrospray ionization
FID	Flame ionization detection
FMOC-Cl	9-Fluorenyl methoxycarbonyl chloride
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GCB	Graphitized carbon black
LAS	Linear alkyl benzene sulfonate
LC	Liquid chromatography
LLE	Liquid–liquid extraction
MIP	Molecular imprinted polymer
MS	Mass spectrometry
PAH	Polyaromatic hydrocarbon
PGC	Porous graphitic carbon
PS–DVB	Polystyrene–divinylbenzene
SAX	Strong anion exchanger
SPE	Solid-phase extraction

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