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Review

Graphitized carbons for solid-phase extraction

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Abstract

The objective of this review is to provide updated information about the most important features of graphitized carbonaceous sorbents used for solid-phase extraction (SPE) of organic compounds from liquid natural matrices or extracts. The surface characteristics of graphitized carbon blacks and porous graphitic carbons are described which are responsible for the various types interactions (hydrophobic, electronic and ion-exchange) with analytes. The method development is given which is based on the prediction from liquid chromatographic retention data obtained using porous graphitic carbon. Emphasis is placed on their capability for trapping very polar and water-soluble analytes from aqueous samples. Comparison is made between carbon-based SPE sorbents and other reversed-phase materials such as octadecyl silicas and highly cross-linked copolymers. Especially, the difficulty encountered for the desorption of some strongly retained analytes is explained by LC data and solutions are given for optimizing the composition and volume of the desorption solution. Many examples illustrate the various common features of graphitized carbons which are the extraction of very polar analytes and multiresidue extractions. Some applications are specific to graphitized carbon black due to the presence of surface functional groups. They include the extraction of anionic compounds such as benzene and naphthalene sulfonates or acidic pesticides. Other applications are specific to porous graphitic carbon due to its flat and homogeneous surface. One example is the trace extraction of coplanar polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins and dibenzofurans from other PCB congeners

Keywords: Reviews; Solid-phase extraction; Porous graphitic carbon; Graphitized carbon black; Pesticides; Atrazines

Contents

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1. Introduction

Solid-phase extraction (SPE) is today widely accepted as an alternative to laborious and time-consuming liquid–liquid extraction (LLE) for the trace determination of non volatile organic compounds in aqueous samples. One reason was the pressure to decrease organic solvent usage in laboratories which has encouraged the requirement for solvent-free procedures. The introduction of survey lists containing very polar analytes such as some degradation products of organic micropollutants has also pointed out the need for alternative methods to LLE because many polar analytes are often partly soluble in water and cannot be extracted with good recoveries whatever the organic solvent selected.

Activated carbon was certainly one of the first material used for extracting medium- to low-polarity organic compounds from water [1]. This sorbent was left because irreversible adsorption and low recoveries were obtained for some analytes. Then, for many years *n*-alkylsilicas have been the universal SPE sorbents. The use of carbonaceous sorbents for SPE has began in the 1980s with the introduction of graphitized carbon blacks (GCBs) obtained by heating carbon blacks. They were applied to the extraction of non polar analytes such as organochlorinated insecticides [2,3] and then of moderately polar analytes such as triazines and phenoxy acids [4,5]. The interest in this sorbent increased when its high ability was demonstrated to isolate polar molecules with high solubility in water (>1 g/l) [6–10]. These type of solutes are the most difficult to extract because of their low affinity for most reversed-phase sorbents. As other carbons made from carbon blacks, GCB was shown to contain various functional groups at the surface following the oxygen chemisorption [10,11]. As a consequence examples have described its use as an ion exchanger for the extraction of aklylbenzene sulfonates [12], naphthalene sulfonates [13] and various acidic pesticides [11]. Di Corcia and co-workers took advantage of the positively charged active centres at the GCB surface for performing multiresidue extraction of pesticides which involved a fractionation between neutral and basic pesticides on the one hand and acidic on the other hand [10,13–17]. However, in addition to ionizable groups, the GCB surface was shown to contain hydroquinone groups able to give rise to irreversible chemisorption if previously not oxidized [10]. All these characteristics explain the ‘‘mysterious’’ nature of GCBs and the occurrence of some strong interactions with some solutes which sometimes are difficult to disrupt [17]. That is certainly the origin of the reputation that GCB and carbons in general have received for being ‘‘difficult to elute’’.

Because of the similarity between the SPE process and the classical elution liquid chromatography (LC), LC data have been used for predicting most of the parameters that describe a SPE sequence [19–24]. GCBs are not sufficiently pressure resistant to be used in LC so that no data indicating the LC behavior of solutes are available. The high potential of graphitized carbons for trapping polar analytes was then confirmed when the first carbon material became available at the end of the 1980s with properties appropriate for a LC stationary phase as well as for a SPE sorbent [25]. This so-called porous graphitic carbon (PGC) has a highly homogeneous crystalline structure made of large graphitic sheets. Although it was made to be the ‘‘perfect reversed-phase material’’, PGC was shown to possess a unique chromatographic behavior. It was first described as a more retentive reversed-phase sorbent

than C_{18} silica, the retention mechanism was shown to be very different and its ability for also providing high retention for polar and water-soluble analytes was first described with the extraction of polyhydroxybenzenes in 1992 [26]. In contrast to C_{18} silicas, a high retention has also been observed with pure organic solvents especially with acetonitrile or methanol and LC data were also used to optimise the desorption step [27]. Relevant examples using PGC have been described for the trace determination of very polar analytes or degradation products such as polar phenolics and aniline derivatives, or very polar pesticides or degradation products [26–31].

All these features show that both GCB and PGC have unique properties, but their use is not as straightforward as that of C_{18} silica or apolar poly(styrene–divinylbenzene) (PS–DVB) sorbents, especially for the desorption step.

The objective of this review is to give up to date information about the most important features of graphitized carbons used in SPE, their interaction modes and their potential for the extraction of very polar analytes from aqueous samples. The analogy between SPE and LC will be given for the method developments as well as a comparison with C_{18} silicas and apolar copolymers. Emphasis will be placed on the desorption step. Various examples illustrate the specific and unique behavior of graphitized carbons as extraction sorbents. In most applications, SPE is performed off-line, the sample preparation being separated from the subsequent chromatographic analysis. A few examples will also be presented where SPE is connected on-line to the chromatographic system. On-line techniques do not require further handling of the samples between the trace enrichment and the separation step and, therefore are highly suitable for fully automated techniques [32–34].

2. Structure and characteristics of graphitized carbons used in solid-phase extraction

2.1. Graphitized carbon blacks

Active carbons with high specific surface areas were shown to be microporous and to contain polar groups at their surface which provided poor LC and SPE performances. The most widely used carbon-based SPE sorbents are GCBs obtained by heating carbon blacks at high temperature (2700–3000°C). The first available GCBs were non porous with a low specific surface area around 100 m^2/g (Carbopack B or ENVI-Carb SPE from Supelco, Carbograph 1 from Altech). Carbograph 4 was recently introduced with a surface area of 210 m^2/g [35].

All carbon blacks contain various functional groups at the surface following the oxygen chemisorption. The surface framework of GCBs used in SPE was shown to be contaminated by oxygen complexes, having a structure similar to hydroquinone, quinones, chromene and benzpyrylium salts. These groups are able to interact so strongly with sufficiently acidic compounds that conventional solvent systems are not able to desorb them [10]. Therefore, GCB has a somewhat positively charged surface that also sorbs by an anion-exchange mechanism.

2.2. Porous graphitic carbons

PGC is available in SPE cartridges (Hypersep PGC) and is similar to the LC-grade Hypercarb, which appeared commercially at the end of the 1980s. In the 1970s, the bonded silicas were developed to a high extent, but some disadvantages rapidly appeared, such as solubility in the eluents or hydrolysis of the bonded chain at low or high pH and the effects of the unavoidable unreacted silanol groups. Several attempts have been made for providing graphite-based sorbents that would not suffer from the disadvantages of bonded silica sorbents [36–42]. Most of them failed until 1979, when Knox and Gilbert patented a method for making a robust porous carbon that met the required properties for use in LC [43]. The porosity of PGC is obtained by impregnating a porous silica with a phenol–formaldehyde mixture which is polymerized within the pores of the silica gel and then carbonized at 1000°C. The silica is then removed by dissolution in a concentrated (5 *M*) sodium hydroxide solution. Graphitization is performed at temperature in the range 2000–2800°C in order to remove the micropores. The resulting macroporous material has a flat crystalline surface. This carbon was improved and

became commercially available in 1988 under the trade name Hypercarb. PGC has a two-dimensional graphite structure composed of layers of hexagonally arranged carbon atoms in the sp^2 hybridization. The graphitic sheets are closely intertwined together, which provides the rigidity and mechanical stability.

PGC has an average specific surface area of 120 m^2/g, a uniform pore structure with mean pore diameter of 25 nm and a porosity of 75%. Designed to withstand pressures of more than 400 bar, it is geometrically stable and free from any swelling or shrinking. It is inert to usual organic eluent and to extreme pH. The flat homogeneous surface of the PGC is responsible for its unique selectivity to geometrical isomers. The large layers of carbons containing delocalized π electrons and the high polarizability are responsible for a different retention mechanism. In contrast to GCB, the surface is highly homogeneous and up to now, there was no evidence for ionized groups at the surface frameworks of the PGC.

Table 1
Recovery data obtained by LLE and SPE for the extraction of some polar pesticides added to 2 l of municipal water samples[a]

Compound	Recovery (%)±RSD (%)		
	LLE	C_{18}	GCB
Omethoate	58±8	3±45	83±6
Butocarboxim sulfoxide	13±14	3±42	102±5
Aldicarb sulfoxide	16±17	4±29	93±5
Butoxycarboxim	74±7	4±32	98±3
Aldicarb sulfone	58±11	6±21	75±8
Oxamyl	51±10	24±12	101±2
Methomyl	64±11	10±20	100±2
Monocrotophos	68±5	42±16	98±3
Deisopropylatrazine	87±4	15±14	102±4
Fenuron	60±8	19±12	99±3
Metamitron	79±4	28±12	95±5
Isocarbamid	74±10	78±6	97±3
Deethylatrazine	85±4	30±13	97±4
Chloridazon	75±4	31±11	100±3
Dimethoate	78±6	22±14	98±4
Cymoxanil	89±9	28±11	94±4
Butocarboxim	82±5	63±9	95±4
Aldicarb	68±12	55±9	99±4
Metoxuron	83±5	101±3	97±3
Hexazinone	75±11	88±4	98±3

[a] SPE using a 1-g C_{18} cartridge and a 1-g GCB cartridge (spike level: 1–4 μg/l; mean values from four determinations). Adapted from Ref. [44].

Although one or two other carbons made by the Japanese are sometimes mentioned, most of the studies and applications described in the literature utilize the PGC Hypercarb.

For off-line SPE applications, the syringe-barrel and/or cartridge types are still the most popular format with typically 40–60 μm d_f packing materials. Another available format is the disk which allows higher flow-rates without channelling effects thanks to their large cross-sectional area and thin bed.

3. High potential for the extraction of polar analytes

3.1. Comparison of recoveries obtained with C_{18} silica and graphitized carbon black

The simplest measurements for comparing the extraction efficiencies are the recoveries. Extensive studies were performed by Di Corcia et al. for the trace-level determination of polar pesticides in water [44]. In Table 1 the extraction recoveries obtained from 2 l of water using a 1-g GCB cartridge are compared to those obtained with using a 1-g of C_{18} silica with the same sample volume and to those obtained by using LLE with three separate 120-ml portions of methylene chloride. Breakthrough has occurred for most of the pesticides with a sample volume far lower than 2 l on a 1-g C_{18} silica cartridge, but not on GCB even for the polar carbamates methomyl and oxamyl and some degradation products. The GCB used in the example above had a specific surface area of 100 m^2/g. A similar study was performed by the same group using Carbograph 4 with a surface area of 210 m^2/g. The recoveries of 45 pesticides including the polar omethoate, aldicarb sulfone, oxamyl and methomyl were all in the range 95–100% with the handling of 4-l samples of drinking water and using a 0.5 g Carbograph 4 cartridge [16].

3.2. Prediction of solid-phase extraction parameters from liquid chromatography data obtained using porous graphitic carbon

The parameters to be determined are indicated in

the SPE sequence. They are the selection of the type and amount of sorbent, the determination of the sample volume which can be applied without loss in recovery – the so-called ''safe sampling volume'', the composition and volume of the washing or clean-up solution which can be applied without loss of analytes and finally, the composition and the volume of the elution or desorption solution.

The same sorbents as those used in reversed-phase LC are utilized and there is an analogy between the SPE process and classical elution LC. Processes involved in SPE are a frontal chromatographic process during the extraction step and a displacement chromatography during the desorption step. These two modes are well known and to a first approximation, SPE can be described as a simple chromatographic process, the sorbent being the stationary phase. The mobile phase is the obligatory solvent of the sample during the extraction step and an appropriate selected solvent during the desorption step. It is then possible to predict and optimize the main SPE parameters from data generated by LC. The breakthrough volume has received much attention because it represents the maximum sample volume that can be percolated with a theoretical 100% recovery, but is not easy to measure [18–24]. Among the various tools for selecting the sorbent and predicting the recovery according to the percolated aqueous sample volume, the most important is the retention factor of the analyte in water, k_w. Therefore, it was shown that developing a SPE method only requires to know the retention behavior of the analytes using the same extraction sorbent as the stationary phase in the LC process and pure water as mobile phase, as measured by k_w [19,21,45,46]. Both breakthrough curves and recovery curves have been modelled according to the sample volume [21]. The necessary sample volume is usually known after being calculated according to the required quantification level and to the limit of quantification of the chromatographic and detection modes. Using LC with UV diode array detection (DAD), detection and quantification of pesticides at the regulatory level of 0.1 μg/l requires a sample volume in the range 300–500 ml using an off-line procedure. For example, with an amount of sorbent of 500 mg, a recovery in the range 90–100% with a sample volume of 500 ml will require a sorbent providing log $k_w > 3$.

Using C_{18} silica, the retention is primarily governed by hydrophobic interactions between the analyte and the carbonaceous moieties of the alkyl chains at the silica surface. Consequently, a relation has been observed between the retention factors of the analytes and their octanol–water partition coefficient (K_{ow}). In log units, the slope was shown to be close to 1, so that one can estimate the recovery without measurements. Therefore, if a sample volume of 500 ml is required, all moderately and polar analytes characterised by log $K_{ow} < 3$ will not be extracted with a 100% recovery from a 500-mg cartridge packed with C_{18} silica. Using PS–DVB polymers, additional interactions occurs between the numerous π bonds of the sorbent and the organic analytes so that the compounds were shown to be more retained, depending on the PS–DVB surface area. However, there is still a relation between the retention factor and the analyte hydrophobicity and the lower the log K_{ow} values, the less retention is.

The retention mechanism on PGC has been shown to be very different from that observed on C_{18} silica or PS–DVB polymers due to its crystalline structure made of large sheets held together by weak Van der Waals forces. Analytes are retained on PGC by both hydrophobic- and electronic-type interactions, so that non polar but also very polar and water-soluble analytes have been shown to be strongly retained in aqueous mobile phases [26,28,46–60]. Therefore, log k_w cannot be predicted easily and there is no link between log K_{ow} and log k_w except for a series of related analytes such as alkylbenzenes [47].

3.3. Comparison with other reversed-phase sorbents

The affinity of PGC towards very polar and water-soluble polyhydroxybenzenes has been studied [26]. The capacity factor in water of the very polar 1,3,5-trihydroxybenzene (phloroglucinol) was about 1000 with PGC whereas it was found to be 3 (log k_w of 0.5) with PRP-1 (PS–DVB sorbent). This compound is not retained by C_{18} silica and it was even proposed as an experimental probe for determining the void volume of C_{18} columns. Other extrapolated or real experimental log k_w values have been reported for mono- and polysubstituted benzene derivatives with RP-18, PRP-1 and with PGC in Table

Table 2
Comparison of extrapolated log k_w values obtained with RP-18 silica, PRP-1 and PGC[a]

Solute	RP-18	PRP-1	PGC
Monosubstituted			
Benzene	2.2	3.5	1.45
Aniline	1.08	2.5	1.35
Phenol	1.55	2.4	1.8
Benzoic acid	1.9	3.2	2.4
Nitrobenzene	2.05	3.6	2.45
Polysubstituted			
4-Aminophenol	nd	1.1	2.05
1,4-Diaminobenzene	nd	1.2	2.4
4-Aminobenzoic acid	nd	2	2.85
4-Hydroxybenzoic acid	nd	2.3	2.7
3,5-Dihydroxybenzoic acid	nd	1.35	3
1,3-Dihydroxybenzene	nd	1.35	2.35
1,4-Dihydroxybenzene	nd	0.83	2.15
1,3,5-Trihydroxybenzene	nd	0.5	2.7

[a] From Ref. [46].
nd: Not determined.

2. First, when comparing values for monosubstituted benzenes, compounds are more retained by PRP-1 than they are by PGC. The comparison between RP-18 and PGC indicates that solutes are less or more retained by PGC than they are by RP-18. In contrast to results on PRP-1 indicating that retention of all the solutes was higher with PRP-1 than that with C_{18} silicas, no correlation was found between retention of monosubstituted benzenes on PGC and retention on C_{18} silicas. The disubstituted benzenes studied in Table 2 are rather polar compounds and are not, or slightly, retained by C_{18} silicas, explaining why log k_w values have not been reported. The comparison between the retention obtained on PRP-1 and on PGC are interesting. The log k_w values obtained when solutes have two polar substituents using PRP-1 are always lower than those measured for each corresponding monosubstituted benzene whereas the contrary is observed with PGC. For instance, log k_w of aminophenol is 1.1 with PRP-1 and is lower than both log k_w of phenol (2.4) and aniline (2.5). With PGC, log k_w of aminophenol is 2.05 and is higher than log k_w of both phenol (1.8) and aniline (1.35). The retention mechanism is therefore very different for the two sorbents.

High retention is usually obtained for planar molecules containing several polar groups with delocalized electronic charges via π bonds and lone pairs of electrons. When no guide can be given for log k_w prediction, the only rapid and easy means 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.

3.4. Desorption conditions

Desorption problems have been encountered with GCB cartridges: pure methanol, acetonitrile or methylene chloride were shown to be unable to desorb some pesticides as well as other organic pollutants, so that a mixture of methylene chloride–methanol (80:20, v/v) was recommended [10,14,44]. It was also pointed out that residual water had to be reduced to a minimum and, that, when this was not done, low and irreproducible recoveries were obtained because the water can hinder intimate contact between the desorption mixture and the GCB. Since only a fraction of the residual water can be removed by vacuum, the authors recommended that one should wash the GCB cartridge with a small volume of pure methanol before applying the methylene chloride–methanol mixture, but risk of losses may exist for weakly retained compounds. Special care also has to be taken with the elution mixture owing to the problem of double-layers during the subsequent evaporation if the water was not well removed before desorption. Another problem mentioned by the authors is in the removal of methylene chloride when the subsequent analysis is performed by LC and when the desorption mixture cannot be blown down to dryness because of the presence of relatively volatile compounds. Most of the pesticides reported in Table 1 were extracted with good recoveries from 2-l samples using a 300-mg GCB cartridge and 6 ml of the desorption mixture, except for the first seven compounds of the list for which a 1-g GCB cartridge was required. Then, the desorption volume has to be so strongly increased with 1-g cartridges that a backflush desorption was recommended [44].

More recently, Creszenzi et al. described a multiresidue method for 45 neutral and basic pesticides using a 500-mg Carbograph 4 cartridge [16]. After sample application followed by air during 1 min in

order to reduce the amount of residual water, a volume of 0.4 ml of methanol was applied. According to the authors, this volume is critical and even a slightly larger resulted in some loss of the more polar pesticides. Then the cartridge was turned upside down and analytes could be back eluted with 1.5 ml of methanol followed by 8 ml of a mixture of methanol–methylene chloride (10:90, v/v). When omitting to reverse the cartridge before desorption, up to 90% of metabenzthiazuron was not eluted from the extraction cartridge. A cartridge was specially designed allowing this backflush elution [61].

All the problems mentioned above could be overcome using a water-miscible solvent able to desorb all the analytes. The selection of the desorption solution can be achieved from the knowledge of the retention behavior of analytes with pure organic solvent. According to the theoretical basis of SPE, the desorption conditions can also be derived from LC data. This has been achieved using PGC sorbents. The retention factors of some pesticides and other organic pollutants have been measured using a PGC analytical column eluted with methanol, tetrahydrofuran (THF) and methylene chloride and are reported in Table 3. The results show first that the retention factor can be very high with methanol and that THF and methylene chloride are more eluting. Some measurements were also performed with acetonitrile, but the retention factors were similar to those obtained with methanol. Once more, one can observe that there is no relationship between polarity – indicated by corresponding values of log K_{ow} – and the retention of compounds. A polar pesticide such as metamitron is highly retained in pure methanol, and less by THF and methylene chloride. Similarly to the predictions that have been made for the breakthrough volumes during the percolation step, using a 500-mg PGC cartridge, the calculation of the desorption volume for a total recovery of atrazine was made from the retention volume of 7 ml as reported in Table 3 and gave a volume of 12.3 ml [27]. Experimental measurements indicated that a volume of methanol around 12–14 ml was required for a complete desorption. Table 3 clearly indicates that methanol (and acetonitrile) cannot be used for desorption of all analytes as that almost occur using C_{18} silica sorbents. Although THF and methylene chloride are more eluting, some compounds such as

Table 3
Retention factors of various pesticides (with various hydrophobicity) measured in pure organic solvents (methanol, tetrahydrofuran and methylene chloride) with a PGC analytical column and calculated retention volume using a 500-mg PGC cartridge[a]

Compound	Log K_{ow}	Log k			V_r (ml)
		MeOH	THF	CH_2Cl_2	MeOH
Oxamyl	−0.5	−0.51	−1.42	−1.22	2
Methomyl	0.2–1.8	0.04	−0.92	−1.01	3
Metamitron	0.8	>1.4	0.23	0.26	>34
Fenuron	0.5–1.2	0.28	−0.56	−0.66	4
DIA	1.1	0.57	−0.71	−0.28	6
DEA	1.5	0.22	−1.01	−1.04	3
Metoxuron	1.6	1.28	0.05	−0.02	26
Metribuzin	1.6–1.7	−0.35	−1.42	−1.04	2
Aminocarb	1.7	−0.25	−1.35	−1.01	2
Carbendazim	1.4–1.6	>1.4	0.79	nd	>34
Chloridazon	1.1–2.2	0.96	−0.13	−0.05	13
Simazine	1.5–2.3	0.97	−0.49	−0.39	13
Atrazine	2.2–2.8	0.62	−0.82	−0.85	7
Diuron	2.8	>1.4	0.17	nd	>34
Linuron	2.8	1.38	−0.10	−0.16	32
3,5-Dichlorophenol	3.6	0.52	−0.73	−0.51	6
2,4,5-Trichlorophenol	4.1	0.99	−0.12	0.20	14
Anthracene	4.7	>1.6	1.21	nd	>34
Pentachlorophenol	5	>1.4	0.81	nd	>34

[a] From Ref. [27].

metamitron, diuron and carbendazim are still strongly retained. THF gives a lower retention than methylene chloride for the compounds of Table 3, but from LC data, more than 20 ml of THF should be necessary to completely desorb carbendazim. These data obtained on PGC are consistent with experiments achieved using GCB, showing a certain similarity in the retention mechanism, even if the surface is not described as similar.

Because it is not really straightforward to predict which compounds will be strongly retained by THF or methylene chloride for desorption with a low volume, the recommended solution is to always desorb analytes in the opposite way to the sample application (backflush desorption) when using carbonaceous sorbents, whatever the amount of sorbent in the cartridge. Then, methanol can be used with the advantage of being water-soluble and less toxic than THF or methylene chloride. Table 4 shows the recoveries that were obtained by percolating 1 l of water spiked with 13 pesticides through a 500-mg PGC cartridge and desorbing it in the same way as the sample application with 15 ml of methanol and in the opposite way with 5 ml of methanol. Half of the solutes were not desorbed in the forward flush, and the results are in agreement with the LC data of Table 4 whereas all the compounds are desorbed in the backflush way with only 5 ml of methanol. The lower recoveries for aldicarb and carbendazim are explained by loss during the evaporation step. For these compounds, it is necessary to stop the evaporation before dryness.

4. Off-line applications

4.1. Polar analytes and/or multiresidue extraction including very polar analytes

Off-line extractions have been described using GCB cartridges for the extraction of polar analytes such phenols, chlorophenols [62–64] and chloroanilines [7]. Carbon-based membrane extraction disks are also available and have been used for the determination of *N*-nitrosodimethylamine at the ng/l level in ground water [65].

Many applications deal with the extraction of several neutral or basic pesticides over a wide range of polarity and including polar pesticides or their degradation products [9–11,16,35,66,67]. A sensitive and specific LC–mass spectrometry (MS) method for determining 45 widely used pesticides having a broad range of polarity was developed using a cartridge packed with 0.5 g of Carbograph 4 [16].

Table 4
Recoveries obtained when desorption is performed using methanol in the same way (forward) or in the opposite way (backflush) way to sample application[a]

Compound	Recovery (%)±RSD (%)		
	Test of volatility	Forward desorption (15 ml)	Backflush desorption (5 ml)
Oxamyl	100±3	91±8	101±5
Methomyl	95±3	94±6	99±4
Deisopropylatrazine	103±2	103±4	102±6
Monocrotophos	102±3	105±5	100±5
Fenuron	95±4	95±3	101±5
Metamitron	95±3	Non desorbed	99±3
Deethylatrazine	103±2	100±3	101±4
Chloridazon	105±2	Non desorbed	106±5
Carbendazim	65±9	Non desorbed	58±7
Aldicarb	71±3	80±5	79±6
Aminocarb	103±3	Non desorbed	103±3
Metribuzin	102±3	Non desorbed	101±6
Metoxuron	98±4	Non desorbed	101±5

[a] Extraction of pesticides using a 500-mg PGC cartridge from 1 l of LC-grade water; spike level: 3 μg/l; values from three replicate experiments. The volatility test consisted of spiking 5 ml of methanol with 50–100 ng of each pesticide and evaporating to dryness under the same conditions of nitrogen flow at ambient temperature. From Ref. [21].

From 4 l of drinking water, detection limits ranged between 1 and 9 ng/l when calculated from total ion current chromatograms and between 0.06 and 1.5 ng/l when calculated from extraction ion current profiles.

The potential of PGC for the extraction of very polar and water soluble compounds was shown with the trace determination of simazine, atrazine, their degradation products and a few polar pesticides [21,31]. Table 5 compares the retention factors of these polar degradation products using C_{18} silica, PS–DVB with different specific surface areas and PGC. These data are interesting because they clearly show the different behavior of PGC as compared to the other reversed-phase sorbents. Very few data are available in the literature for the characterization of the behavior of solutes using the new highly cross-linked polymers, just because they are not sufficiently pressure resistant for LC and are not available in analytical column form. Some experiments have been done by laboratory-packing small-size analytical columns using the sorbents contained in the SPE cartridges. Results show a large increase in retention factor when increasing the surface area from 400 m^2/g to above 1000 m^2/g, as can bee seen for oxamyl, simazine, deethylatrazine (DEA) or deisopropylatrazine (DIA). These analytes are highly retained by both PS–DVB and PGC, and DEA is even more retained by the PS–DVB than it is by the PGC. When the polarity increases with the molecule degradation, the retention factor decreases for the PS–DVB – due to the hydrophobic retention mechanism – whereas it increases with PGC, so that hydroxy-DEA and hydroxy-DIA (OHDIA) are more retained by PGC than they are by the highly cross-linked PS–DVB. For the three ultime metabolites cyanuric acid, ammeline and ammelide, the retention is too low for being extracted by the highly cross-linked polymer, whereas log k_w values are around 2.5 with PGC. The better capability of PGC for the extraction of some very polar and water-soluble analytes is then demonstrated.

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 obtained similar recoveries [31]. Fig. 1 shows the chromatogram obtained on a C_{18} analytical column when injecting an extract from 300 ml of drinking water spiked with 0.5 μg/l of simazine, atrazine and six metabolites. Ammeline, ammelide and cyanuric acid could not be included in the

Table 5
Comparison of log k_w values obtained with C_{18} silicas, various PS–DVB copolymers with different specific surface areas and porous graphitic carbons[a]

Compound	Log K_{ow}	Log k_w				
		C_{18}	PS–DVB (415)	PS–DVB (350)	PS–DVB (1060)	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
Dethyldeisopropylatrazine (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
Hydroxyatrazine (OHA)	1.4	2.5±0.1	3.0±0.2	nd	nd	3.4±0.2
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±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

[a] From Ref. [5]. 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.

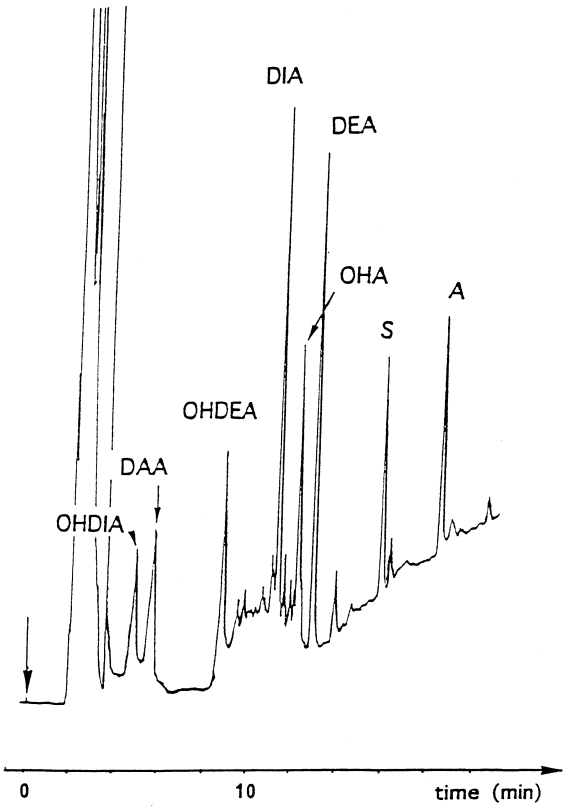

Fig. 1. Off-line analysis of the SPE extract corresponding to 250 ml of drinking water spiked with 0.5 μg/l of atrazine, simazine and six hydroxylated and dealkylated metabolites. From Ref. [31]. Extraction through a 300-mg PGC cartridge and analysis with a Sperisorb ODS-2 (25 cm×0.46 cm I.D.) analytical column; water–acetonitrile gradient at pH 7. Solutes: A, atrazine; S, simazine; DEA, deethylatrazine; OHA, hydroxyatrazine; DIA, deisopropylatrazine; OHDEA, hydroxydeethylatrazine; DAA, deethyldeisopropylatrazine; OHDIA, hydroxydeisopropylatrazine; UV detection at 210 nm.

chromatogram of Fig. 1. They could be separated with an aqueous mobile phase but with retention close to the void volume of the C_{18} analytical column as shown in Fig. 2a. Therefore, when these analytes are to be determined in real samples at the trace level, the extraction and concentration step generates many interfering compounds which hinder the detection of the early eluted analytes as shown in Fig. 2b where peaks marked with the star could correspond to the analytes. The extract was spiked with cyanuric acid and the peak corresponding to the second star increased. Then, in order to confirm, the solution was to take a PGC analytical column which provided the elution of cyanuric acid in 8 min with a mobile phase containing 30% methanol, so that it was possible to discriminate between interferences and cyanuric acid, as shown in Fig. 2c and d.

The use of a PGC analytical column is of particular interest for analyzing extracts containing very polar analytes. This was illustrated when looking at the stable degradation products of atrazine in ground water. According to the work of Thurman et al. [68], atrazine is degraded in soil rapidly to deethylatrazine and more slowly to deisopropylatrazine. The former analyte is stable and being more soluble that the parent molecule rapidly migrates in ground water, whereas the latter is not stable and rapidly degraded in the didealkylated product DEDIA which is stable and water-soluble (log $K_{ow}=0$). Whereas DEA is often reported, the occurrence of DEDIA has never been reported because it is not extracted by current procedures or is co-eluted in the interfering peak due to humic substances. Fig. 3a shows the analysis of an extract from drinking water using a PGC analytical column. A 200-mg PGC cartridge was used for the handling of 500 ml spiked with 0.3 μg/l of each compound. Recoveries were in the range 90–95% for the five analytes. One can see the great difference in the retention mechanism since DEA is eluted before the less hydrophobic DIA and DEDIA has a retention time around 10 min with an acetonitrile–water gradient from 10% to 70% acetonitrile from time 10 to 35 min. Fig. 3b correspond to the extract from 500 ml of ground water and shows the occurrence of DEDIA, DEA and atrazine. The concentration of DEA (0.65±0.05 μg/l) is higher than that of the parent molecule atrazine (0.045±0.05 μg/l). The concentration of DIA is low (0.06 μg/l) as compared to that of DEDIA (0.30±0.05 μg/l) and this result confirms the experiments of Thurman et al. who have observed these preferential dealkylation reactions of atrazine in the unsaturated zone [68].

Hydroxyatrazine (OHA or HA) is a metabolite of environmental concern in surface water. Good recovery for this analyte was obtained using a 250-mg GCB cartridge from 2 l of water [69]. In another study, using the same cartridge, it was possible to determine DEA, DIA and HA at the ng/l levels from 1 l of lake water [70]. Carbograph 4 with its higher specific surface area was shown to be even more

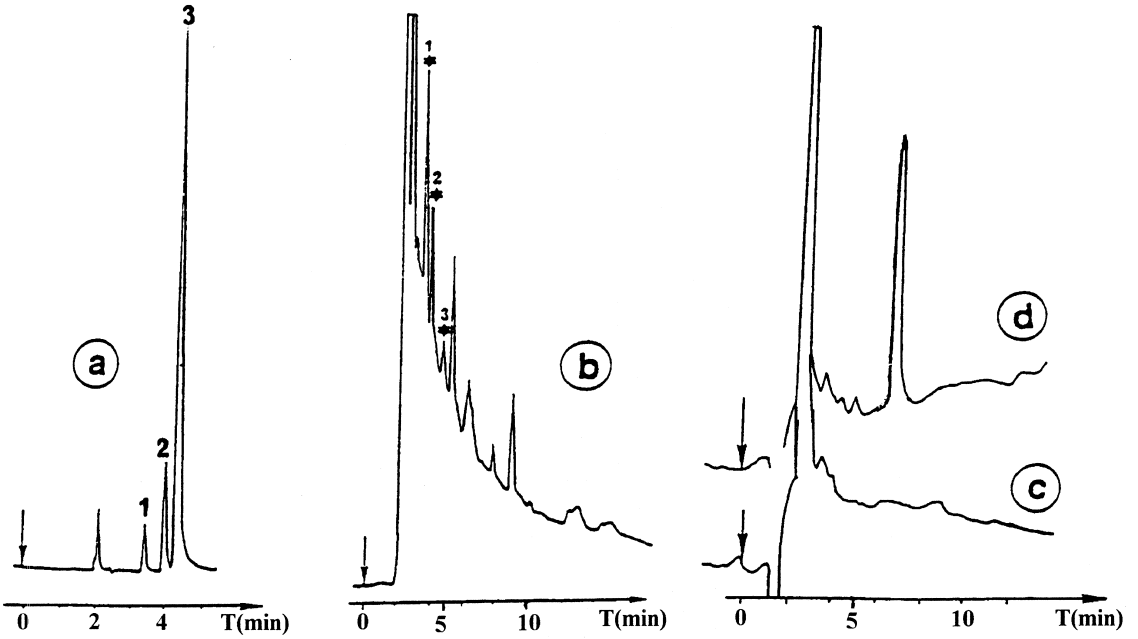

Fig. 2. (a) Analytical separation of ammeline (peak 1), cyanuric acid (2) and ammelide (3) using Sperisorb ODS-2 (25 cm×0.46 cm I.D.) analytical column eluted with a 10^{-3} *M* perchloric acid solution. (b) Analysis of a water extract from 250 ml of drinking water. (c) Analysis of the same sample as in (b) using a Hypercarb analytical column eluted with methanol–0.05 *M* phosphate buffer at pH 7 (30:70, v/v). (d) Same sample as in (c), but spiked with 5 μg/l of cyanuric acid. SPE using Hypersep PGC cartridges. Adapted from Ref. [31].

capable than Carbograph 1 (210 m^2/g instead of 100 m^2/g) to extract very polar compounds from water [71]. The extraction of atrazine and its six major metabolites followed by LC–electrospray (ES)-MS has been also described using Carbograph 4 [72]. In order to detect ng/l levels, 4 l of drinking water and 1 l of river water were handled and desorption occurred by 0.5 ml of methanol, followed by air during 1 min and back elution with 1.5 ml of methanol and 6 ml of methanol–methylene chloride, (20:80, v/v) containing 5 mmol/l HCl. When the eluate was not acidified poor recoveries wee obtained for OHDIA and DEDIA. With this procedure, recoveries were excellent when 4 l of drinking water were spiked at the 200 ng/l and at the 3 ng/l level. Thanks to the study with water spiked at the low 3 ng/l level, the author could conclude that no effect of irreversible adsorption was produced by the extraction device. Fig. 4a shows the total ion current chromatogram corresponding to the analysis of 1 l of a river water spiked with the seven analytes at the individual level of 0.4 μg/l. Acquisition in time-scheduled single ion monitoring (SIM) mode and extracted from 4 l of drinking water afforded higher sensitivity as shown by Fig. 4b where the two-ion LC–ES-MS-SIM chromatogram is represented which corresponded to the analysis of an extract spiked with 1 ng/l of each analyte.

4.2. Potential for in-site sampling: analyte stability and storage

The sample handling, transport and storage of samples can be greatly improved because of the small volume of the cartridges. Transport from the sampling site with storage at cool temperature such as −20°C and even 4°C is difficult for water samples in glass bottles. The in-the-field sampling and analyses in laboratory can also be advantageous for monitoring in remote areas. The use of SPE cartridges and disks has been shown to be an alternative to storage of original samples or for analysis of samples collected in remote sites [73–78]. Few studies have been devoted to stability studies on

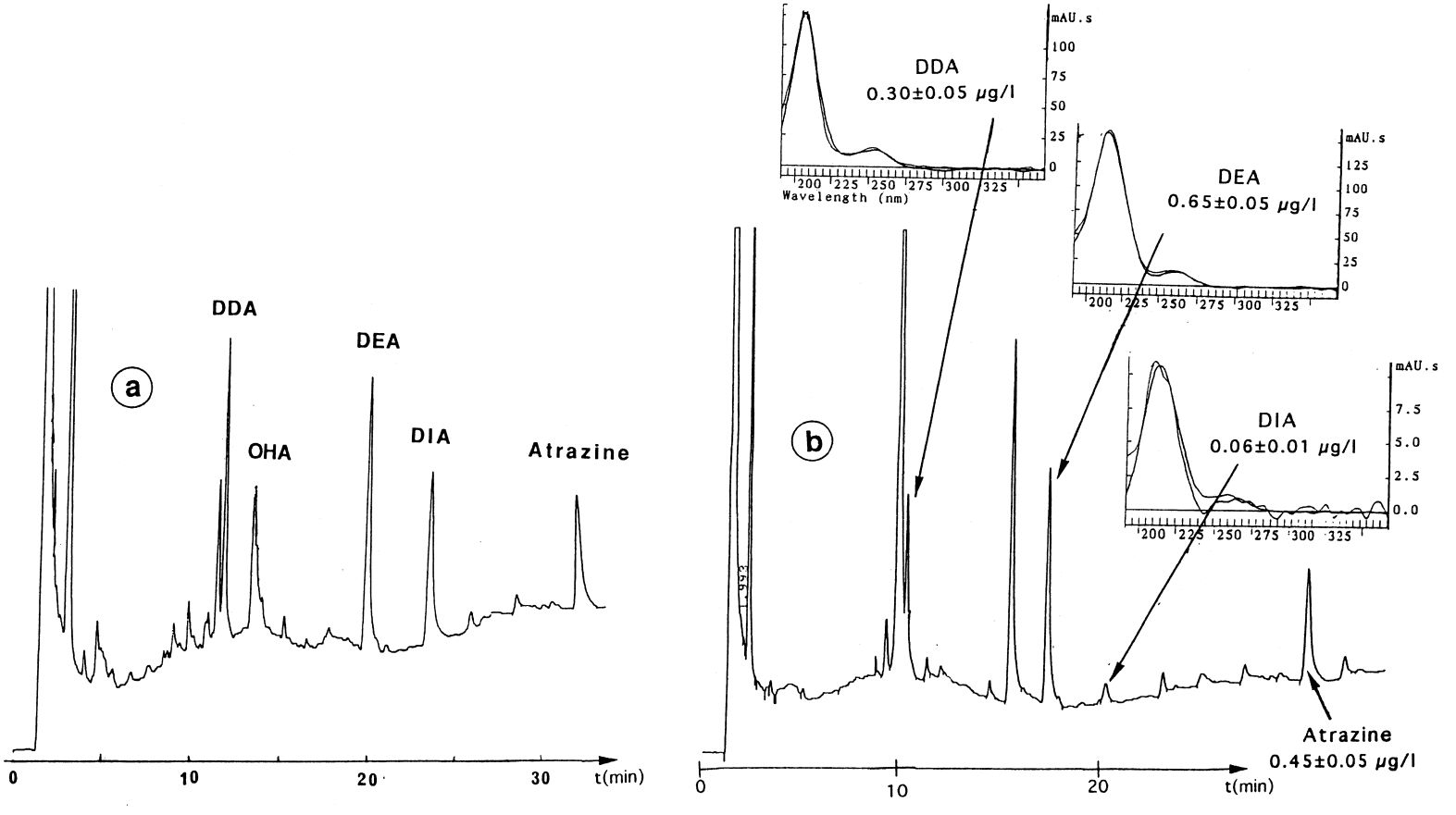

Fig. 3. Off-line SPE followed by LC using PGC. Extracts from 500 ml of (a) drinking water spiked with 0.3 μg/l of each analyte and (b) ground water in an agricultural area. SPE on a 200-mg Hypersep PGC cartridge; analysis using a Hypercarb analytical column (100×4.6 mm), acetonitrile gradient with 0.005 *M* phosphate buffer at pH 7 from 10% to 70% acetonitrile from 10 to 35 min, UV detection at 220 nm. Peaks: 1=deethyldeisoprolylatrazine; 2=hydroxyatrazine; 3=deethylatrazine, 4=deisopropylatrazine, 5=atrazine.

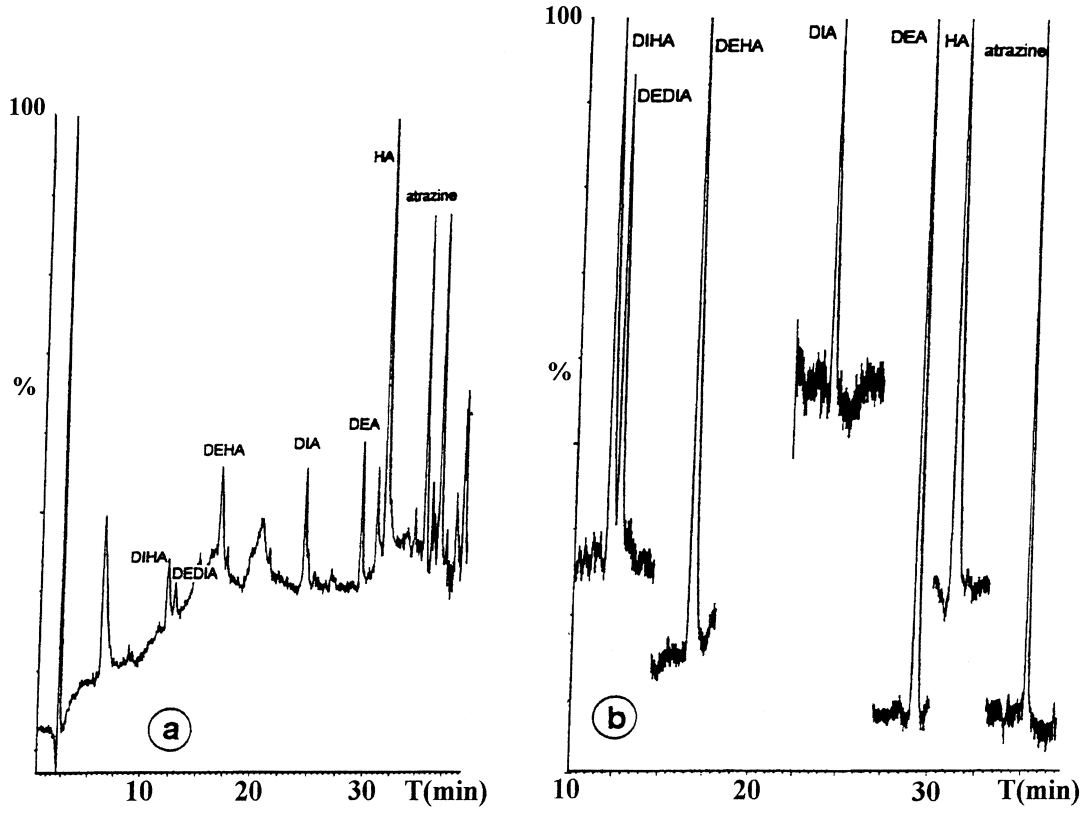

Fig. 4. (a) Total ion current (TIC) LC–MS collision induced dissociation (CID) chromatogram obtained by analyzing 1 l of a river water sample spiked with atrazine and its six major metabolites. Off-line SPE using a 0.5-g Carbograph 4 cartridge. LC using a C_{18} Alltima (25 cm×0.46 cm I.D.) analytical column eluted with a methanol–water gradient with formic acid 10^{-5} *M*. (b) Two-ion LC–ES-MS-SIM obtained by analyzing 4 l of a drinking water sample spiked with the analyte at the individual level of 1 ng/l. Adapted from Ref. [72].

GCB or PGC. Atrazine an simazine adsorbed on Carbopack B have been stored at ambient temperature during 15 days without significant loss in recoveries [4]. However, the GCB surface is contaminated by a small number of oxygen chemical complexes and the adsorption of more polar analytes on the active centres may affect their stability. Traces of chloroanilines were lost after 1-day storage on the adsorbent unless hydrazine was added to the water samples [7]. The stability of 34 selected pesticide extracted from water onto the GCB surface was evaluated under various conditions of storage [78]. The best results were obtained by first minimizing the water content into the GCB extraction cartridge by a suitable methanol washing and then freezing the cartridge. Under these conditions and over a storage period of 3 weeks, the stability of pesticides extracted from four river water samples onto the GCB surface was assessed and compared with that in water at 4°C with and without an inhibitor of biodegradation agent, such as $HgCl_2$. Results indicated that storage on the GCB material was a far better preservation procedure than storage in water at 4°C. Several of the pesticides were degraded when stored in water in the presence of $HgCl_2$.

4.3. Two-trap tandem extraction systems involving graphitized carbon black

The coupling of C_{18} silica membrane extraction layered over a carbon-based extraction disk was employed for the trace determination of *N*-nitro-

sodimethylamine in water samples [65]. The C_{18} disk removed non polar and water-insoluble neutral compounds and was set aside whereas the carbon disk was extracted with a small volume of dichloromethane. Using gas chromatography (GC) and a chemiluminescence detector, detection limits were 300 ng/l in heavily contaminated samples. This procedure offered a 50-fold saving time and 100-fold reduction in dichloromethane consumed as compared to the previous LLE procedure which was overnight because of the high water-solubility of the analyte.

The coupling of a reversed-phase sorbent with an ion exchanger was shown to be very efficient for the selective determination of ionizable analytes [19]. A first cartridge packed with the non specific graphitized carbon black sorbent traps the analyte of interest and many other compounds, but only ionized analytes are transferred and reconcentrated into a second cartridge packed with a more specific sorbent such as a cation exchanger. Selective determination of triazine herbicides [5] and chloroanilines [44] could thus be achieved at the ppt level. By percolating of 2 l of drinking water through a cartridge packed with 250 mg of graphitized carbon black, and then connecting this cartridge to a second one packed with a cation exchanger and flushing of the two columns with a mixture of dichloromethane and methanol, 14 phenylurea herbicides could be determined in drinking water with detection limits at the ng/l level. Phenylureas were eluted while all basic interferences such as chlorotriazines and anilines were trapped by the ion exchanger [79].

A similar two-trap tandem was described for the selective determination of phenols [9]. The phenols were isolated from base–neutral species. After the sample had passed through the 300-mg GCB cartridge, the latter was connected to a strong anion exchanger (SAX) cartridge (50 mg) and base–neutral species were removed from the GCB surface by a neutral eluent. Co-eluted very weakly acidic phenols were selectively re-adsorbed on the SAX sorbent. An acidified eluent was allowed to flow through the two cartridges still in series, to recover the most acidic phenols from the GCB cartridge and the least acidic from the SAX cartridge. Recoveries of 17 priority phenols from 2 l of spiked drinking water samples were higher than 90%.

4.4. Extraction of anionic analytes using graphitized carbon black acting as an ion exchanger

Although GCB is shown to behave as a reversed-phase, it contains positively charged oxonium groups which can act as anion-exchange sites. That property was exploited for the extraction of anionic linear alkylbenzene sulfonates (LASs) [12,13,80]. The common approach for the separation of these highly polar aromatic sulfonated analytes is ion-pair chromatography. An on-line ion-pair-based SPE for their trace enrichment from water samples followed by ion-pair LC has been described using precolumns prepacked with C_{18} silica or the copolymer PLRP-S as sorbent and tetramethyl- or tetrabutylammonium bromide as ion-pair reagent [81–84]. However, the extraction of the more hydrophilic benzenesulfonate such a few amino-substituted and amino-hydroxy was incomplete. Moreover, the co-extraction of interfering dissolved organic compounds was problematic. The potential of the combined anion-exchange and hydrophobic mechanisms was investigated with respect to the hydrophilic amino- and hydroxybenzenesulfonates and the elimination of humic substances [13]. The authors have shown that the ability to extract aromatic sulfonates from water and the possibility to elute it later from GCB strongly depended on the type and amount of functional groups and the size of the aromatic structure. Benzene- and naphthalenesulfonates without protonated functional groups were easily eluted with 50 m*M* ammonium acetate in dichloromethane–methanol (80:20, v/v). Compounds with amino groups were more difficult to recover. According to a previous study by Di Corcia and Marchetti [10], irreversible interactions can take place between free amino groups and quinone groups of the GCB surface and the solution was to pretreat it with ascorbic acid to reduce the quinones to the corresponding hydroquinones. Therefore, after washing the GCB cartridges (Carbopack B, 500 mg) with 3 ml of the desorption solution and 3 ml of methanol, a further conditioning was performed using 20 ml of ascorbic acid in 0.1 *M* hydrochloric acid. With this procedure, satisfactory recoveries were obtained with most of the tested sulfonates including those containing one

amino group [13]. Only those containing two amino or hydroxy groups could not be completely recovered. The irreversible addition of amino compounds was investigated and the authors concluded that the potential of GCB to form hydrogen bridges may negatively affect their recoveries and that the reduction with ascorbic acid eliminated only partially the hydrogen binding functions. In the same study, they observed that larger aromatic structures such as stilbene- and anthraquinonesulfonates could not be eluted from GCB. The interest was that interferences caused by humic substances were also removed. This is illustrated in Fig. 5 where the chromatograms of an extract from river water samples are compared, one (A) being obtained by ion-pair extraction on C_{18} silica with tetrabutylammonium and the other one (B) using GCB. The characteristic hump formed by humic substances is almost absent from the chromatogram of the GCB extract. The detection limits for 100-ml samples were between 0.1 and 1.0 μg/l using reversed-phase ion-pair LC in combination with a UV DAD. Twelve aromatic sulfonates were identified and quantitatively determined by applying the whole procedure to wastewater from a textile manufacturing plant. A similar procedure was applied to the selective determination of aromatic sulfonates in landfill leachates and ground water using microbore LC coupled with mass spectrometry [85]. The minor modification was the use of 1-g Envi-Carb cartridge preconditioned with 5 ml of the

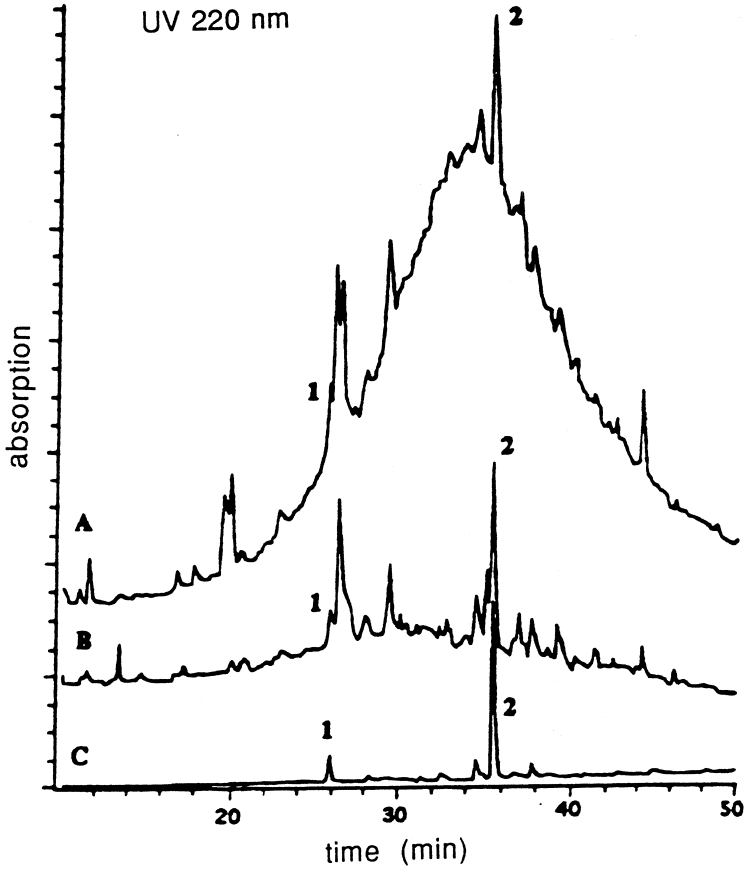

Fig. 5. Chromatograms of extracts from 1 l of river water spiked with 1 μg/l 3-nitrobenzenesulfonate (1) and naphthalenesulfonate (2). The samples were extracted with (A) 1 g of C_{18} adsorbent and 5 m*M* tetrabutylammonium bromide and (B) 1 g of Carbopack B. (C) Standard solution. LC analysis with a C_{18} analytical column (Hypersil ODS, 240×4 mm I.D.) operating in ion-pair mode. From Ref. [13].

eluent, 3 ml methanol and 75 ml of ascorbic acid (57 m*M* in 0.1 *M* aqueous HCl).

4.5. Class fractionation using a single graphitized carbon black cartridge by sequential elution

The fact that GCB can behave as both a non specific and an anion exchanger made possible extraction, concentration and class fractionation using a single sorbent cartridge. By taking advantage of the positively charged active centres on the Carbopack B surface, a stepwise elution system allowed the complete separation of base–neutral pesticides from acidic ones [10,14]. The procedure was applied to the monitoring of 89 pesticides (71 base–neutral and 18 acidic) [14]. After passing the water samples through a 300-mg Carbopack B cartridge, the base–neutral pesticides were eluted in a first vial by 1 ml of methanol followed by 6 ml of methylene chloride–methanol (90:10, v/v). Then, acidic pesticides were collected in a second vial by passing through the sorbent bed 4 ml of methylene chloride–methanol (90:10, v/v) acidified by trifluoroacetic acid (TFA; 0.2%, v/v). Satisfactory recoveries were obtained for all the 89 compounds with 2 l of spiked tap water. A very similar procedure was recently described allowing the simultaneous determination of base–neutral and acidic pesticides at the ppt level (ng/l) using Carbograph 4 followed by sequential back elution and LC–MS analysis [15]. Fig. 6 represents the chromatogram corresponding to the two fractions obtained from 2 l of drinking water samples spiked with pesticides at level of 50 ng/l each.

The determination of 15 of most representative

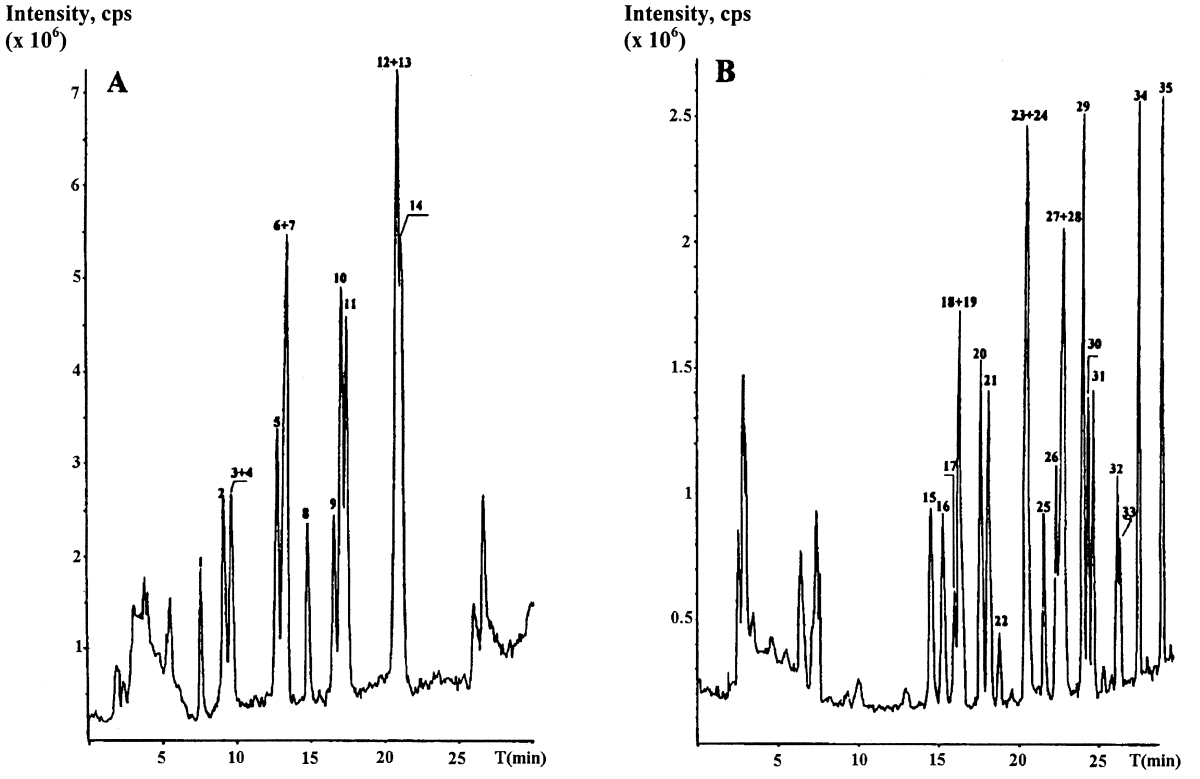

Fig. 6. TIC chromatogram for (A) neutral and (B) acid fraction obtained by injecting 50/200 of a final extract relative to 2 l of drinking water spiked with the herbicides at a level of 50 ng/l each. SPE through a 0.5-g Carbograph 4 cartridge, see text for fractionation scheme; LC using a C_{18} Alltima (25 cm×0.46 cm I.D.) analytical column eluted with a methanol–water gradient. From Ref. [15].

compounds of a new class of post-emergence pesticides (sulfonylureas, imidazolinones, arylphenoxypropionic acids) was possible with detection limits of 5 ng/l in drinking water [17]. The fractionation was not performed and after sample application the procedure for acidic pesticides (elution with methanol chloride–methanol containing TFA) was applied. Recoveries were all in the range 85–107% with 4-l samples spiked at the 100 ng/l level without sample pretreatment. Comparison was made when using C_{18} silica for the preconcentration step. The difference was that acidification of samples was required because retention was obtained with pesticides in their acidic form. But some of them like imazethapyr, haloxyfop, quizalofop and fenoxaprop were unstable in acidic environment.

The sequential elution was also applied to the extraction and fractionation of nonylphenol polyethoxylates and LAS surfactants and their degradation products [80,86].

When only acidic analytes are to be isolated, the first step of the sequential elution can act as a clean-up step, removing the non acidic compounds present in the sample. This was applied to the extraction of arylphenoxypropionic acid herbicides [67]. In term of recovery and selectivity the effectiveness of Carbograph 1 was compared with that of two PS–DVB sorbents (LiChrolut-EN and Empore disk). Fig. 7 shows the chromatograms corresponding to the three extracts and illustrate the potential of the sequential elution in removing potential interferences. Samples have been acidified before extraction using the two PS–DVB sorbent whereas they were not using Carbograph 1.

Another application has been described for the characterization of biodegradation intermediates of branched alcohol ethoxylate surfactants [87,88]. The sequential elution allowed the separation of neutral analytes and acidic metabolites.

4.6. Shape-based fraction between planar and non planar polychlorinated biphenyls

The flat PGC surface provides unique ability to

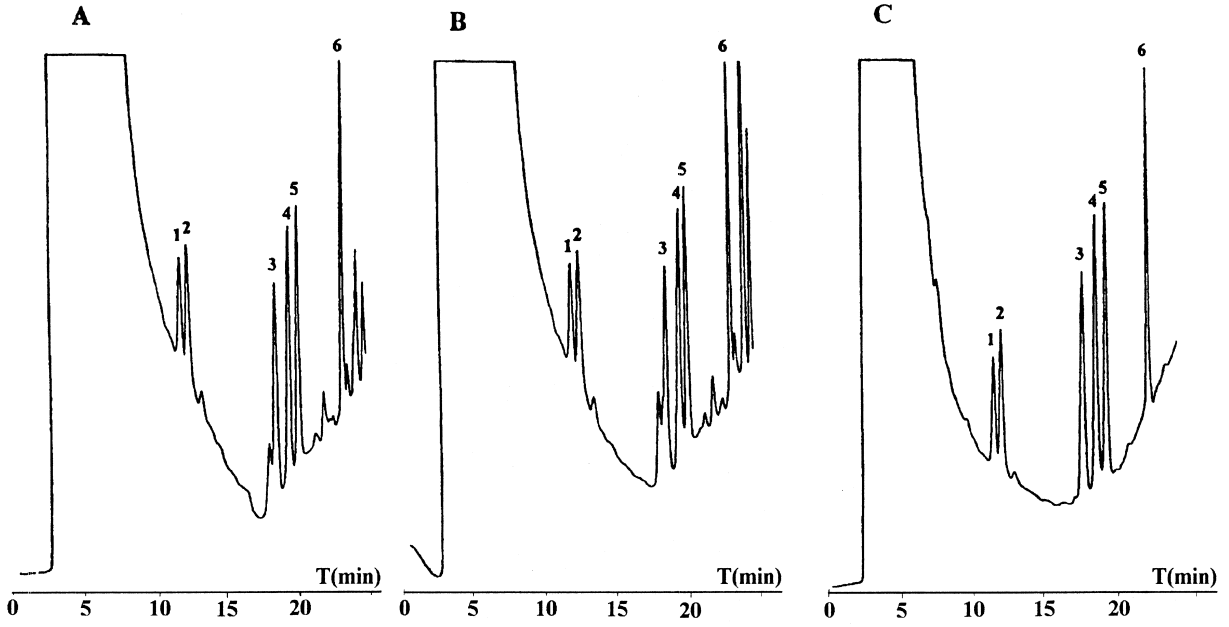

Fig. 7. Chromatogram obtained on analyzing 1 l of ground water sample spiked with arylphenoxypropionic acids at the individual level of 100–200 ng/l by three procedures involving the use of (A) the PS–DVB LiChrolut-EN cartridge; (B) a PS–DVB Empore disk and (C) the Carbograph 1 cartridge. LC using a C_{18} Supelco (25 cm×0.46 cm I.D.) analytical column eluted with a water–methanol–acetonitrile gradient. Analytes: 1=fluazifop, 2=clodinafop, 3=quizalofop, 4=fenoxaprop, 5=haloxyfop, 6=doclofop. UV detection at 240 nm. From Ref. [67].

resolve isomeric and closely related compounds [89]. One interesting application was the fractionation of polychlorinated aromatic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs) with hexane as eluting mobile phase [90]. In this fractionation scheme, PGC is used in normal-phase chromatography with apolar solvent such as hexane. A 50×4.6 mm column has been designed for this purpose (Hypercarb PCB). The determination and quantification of the planar PCBs (non-*ortho* substituted and mono-*ortho* substituted congeners) as well as that of PCDDs and PCDFs is important because of their higher toxicity, as compared to the other congeners. But it is also a very difficult analysis because their concentration is typically 10^{-9}–10^{-6} lower than that of other PCBs. PCG is well suited for this fractionation because of the planar structure of these toxic congeners. These fractionation has been described using hexane or mixture of hexane with dichloromethane or toluene [91–94]. A linear gradient from hexane to a mixture of hexane–toluene (60:40, v/v) was used to fractionate di-*ortho*, mono-*ortho* and non-*ortho* PCBs [95]. PCDDs and PCDFs were so strongly retained that they were only eluted using pure toluene in the reverse flow.

5. On-line coupling with liquid chromatography

Advantages of on-line coupling SPE to chromatographic separations are mainly that no risk of loss or contamination exists and the automation potential. A typical on-line arrangement is easy to perform in any laboratory using simple switching valves and commercial precolumns and their holder [21,32–34]. Two automated devices are commercially available (Prospekt and OSP-2) which possess the capability of using a fresh disposable precolumn for every sample. The trace enrichment is carried out similarly to the off-line sequence using a solvent delivery unit which provides the solvent necessary to purge, wash and activate the precolumn and applies the required volume of sample. The main difference is in the desorption since the trapped compound are eluted directly from the precolumn into the analytical column by a suitable mobile phase which also brings about the chromatographic separation.

5.1. Compatibility of porous graphitic carbon precolumns with C_{18} and porous graphitic carbon analytical columns

Since the precolumn is part of the analytical column in the transfer and separation process, a first requirement is that it should be pressure-resistant. The size of the precolumn is also of prime importance because the profile of the concentrated species transferred from the precolumn to the analytical column should be as narrow as possible at the beginning of the separation in order to avoid band-broadening. The quality of the coupling can be easily controlled by comparing chromatograms obtained by direct injection with those obtained by on-line preconcentration. The dimensions of the precolumn should be adapted to those of the analytical column and are typically 2–15 mm long and 1–4.6 mm I.D. for a classical 15–25 cm long analytical column [32].

Although the basic principles of SPE are similar in off-line and on-line methods, there are two serious limitations of on-line SPE–LC systems for the method development. The first one is that they use small precolumns which contain a small amount of sorbent. In off-line SPE, there is the possibility of increasing the breakthrough volumes by increasing the amount of the sorbent up to 1 or 2 g without increasing the volume of the desorption solution too much. This is not possible in on-line techniques and typical amounts of sorbents in precolumns are in the range 20 to 100 mg, so that when analytes are poorly retained in the precolumn, the only solution is to select a more retentive sorbent. The second limitation is that compatibility should occur between the sorbents in the precolumn and in the analytical column. In theory, the analyte retention should be ideally similar to, or lower than that on the analytical column for a perfect coupling. Therefore, the most efficient system is ideally obtained from a precolumn and an analytical column of the same nature. When many compounds are to be separated over a wide range of polarity, their separation requires a highly efficient analytical columns with both water- and organic-rich mobile phases. At present, only C_{18} silica columns meet this requirement. Analytical columns prepacked with polymeric styrene–divinylbenzene or porous graphitic carbon are very

efficient in organic-rich mobile phases but less in water-rich mobile phases depending on the nature of the analytes.

The on-line coupling of a PGC precolumn with a C_{18} analytical column was reported for the trace analysis of a mixture of 12 polar pesticides and degradation products [30]. The relatively high polarity of the mixture is shown in Fig. 8a by the gradient used for their separation. It starts with 5% acetonitrile, increases to 15% at 50 min and 30% at 60 min. The chromatogram corresponding to the on-line procedure is also represented in Fig. 8a. Backflush desorption only slightly improved the transfer. The alone analytes aldicarb (peak 10) and metribuzin (peak 12) are transferred with band broadening, whereas the other ones are not desorbed at all. That can be easily explained by the difference in log k_w values as shown in Table 6. Analytes are too strongly retained by the PGC in the precolumn to be desorbed by the mobile phase allowing their sepa-

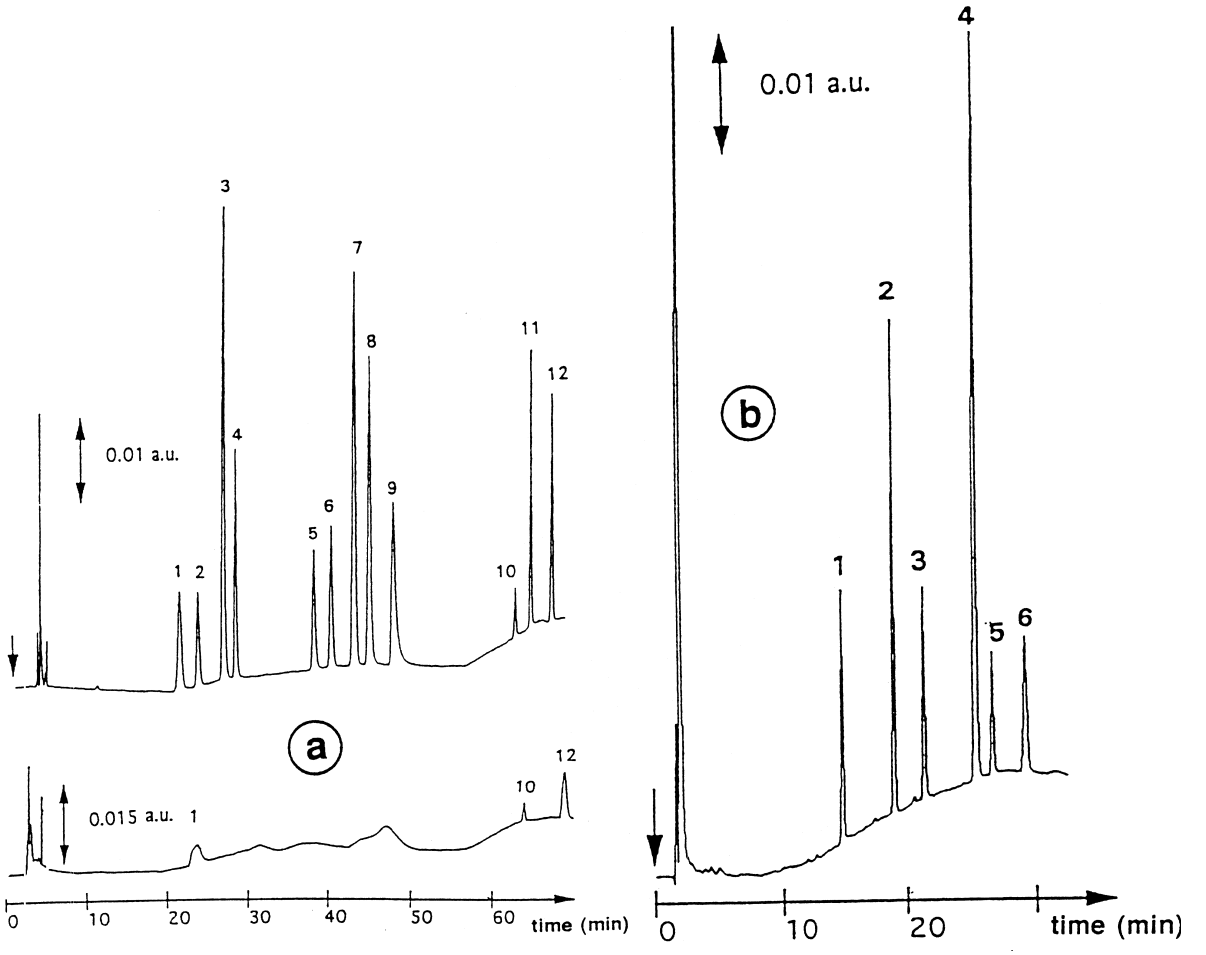

Fig. 8. (a) On-line coupling of a PGC precolumn and a C_{18} silica analytical column by comparison with the direct injection of a mixture and (b) on-line coupling of a PGC precolumn with a PGC analytical column. (a) On-line preconcentration of 100 ml of water spiked with 1.5 μg/l of each analyte; C_{18} Supelcosil LC-18-DB (25 cm×0.46 cm I.D.), acetonitrile gradient with a $5\cdot10^{-3}$ *M* phosphate buffer at pH 7, 5% acetonitrile from 0 to 15 min, 10% at 20 min, 15% from 40 min to 50 min, 30% at 60 min and 65% at 65 min. Flow-rate 1 ml/min; UV detection at 220 nm; solute numbering according to Table 6. (b) Water sample of 25 ml spiked with 6 μg/l of each compound; Hypercarb column (10 cm×0.46 cm I.D.), acetonitrile gradient with a $5\cdot10^{-3}$ *M* phosphate buffer at pH 7, 10% acetonitrile from 0 to 5 min, 15% at 10 min, 55% at 25 min. Flow-rate: 1 ml/min, UV detection at 220 nm. Analytes: 1=oxamyl, 2=methomyl, 3=monocrotophos, 4=fenuron, 5=deethylatrazine, 6=aminocarb. Adapted from Ref. [30].

Table 6
Comparison log k_w values estimated for a C_{18} analytical column and a PGC analytical column (Hypercarb)[a]

	Compound	Log k_w on C_{18}	Log k_w on PGC
1	Oxamyl	1.9±0.1	2.3±0.1
2	Methomyl	1.7±0.1	2.9±0.2
3	DIA	2.1±0.1	>3.5
4	Monocrotophos	2.0±0.1	2.9±0.2
5	Fenuron	2.1±0.1	>3
6	Metamitron	2.1±0.1	Not eluted
7	DEA	2.6±0.1	3.2±0.2
8	Chloridazon	2.0±0.1	>5
9	Carbendazim	2.2±0.1	Not eluted
10	Aldicarb	2.3±0.1	2.3±0.1
11	Aminocarb	2.9±0.2	3.3+0.2
12	Metribuzin	2.9±0.2	3.0+0.2

[a] Log k_w values extrapolated from the curves log k versus percentage of methanol. From Ref. [30].

ration on a C_{18} silica column starting at with 5 to 15% acetonitrile. When possible, the replacement of the C_{18} analytical column by an Hypercarb analytical column can solve the problem. Fig. 8b shows clearly that when both precolumn and column have the same nature, the on-line coupling is excellent and no difference is detected between the chromatogram obtained by direct injection and by on-line preconcentration, but not all the analytes of Fig. 8a could be separated using the Hypercarb analytical column.

In the literature, some examples show an acceptable PGC/C_{18} coupling. A close look indicates that the slope of the gradient used for the on-line transfer and separation is important. An example described the on-line use of Carbopack with a C_{18} analytical column for the trace enrichment of a mixture of polar carbamates and phenols [96]. The slope of the gradient used was much higher than that used in Fig. 8a as shown by the gradient which was linear from 20% acetonitrile to 40% in 20 min and 100% at 25 min. This gradient can be more rapid than that of Fig. 8 because there a few polar analytes mixed with rather moderately polar ones. Therefore, there is no general rule and the apparent compatibility between sorbents depends strongly on the polarity of the analytes to be separated.

5.2. Selected examples

The on-line system PGC/PGC can solve the accurate determination of some polar analytes. In a long-term survey of a ground water source, monitoring using the PLRP-S precolumn/C_{18} analytical column on-line system indicated constant and rather high amounts of atrazine and deethylatrazine with average concentrations of 0.5 and 0.6 μg/l, respectively [29,30]. With this system, a bad recovery is obtained for the metabolite deisopropylatrazine because its breakthrough volume on PLRP-S is 25 ml. Fig. 9 shows the advantage of using the coupling PGC/PGC since deisopropylatrazine is eluted after deethylatrazine and can be easily delayed to 40 min in the chromatogram, after the interfering compounds. Breakthrough volume of DIA on PGC is above 100 ml so that detection limits using 100-ml samples are in the low 0.1 μg/l in LC-grade water as shown in Fig. 9a and b. In the non spiked ground water (Fig. 9c and d), DEA was confirmed at concentration of 0.6 μg/l and the concentration of DIA was 0.05±0.01 μg/l.

On-line determination of hydroxychloroanilines, aminophenols and cyanuric acid was reported using both a PGC precolumn and a PGC analytical column [28]. Hypercarb analytical columns are available up to 10-cm long and even when packed with 5-μm particles, they are not as efficient as C_{18} silica columns, especially in water-rich mobile phases. If the pesticides of interest are not too numerous, the efficiency of Hypercarb analytical column may be sufficient. The on-line SPE and LC determination of diquat, paraquat and difenzoquat from environmental water was accomplished using the automated on-line device OSP-2 with a precolumn laboratory packed with Carbograph and a Hypercarb analytical column [97]. Sometimes, the on-line transfer in the backflush way was shown to improved the coupling [98].

6. Conclusion

Carbonaceous sorbents have effectively unique properties in retention. They behave as normal-phase, reversed-phase and ion exchanger sorbents. The LC data obtained with PGC are an important tool which greatly help in the prediction and understanding of the SPE properties of carbon-based sorbents. It is clear that more work is necessary for a full understanding of the interactions involves with PGC or GCB.

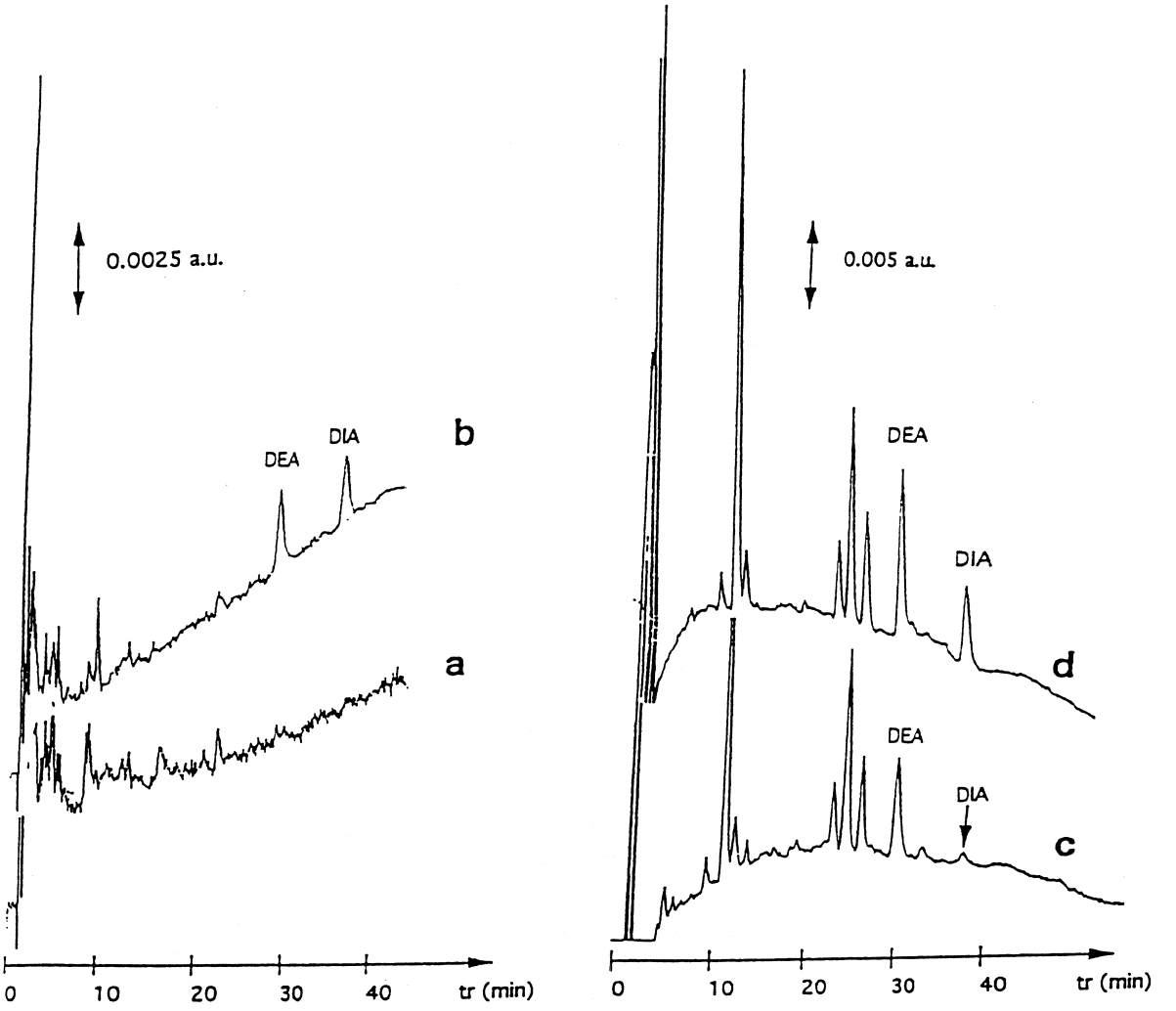

Fig. 9. On-line preconcentration of different aqueous matrices using the on-line coupling PGC precolumn/PGC analytical column. (a) 100 ml of non spiked LC-grade water and (b) spiked with 0.2 μg/l of DEA and DIA; (c) 100 ml of non spiked ground water and (d) spiked with 0.5 μg/l of DEA and DIA. Hypercarb column, 10 cm×0.46 cm I.D., acetonitrile gradient with a $5 \cdot 10^{-3}$ *M* phosphate buffer at pH 7, 15% to 35% acetonitrile from 0 to 40 min; flow-rate: 1 ml/min, UV detection at 220 nm. Adapted from Ref. [30].

It is clearly established now that SPE using graphitized carbonaceous sorbents can be a powerful method for the sample preparation of very polar analytes. Identifying new environmental problems and looking at the responsible compounds or metabolites involves the availability of such SPE sorbents which are capable to extract water-soluble analytes in aqueous samples. Some metabolites are not known just because they are not taken into account by conventional sorbents. For this purpose, carbonaceous are today the unique sorbents capable of extracting some highly water-soluble analytes.

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