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Evaluation of two new examples of graphitized carbon blacks for use in solid-phase extraction cartridges

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Abstract

The performances of two new examples of graphitized carbon blacks (GCBs), Carbograph 4 and Carbograph 5, filling solid-phase extraction cartridges were evaluated. Compared to an older GCB, Carbograph 1, the two new GCBs exhibited far larger abilities in extracting very polar compounds from both 4 l of drinking water and 1 l of water containing an amount of humic materials equivalent to 20 mg/l dissolved organic content. Like older GCB material, the new examples of GCBs have on their surfaces anion-exchange adsorption sites. However, Carbograph 5 partly failed to isolate acidic species from co-extracted non-acidic species by stepwise elution. Moreover, the surface of this sorbent material is more contaminated than those of both Carbograph 1 and 4 by sites able to bind irreversibly particular adsorbates. The extraction efficiencies of the two new GCBs were also compared with those of two recently introduced polystyrene–divinylbenzene (PS–DVB)-based materials. Recovery data showed that the carbonaceous materials were abler than PS–DVB ones in isolating very polar compounds from large water volumes, such as phenol, water-soluble pesticides, and low-molecular-mass biointermediates of linear alkylbenzenesulfonate surfactants. The positive features of including Carbograph 4 extraction cartridges in analytical schemes for determining traces of very polar pollutants in natural waters are demonstrated by three practical applications.

Keywords: Solid-phase extraction; Graphitized carbon black; Water analysis; Adsorbents; Environmental analysis; Polystyrene–divinylbenzene sorbents; Pesticides; Phenols; Surfactant biointermediates

1. Introduction

Recent regulations enacted in many European countries state that many organic pollutants, such as pesticides and phenols, cannot be present in waters destined for human consumption at individual levels exceeding 100 ng/l. To satisfy this stringent requirement, analytical methods able to detect 20–30 ng/l of a large number of these compounds are needed. An additional problem arises from the fact that several of the very polar compounds to be monitored are difficult to extract from the aqueous matrix. Moreover, there is a growing interest in assessing the fate in aquatic environments as well as the ecotoxicological impact on the aquatic life not only of a large variety of pollutants, such as pesticides,

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phenols and surfactants, but even of their chemical and biochemical degradation products, these often being more polar than their parent compounds.

To meet all these challenging demands, analytical chemists are developing routine analytical methods which are very sensitive, versatile, sufficiently rapid and simple. This goal may be achieved by coupling instrumentations with a high confirmational power, such as GC–MS and LC–MS, to sample preparation procedures able to give enrichment factors of 5000–10 000, even for highly hydrophilic target compounds. To obtain such high concentration factors, extraction of analytes from large water volumes, say 1–4 l, is a prerequisite.

A traditional approach to the preparation of water samples has involved liquid–liquid extraction (LLE). In addition to being a laborious and time-consuming technique, LLE is unable to solve the problem of extracting very polar compounds from water [1]. Solid-phase extraction (SPE) with inexpensive, commercially available sorbent cartridges offers a number of well-known advantages over LLE. Among the sorbent materials available for LSE of pollutants from water, octadecyl-bonded silica (C_{18}) has become by far the most popular one. However, there is an increasing awareness, supported by experimental data [1–8], that C_{18} cartridges are inadequate to solve the problems of isolating polar contaminants from large water volumes. This failure has urged investigators to evaluate alternative sorbent materials, such as highly cross-linked styrene–divinylbenzene copolymers (PS–DVB) [9–13]. The common feature of these materials is high surface area, i.e. 800–1200 m^2/g. Another emerging material is graphitized carbon black (GCB), commercially referred to as Carbopack or Carbograph 1. GCBs are obtained from heating carbon blacks at 2700–3000°C in an inert atmosphere. Carbograph 1 is essentially a non-specific, non-porous sorbent with a surface area of about 100 m^2/g. Carbograph 1 has proved to be a valuable adsorbent of a number of polar contaminants in water for SPE [1,4–8,14,15]. It has been shown that a GCB cartridge is much more efficient than either a C_{18} cartridge or LLE for extracting very polar pesticides from aqueous samples [1]. Owing to the presence on its surface of chemical heterogeneities bearing a positive charge [16], a singular feature of GCB is that it can behave as both a reversed-phase sorbent and an anion exchanger [17]. By exploiting this double nature, the separation of acidic compounds from co-extracted base/neutral ones can be easily performed by differential elution, passing suitable eluent phases sequentially through the cartridge [4,14,15]. In this way, extraction, preconcentration and class fractionation of analytes can be performed with a single cartridge.

Compared with other recent sorbent materials available for SPE, Carbograph 1 has a low surface area. Thus, the ability of Carbograph 1 to extract very polar species from large water volumes is due to an abnormally large adsorption of organics to its surface. However, the limited number of adsorption sites on the Carbograph 1 surface can create serious problems when extracting target compounds from an aqueous environmental sample with a high dissolved organic content (DOC). In this case, saturation effects of the SPE cartridge can lead to an unpredictably low recovery of the most polar analytes [7,14]. Such an unwelcome effect could be circumvented by increasing the weight of Carbograph 1 filling in the extraction cartridge [1,8]. This is reflected, however, in a decrease of the permeability of the cartridge to water and an increase of the time needed for extracting aqueous samples. This parameter is of relevant importance when conducting extensive environmental surveys, which require extraction of a large number of samples.

This work had two objectives. The first one was that of characterizing two new GCB examples with surface areas greater than that of Carbograph 1, in order to assess whether they could completely and advantageously replace Carbograph 1 in SPE cartridges. The second was that of comparatively evaluating the abilities of the two new GCBs and two recently introduced PS–DVB resins in quantitatively extracting selected polar compounds of environmental interest from large water samples.

2. Experimental

To achieve the objectives mentioned above, various choices concerning the design of the extraction cartridge, the analytes as well as the types of aqueous matrices to be assumed as models had to be made.

Cartridge design

To extract water samples in a relatively short time, large-diameter (1.3 cm I.D.), syringe-like, polypropylene tubes were filled with 0.5 g of each adsorbing material considered. Polyethylene frits were placed above and below the sorbent bed.

Model compounds

For this study, model compounds were selected from three classes of contaminants of significant environmental interest, i.e. phenols, pesticides, and surfactant biointermediates. Among these classes of contaminants, we selected as model compounds those with particularly high solubilities in water, which are supposed to be not easily prone to extraction from large water volumes.

Model aqueous matrices

Recovery studies were performed by extracting model compounds from two different types of aqueous matrices that, in terms of complexity, represent two opposite situations, that is drinking water and drinking water spiked with a concentration of humic acids (Aldrich Chemical, Milwaukee, WI, USA) equivalent to a DOC of about 20 mg/l. This latter matrix was prepared following a previously reported procedure [18] and was used for simulating a river water sample. This choice was based on two considerations. One is that humic materials account for up to 80% of DOC in surface waters [19]. The second was that, depending on a number of factors, the composition of river water can vary to such a large extent that no sample collected in a particular place and at a particular season can be assumed to be representative. Typical surface waters have DOC values significantly lower than 20 mg/l. Therefore, the humic acid-spiked drinking water chosen by us as a model matrix should be regarded as an anomalous aqueous sample that may eventually be encountered while monitoring pollutants in surface waters.

2.1. Reagents and chemicals

The test compounds selected were the following: O,O-dimethyl *S*-methylcarbamoylmethyl phosphorothioate (omethoate); 3-methylsulfonylbutanone O-methylcarbamoyloxime (butoxycarboxim); 2-methyl-2-(methylsulfonyl)-propionaldehyde O-(methylcarbamoyl)-oxime (aldicarb sulfone); 3-methylsulfoxylbutanone O-methylcarbamoyloxime (butocarboxim sulfoxide); 2-methyl-2-(methylsulfoxy)-propionaldehyde O-(methylcarbamoyl)-oxime (aldicarb sulfoxide); *S*-methyl 1-(dimethylcarbamoyl)-N-[(methylcarbamoyl)oxy]thioformimidate (oxamyl); *S*-methyl N-(methylcarbamoyloxy)-thioacetoamidate (methomyl); dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate (monocrotophos); 2-chloro-4-ethylamino-6-amino-1,3,5 triazine (atrazine, deisopropyl); 5-amino-4-chloro-2-phenylpiridazin-3-one (chloridazon); 4-amino-6-*tert.*-butyl-3-(methylthio)-1,2,4-triazin-5-one (metribuzin); 4-amino-3-methyl-6-phenyl-1,2,4-triazine-5-(4H)-one (metamitron); 2,4 dinitrophenol; 4,6-dinitro-2-methylphenol (DNOC); pentachlorophenol (PCP); 2-methyl-2-(methylthio)-propion-aldehyde *o*-methylcarbamoyloxime (aldicarb); 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron); 2-chloro-4-ethylamino-6 isopropylamino-1,3,5-triazine (atrazine); 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop); 2,4,5-thrichlorophenoxy-acetic acid (2,4,5-T); 4-hydroxy-3,5-diiodophenyl cyanide (ioxynil); (2,4-dichlorophenoxy) acetic acid (2,4-D); (2,4-dichlorophenoxy)butyric acid (2,4-DB); 2-(4-chloro-2-methylphenoxy)-propionic acid (mecoprop); 4-nitrophenol; 2-chlorophenol; 2-nitrophenol; 4-amino-3,5,6-trichloropyridine-carboxylic acid (pichloram); 3-amino-2,5-dichlorobenzoic acid (chloramben); 3,6-dichloro-2-methoxy-benzoic acid (dicamba); 2-isopropyl-(1H)-benzo-2,1,3-thiadiazin-4-one-2,2′-dioxide (bentazone); phenol; sulfophenyl-4-propionic acid (SPP); sulfophenyl-4-butyric acid

(SPB); sulfophenyl-4-valeric acid (SPV); nonylphenoxyacetic acid (NP1EC); nonylphenoxyethoxyacetic acid (NP2EC); O,O-dimethyl *S*-(N-methylcarbamoylmethyl) phosphorodithioate (dimethoate); 3-(4-chlorophenyl)-1,1-dimethylurea (monuron); 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine (simazine); 2-isopropoxyphenyl methylcarbamate (propoxur); 3-(4-isopropylphenyl)-1,1-dimethylurea (isoproturon).

The compounds (90–99%, purity) listed above were in part supplied by Riedel-de Haën (Hannover, Germany) and in part by Aldrich. SPP, SPB, SPV, NP1EC, NP2EC were obtained by synthesis according to procedures previously reported [20]. Individual standard solutions were prepared by dissolving 100 mg of each compound in 100 ml of acetonitrile.

Trifluoroacetic acid (TFA) and tetrabutylammonium chloride (TBACl) were purchased from Aldrich. For liquid chromatography (LC), distilled water was further purified by the Milli-Q RG apparatus (Millipore, Bedford, MA, USA). Methanol "plus" and acetonitrile "plus" of LC gradient grade were from Carlo Erba (Milan, Italy). All other solvents were of reagent grade (Carlo Erba) and were used as received.

2.2. Sorbents

Carbograph 1 and two new experimental examples of GCBs, Carbograph 4 and Carbograph 5, were kindly supplied by Carbochimica Romana (Rome, Italy). The particle size range of the three GCBs was 37–150 μm. No particular precaution was taken on storing GCBs. LiChrolut and Envichrom P are two PS–DVB materials. LiChrolut has a surface area of about 1200 m^2/g and a particle size range between 40 and 120 μm [13], and was kindly supplied by Merck (Darmstadt, Germany). Envi-Chrom P has a surface area of about 900 m^2/g, a particle size range between 80 and 160 μm [12], and was supplied by Supelco (Bellefonte, PA, USA).

2.3. Cartridge preparation

In all cases, extraction cartridges were prepared as mentioned above. Cartridges containing GCBs were pretreated as previously reported [1], while those containing LiChrolut and Envi-Chrom P were pretreated following procedures reported elsewhere [12,13].

Aqueous sample preparation

Before adding analytes to drinking water samples, hypochlorite was reduced by adding 0.5 g/l $Na_2S_2O_3 \cdot 5\ H_2O$. Simulated river water samples were prepared by adding Aldrich humic acids to hypochlorite-free drinking water and adjusting the pH of the solution to 8 by adding 20 mg/l of $NaHCO_3$. Samples were then artificially contaminated by spiking them with suitable volumes of the various working standard solutions. After agitating for 2 min, samples were submitted to the extraction procedure. When extracting acidic compounds with PS–DVB materials, the aqueous samples were acidified in advance to pH 2, as these materials are unable to retain deprotonated acidic species dissolved in water. On the contrary, no pH adjustment of the sample was necessary when using GCB extraction cartridges.

2.4. Extraction elution and solvent removal procedures

Cartridges were fitted into side-arm filtering flasks, and liquids were forced through the cartridges under vacuum from a water pump. When passing samples through the cartridges, the vacuum was reduced to the minimum. After passage of water samples and cartridge washing with 7 ml distilled water, different reextraction and solvent removal procedures were followed, depending upon the type of the material filling the extraction cartridge.

With GCB cartridges

Most of the water remaining in the cartridge was expelled under vacuum for 1 min. The residual water content was further decreased by slowly passing 0.4 ml of methanol through the cartridge. After the cartridge was air-dried for 1 min, a Teflon piston with a Luer tip and a conically indented base was forced to enter the tube until it reached the upper frit [21]. Thereafter, the cartridge was turned upside down, and adsorbates were recovered by back-flushing elu-

tion. Unless specified otherwise, when analyzing analyte mixtures both acidic and neutral in nature, a differential elution scheme was adopted. Base/neutral compounds were firstly eluted by 1 ml of methanol followed by 6 ml of CH_2Cl_2–CH_3OH (80:20, v/v). Acidic compounds were successively eluted and collected separately by passing 6 ml of the solvent mixture having the same composition as that mentioned above, but containing 10 mmol/l TBACl, through the cartridge. Extracts were dried in a water bath at 30°C by allowing a gentle nitrogen stream to flow into the tubes. Residues were reconstituted with known volumes of a water–methanol mixture, and suitable aliquots were injected into the LC apparatus.

With LiChrolut and Envichrom P cartridges

With both materials, after the passage of the water sample, the last part of a previously reported procedure involving the use of a LiChrolut cartridge [13] was appropriately modified to shorten the analysis time. After partial water removal by air-drying cartridges for 5 min, analytes were eluted from both LiChrolut and Envichrom cartridges by 2×5 ml of a methanol–acetonitrile (50:50, v/v) mixture. To save time, eluates were concentrated down to about 0.5 ml by the procedure reported above. Before concentrating phenol-containing extracts, they were made slightly basic by methanolic KOH to avoid evaporative losses of the most volatile phenols. After measuring the exact volumes of partially concentrated extracts, suitable amounts were injected into the LC apparatus.

All of the extracts were analyzed by LC with UV or fluorometric detection, following chromatographic conditions reported elsewhere [1,8,15].

3. Results and discussion

3.1. Comparative evaluation of cartridges filled with the three GCBS

The first objective was that of evaluating whether Carbograph 4 and 5 materials could advantageously replace Carbograph 1 in SPE cartridges. Some properties and characteristics of the former sorbents were measured and compared with those of the latter. We were particularly interested to ascertain whether, analogously to Carbograph 1, adsorption sites able to exchange anions were present even on the surfaces of the two new GCBs and the abundance of these specific adsorption sites. The anion-exchange capacities were measured by following a procedure described elsewhere [17]. Briefly, this method is based on determination of the amount of an organic anion, octylbenzene sulphonate, adsorbed via Coulombic forces on the GCB surface. In order to evaluate batch-to-batch reproducibility, measurements were performed by taking any GCB-type from three different batches. For each batch, duplicate measurements were made. Results reported in Table 1 show that even Carbographs 4 and 5 possess specific adsorption sites able to exchange anions. The surface concentrations of the anion-exchange sites were calculated to be 0.075, 0.078 and 0.031

Table 1
Some properties of the GCBs evaluated in this study

Sorbent	Surface area (m^2/g)	Flow-rate[a] (ml/min)	pH[b] (mean[c] ± S.D.)	Exchange capacity (μequiv./g, mean[c] ± S.D.)
Carbograph 1	100	57	10.5 ± 0.3	7.5 ± 0.4
Carbograph 4	210	87	11.0 ± 0.4	16.4 ± 0.9
Carbograph 5	560	55	6.5 ± 0.5	17.6 ± 0.8

[a] Flow-rate at which drinking water passed through a 1.3-cm I.D. cartridge filled with 0.5 g of a sorbent material.
[b] pH of the supernatant measured by immersing GCBs in distilled water (5% by weight) after 4 h continuous stirring.
[c] Average values calculated from duplicate measurements for each of the three GCB batches.

equiv./m^2, respectively, for Carbographs 1, 4 and 5. From these data it appears that the Carbograph 5 surface is substantially less densely populated by exchange sites than the other two GCBs. Interestingly, unlike Carbographs 1 and 4, we observed that when Carbograph 5 was immersed in water, a virtually neutral pH value of the supernatant was obtained. In previous works [17,22], we suggested that in the presence of water and oxygen, the generation of positively charged active centers on a GCB surface could result from rearrangement of an oxygen-containing impurity included in the graphitic surface framework to give benzpyrilium salts with simultaneous liberation of hydrogen peroxide and OH^- ions. Therefore, the anomalously low pH value measured for the aqueous suspension of Carbograph 5 might be due to the fact that exchange sites on the surface of this GCB are weak in nature. Or, when immersed in water, Carbograph 5 is able to release both OH^- and H^+ ions. If this is true, then Carbograph 5 should act as a cation exchanger and an anion exchanger as well as behaving as a non-specific sorbent. Work is in progress to ascertain the presence, nature, and behavior of these cation-exchange sites.

When extracting large water volumes and/or when many aqueous samples are to be analyzed, having SPE cartridges with a large permeability to water is desirable to shorten the analysis time. The permeabilities of cartridges packed with the three GCBs were assessed by measuring flow-rates at which tap water passed through them (Table 1). As can be seen, the Carbograph 4 cartridge exhibited the highest permeability. This result could be probably due to the fact that, among the three GCBs, Carbograph 4 particles are the most spherical in shape.

The abilities of the two new GCBs in quantitatively extracting very polar compounds from water was evaluated and compared with that of Carbograph 1. For this purpose, we selected some pesticides and their metabolites that have relatively large mobilities on a Carbograph 1 bed. A tap water sample was spiked with the analytes mentioned above at a level of 200 ng/l each, divided then in 4-l aliquots, and analyzed by extracting with cartridges filled with the three GCB materials. Measurements were made in triplicate (Table 2). Although the surface area of Carbograph 4 is only two times larger than that of Carbograph 1, the former material is far more efficient in extracting very polar compounds than the latter one. Evidently, adsorbates can establish interactions with the Carbograph 4 surface which are stronger than those with the Carbograph 1 surface. Among sorbents of the same chemical nature, stronger interactions with adsorbates can be generated by an increased

Table 2
Recovery (%) of some very polar pesticides and pesticide metabolites from 4 l of drinking water by extracting with cartridges filled with three different GCB examples

Compound	Sorbent material		
	Carbograph 1	Carbograph 4	Carbograph 5
Omethoate	32	91	97
Aldicarb sulfone	28	86	95
Butocarboxim sulfoxide	55	96	97
Aldicarb sulfoxide	32	97	97
Butoxycarboxim	50	98	97
Oxamyl	87	98	99
Methomyl	92	101	99
Monocrotophos	93	100	98
Atrazine, desethyl	95	96	101

Mean recovery values obtained from three measurements.

surface concentration of chemical and/or geometrical heterogeneities. From a practical point of view, it appears that Carbograph 4 and, even to a larger extent, Carbograph 5 are remarkably more effective than Carbograph 1 in extracting highly hydrophilic compounds from large water volumes.

In the recent past, we had experimental evidence [1,4] for some kind of irreversible adsorption occurring on extracting from water extremely low amounts of some pesticides, i.e. metamitron, metribuzin, and chloridazon. Quinone groups contaminating the sorbent surface [16] were supposed to be responsible for this adverse effect [1,4]. Analyte loss by chemisorption was circumvented by both pretreating the Carbograph 1 extraction cartridge with an ascorbic acid solution to reduce quinones and reversing the cartridge before analyte elution [1]. Moreover, it was observed that some phenol derivatives, e.g. 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol, had such a large affinity for some unknown active centers contaminating the Carbograph 1 surface that their quantitative reextraction from the cartridge could be achieved only by eluting them with abnormally high eluent phase volumes [17]. Even this problem was circumvented by eluting phenols in the back-flushing mode. In order to assess whether these anomalous effects could be produced upon adsorption of the compounds mentioned above on the new examples of GCBs, two suitable sets of experiments were conducted. The first set of experiments was conducted by spiking a tap water sample with the three pesticides mentioned above at two concentrations, 12.5 and 50 ng/l, dividing this sample in 4-l aliquots, and analyzing them by extracting alternatively with cartridges filled with the three GCBs. Back-elution was performed by passing the solvent mixture designed for eluting base/neutral species through the cartridges (see Section 2). In the second set of experiments, aliquots of 4 l of tap water samples spiked with the three phenols at 50 ng/l each were analyzed by extracting alternatively with the three GCB materials. Back-elution of phenols was carried out according to a recently reported method [8], that is by passing through cartridges 6 ml of CH_2Cl_2–CH_3OH (80:20, v/v) acidified with TFA (10 mmol/l) or, alternatively, by using as eluent phase the same one employed in this work for eluting acidic species (see Section 2). In both sets of experiments, each measurement was done in triplicate, and the results are reported in Table 3. In spite of the precautions taken, including pretreatment of the cartridge with ascorbic acid and back-elution of the analytes, a severe loss of

Table 3
Recovery (%) of some particular analytes on extracting them from water onto surfaces of three different examples of GCBs at two analyte concentrations

Compound	Sorbent Material					
	Carbograph 1		Carbograph 4		Carbograph 5	
	12.5 ng/l	50 ng/l	12.5 ng/l	50 ng/l	12.5 ng/l	50 ng/l
Metamitron	89[a]	96	81	94	45	83
Metribuzin	98	97	91	97	85	95
Chloridazon	97	96	100	98	82	101
2,4-Dinitroph		94[b] (99)[c]		60 (93)		43 (92)
DNOC		90 (98)		45 (95)		32 (93)
PCP		93 (98)		72 (99)		58 (96)

Mean recovery values obtained from three determinations.
[a] Eluent phase: 6 ml CH_2Cl_2–CH_3OH (80:20, v/v).
[b] Eluent phase: 6 ml CH_2Cl_2–CH_3OH (80:20, v/v) + 10 mmol/l TFA.
[c] Eluent phase: 6 ml CH_2Cl_2–CH_3OH (80:20, v/v) + 10 mmol/l TBACl.

metamitron was observed on extracting it with the Carbograph 5 cartridge from the most diluted aqueous solution. No increase of the percentage recovery of metamitron was observed upon reducing the water volume or doubling the volume of the eluent phase. Vice versa, satisfactory recovery of metamitron was obtained by using the Carbograph 1 and 4 cartridges. From these results, it can be deduced that among the GCBs under study, Carbograph 5 has the largest surface density of active centers able to bind irreversibly metamitron. From an absolute point of view, however, these anomalous adsorption sites on the Carbograph 5 surface are very few in number, as recovery of metamitron significantly increased by extracting it from the 50 ng/l-spiked water sample.

Only partial re-extraction of the three phenols from Carbograph 4 and 5 cartridges was obtained by eluting them with 6 ml of the acidified mobile phase. These phenols appeared to be eluted as badly tailed peaks, as progressively decreasing amounts of the three phenols were found in three successive 6-ml fractions of the TFA-acidified solvent mixture passed through the beds of the two sorbents cited above. Compared with Carbograph 1, it appears that Carbograph 4 and, to a greater extent, Carbograph 5 contain on their surfaces a higher number of anomalous adsorption sites able to establish strong interactions with particular phenoxy ions. No systematic investigation was conducted in order to elucidate the nature of these anomalous adsorption sites. Bearing in mind that these three phenols are weakly acid in nature and that TFA is a strong acid, it could be speculated that, even in protonated form, the three phenol derivatives are still able to interact strongly with those active centers bearing a positive charge. This hypothesis is somewhat substantiated by the fact that the three phenols were readily desorbed from both Carbographs 4 and 5 by replacing TFA with a quaternary ammonium salt (Table 3). As reported elsewhere [17], addition of an ion-pair-forming agent to a suitable solvent mixture is more effective than an acidic agent in displacing organic anions from anion-exchange sites present on the GCB surface.

As mentioned above, among adsorbents commercially available for SPE, the uniqueness of Carbograph 1 is that acidic compounds can be isolated from co-extracted base/neutral ones by differential elution. When analyzing complex aqueous matrices, this peculiarity can be advantageously exploited for decreasing the probability of interferences with the analysis of target compounds and for simplifying the interpretation of chromatograms. We evaluated which of the three GCBs under study was the most suited for accomplishing neutral–acid fractionation. For the purpose, the simulated river water (20 mg/l DOC) sample was spiked with a selected mixture of pesticides, some acidic and others neutral in nature. The spike level was 10 μg/l. This sample was then divided into 1-l aliquots and analyzed by extracting alternatively with cartridges containing the three GCB materials. Irrespective of the GCB-type filling the cartridge, after sample extraction and washings with 5 ml of distilled water followed by 0.4 ml of methanol, the cartridge was reversed, and stepwise desorption was performed to separate non-acidic adsorbates from acidic ones. Measurements were made in triplicate. Recovery data are reported in Table 4. In all cases, there was some carryover of 2,4-DB, which is the most weakly acidic compound included in this experiment. Unexplainably, Carbograph 5 failed to isolate dichlorprop quantitatively from neutral compounds. Carryover of 2,4-DB can be explained considering that large amounts of humic acids can in part saturate positively charged active centers on the GCB surface with the result that adsorption of a certain fraction of a weakly acidic analyte can also occur on the non-specific adsorption sites. It follows that this fraction is eluted on passing the eluent phase designed for reextracting neutral species through the cartridge. As a matter of fact, when extracting model compounds from 4 l of tap water with the Carbograph 4 cartridge, only 3% of 2,4-DB was found in the fraction designed for eluting non-acidic species. Among the GCBs under study, Carbograph 4 appears the most suited for isolating acidic species from non-acidic ones, even in aqueous environmental samples with abnormally high DOC values.

Table 4
Base/neutral–acid fractionation by differential elution of selected compounds with cartridges containing three different types of GCBs at two eluents

Compound	Sorbent material					
	Carbograph 1		Carbograph 4		Carbograph 5	
	Eluent A[a]	Eluent B[b]	Eluent A	Eluent B	Eluent A	Eluent B
Base/neutral						
Atrazine	97	–	95	–	94	–
Linuron	99	–	98	–	95	–
Aldicarb	92	–	92	–	92	–
Acidic						
Dichlorprop (3.5)[c]	–	95	–	97	30	73
2,4,5-T (2.2)	–	97	–	102	–	99
Ioxynil (3.9)	–	101	–	102	–	93
2,4-D (2.6)	–	99	–	100	–	93
2,4-DB (4.8)	40	63	18	81	50	49
Mecoprop (3.7)	–	99	–	99	–	96

Extraction from 1 l of Aldrich humic acid-spiked drinking water (spike level: 10 μg/l). Mean recovery values obtained from three measurements.
[a] Eluent phase: CH_2Cl_2–CH_3OH (80:20).
[b] Eluent phase: CH_2Cl_2–CH_3OH (80:20) + 10 mmol/l TBACl.
[c] In parentheses are reported pK_a values of the acidic compounds.

3.2. Comparison of the extraction efficiencies of the two new GCBs and two new PS–DVB-type sorbents

The abilities of Carbographs 4 and 5 adsorbing media in extracting very polar compounds from the two aqueous matrices taken as models, drinking water and Aldrich humic acid-spiked drinking water, were compared with those of two recently introduced PS–DVB sorbent materials, commercially referred to as LiChrolut and Envichrom P. For the purpose of comparison, very polar model compounds to be extracted from the two types of aqueous matrices considered were selected from three classes of contaminants of significant environmental interest, namely pesticides, phenols, and surfactant biointermediates.

Phenols

The abilities of cartridges filled with the four sorbent materials considered were comparatively evaluated by passing through them 4 l and 1 l of drinking water and simulated river water spiked with the most polar terms of the USEPA priority pollutant phenols, respectively. When extracting with cartridges containing the two GCBs, no pH adjustment of the two water samples was done before extraction. On the contrary, when using the two polystyrene–divinylbenzene-type materials, the pH of water was adjusted to 2 with concentrated HCl, because these sorbents were unable to retain the most acidic phenols at the original pH value of the water samples. Results are reported in Table 5. Compared with Lichrolut and Envichrom P, the two GCB materials could retain phenol significantly better from large volumes of drinking water, in spite of the fact that the two carbonaceous materials have a far smaller surface area. The astonishing ability of the two carbonaceous materials in trapping phenol from an aqueous solution may be due to adsorption of phenol on particular high-energy sites present on the surfaces of the two sorbents mentioned above. The high affinity of phenols for a GCB surface could probably be accounted for by specific interactions taking place between

Table 5
Recovery (%) of selected phenols and pesticides with four different adsorbing media and three spiking levels

Compound	Sorbent material							
	Envichrom P		LiChrolut		Carbograph 4		Carbograph 5	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
Phenols								
Phenol	30	46	66	96	93	84	96	95
4-Nitroph	98	92	98	100	99	98	98	101
2-Chloroph	98	82	95	84	97	97	98	99
2,4-Dinitroph	96	99	82	100	98	95	96	94
2-Nitroph	98	74	92	82	102	96	101	96
Pesticides								
Omethoate	17	52	65	82	88	93	95	99
Butoxycarboxim	66	88	93	91	99	99	94	96
Aldicarb sulfon	68	90	90	92	83	91	94	91
DIA	76	93	94	96	95	95	97	96
Metamitron	93	96	95	98	94	96	96	98
Dimethoate	97	94	95	95	96	94	97	97
Pichloram[a]	69	96	78	102	100	102	76	71
Aldicarb	96	97	98	94	99	101	98	100
Chloramben[a]	80	46	79	83	102	83	100	85
Monuron	97	98	98	96	98	96	99	96
Simazine	98	97	97	96	96	96	95	95
Propoxur	97	96	97	98	95	96	97	96
Dicamba[a]	80	80	91	90	102	93	102	101
Isoproturon	95	96	97	97	98	99	98	97
Bentazone[a]	87	85	93	95	98	96	99	101

Extraction from 4 l drinking water (sample A, spike level = 250 ng/l) and 1 l Aldrich humic acid-amended drinking water (sample B, spike level: 2 μg/l with Carbograph sorbents and 30 μg/l with PS–DVB-type sorbents). Mean recovery values obtained from three measurements.
[a] Pesticides acidic in nature.

quinone-type adsorption sites present on GCB surfaces and phenols. In the past, strong interactions leading ultimately to chemisorption of 2,4-dimethyl phenol upon adsorption on a GCB surface in a basic ambient [7] was explained by considering that the derivative phenol cited above is able to react with quinones [23].

As an example of the effectiveness of a 0.5-g Carbograph 4 cartridge as an extraction device for analyzing traces of phenols in aqueous samples, in Fig. 1 is shown a LC chromatogram obtained by analyzing 4 l of a phenol-free drinking water sample artificially contaminated with phenol at 5 ng/l level. Detection of phenol was performed by a fluorometer (FL). The analytical scheme followed was the same as that described elsewhere [21].

Pesticides

For comparative purposes, we selected 15 high- and medium-polar pesticides, some acidic in nature. This selection was made with the purpose of simulating a multi-component analysis of pesticides in aqueous samples involving SPE cartridges. When extracting with cartridges filled with both Carbograph 4 and 5 materials, recovery experiments were conducted by spiking 4 l of drinking water and 1 l of the simulated river water sample with the pesticides at the respective concentration levels of 0.25 and 2 μg/l.

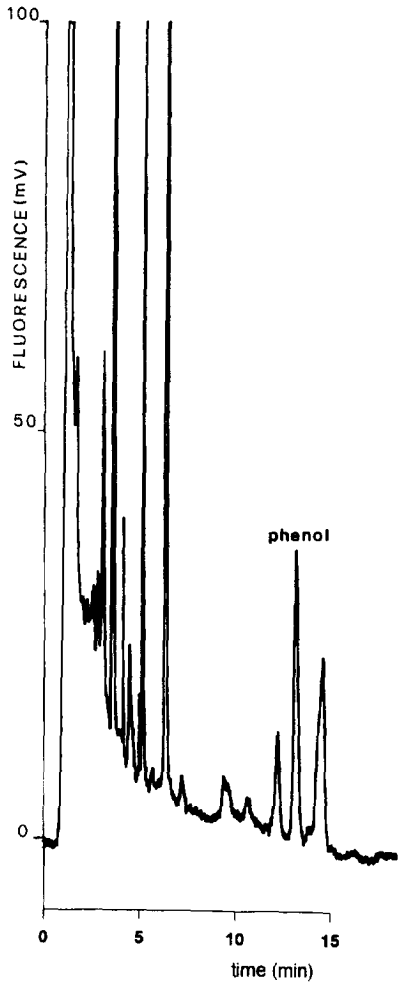

Fig. 1. LC–FL chromatogram obtained by analyzing 4 l of a drinking water sample spiked with 5 ng/l phenol. Sample extraction was performed by a 0.5 g Carbograph 4 cartridge.

On the contrary, when the analytical scheme involved the two PS–DVB-type sorbents, the Aldrich humic acid-spiked drinking water sample was fortified with pesticides at 30 μg/l. The reason for this modification will be made clear later. Before extracting with both LiChrolut and Envichrom P, water samples were acidified to pH 2. When operating with extraction cartridges containing the two GCB materials, neutral species were separated from acidic ones by stepwise desorption (see Section 2). Separation and quantification of the analytes was performed according to a slightly modified LC chromatographic procedure reported elsewhere [14]. Vice versa, eluates containing both acidic and non-acidic pesticides coming from cartridges filled with the two PS–DVB-type sorbents were chromatographed in the ion-suppression mode under the same chromatographic conditions followed for analyzing the acid-containing fraction obtained by extracting with GCB cartridges. Measurements were made in triplicate. Of the four sorbent materials considered, Envichrom P appeared to be the least suitable to extract very polar species from large water volumes (Table 5). Bearing in mind that Carbograph 5 has a surface area more than two times larger than that of Carbograph 4, it appears at first surprising that the former sorbent was less effective than the latter at extracting pichloram. However, the lost fraction of this acidic pesticide was found in the neutral pesticide-containing fraction. This gave further evidence for the fact that Carbograph 5 is scarcely suitable to isolate acidic species from non-acidic ones.

When analyzing simulated river water samples fortified with the 15 model compounds at 2 μg/l each by extracting with the LiChrolut cartridge, co-extracted humic acids interfered greatly with the analysis of many analytes. In fact, a huge peak for humic acids obscured those for early-eluted compounds (Fig. 2). This interference could be almost completely eliminated by avoiding acidifying the sample. By doing so, however, the analysis of acidic analytes was precluded, as they passed unretained through the pure reversed-phase sorbent cartridge together with fulvic acids.

Fig. 3 shows chromatograms obtained by injecting into the LC column the two final extracts obtained by stepwise elution from the Carbograph 4 cartridge after extracting analytes from 1 l of the simulated river water sample. In this case, co-extracted humic acids were co-eluted with acidic pesticides with the result that the quality of the analysis of very polar, non-acidic pesticides was unaffected by the presence of humic acids (Fig. 3A). Moreover, by comparing the chromatogram in Fig. 3B with that in Fig. 2, it appears that the amount of humic acids extracted by the GCB cartridge was far lower than

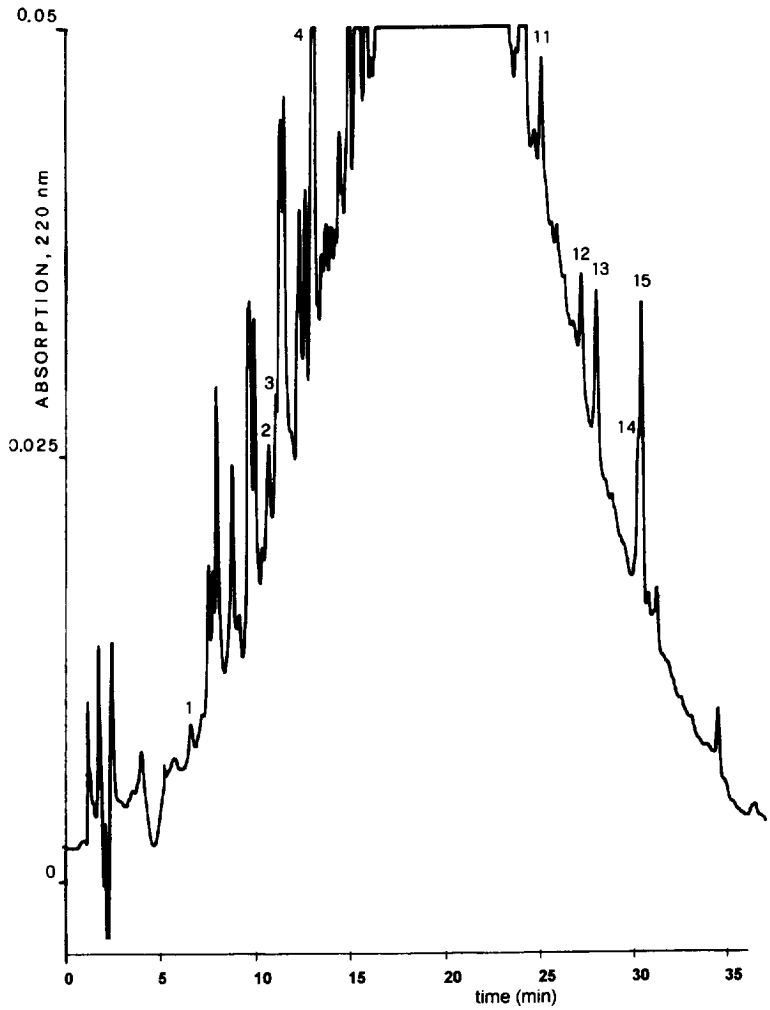

Fig. 2. LC–UV chromatogram obtained by analyzing 1 l of Aldrich humic acid-spiked drinking water (20 mg/l DOC) spiked with selected acidic and non-acidic polar pesticides at 2 μg/l. Sample extraction was performed by a 0.5-g LiChrolut cartridge. Chromatographic conditions: solvent A: H_2O + 0.05% TFA; solvent B: CH_3CN + 0.03% TFA. Initially, solvent B was 10%, and was increased to 48% after 35 min. Wavelength of the UV detector: 220 nm. Peaks: 1 = omethoate; 2 = butoxycarboxim; 3 = aldicarb sulfone; 4 = deisopropylatrazine; 5 = metamitron; 6 = dimethoate; 7 = pichloram; 8 = aldicarb; 9 = chloramben; 10 = monuron; 11 = simazine; 12 = propoxur; 13 = dicamba; 14 = isoproturon; 15 = bentazone. Peaks 5–10 are not shown in the figure, as they were obscured by that for humic acids.

that extracted by the LiChrolut cartridge. This effect may be explained by considering that when extracting with the GCB cartridge, the water sample was not acidified, so that humic acids were in the deprotonated form. Consequently, only that fraction of humic acids which were adsorbed on the relatively few anion-exchange sites of the GCB surface was carried through the rest of the procedure. Definitively, the use of a GCB cartridge offers advantages over that filled with a pure reversed-phase sorbent in that extraction and purification can be achieved by a single cartridge, no pH adjustment of water is necessary before extraction, and last but not

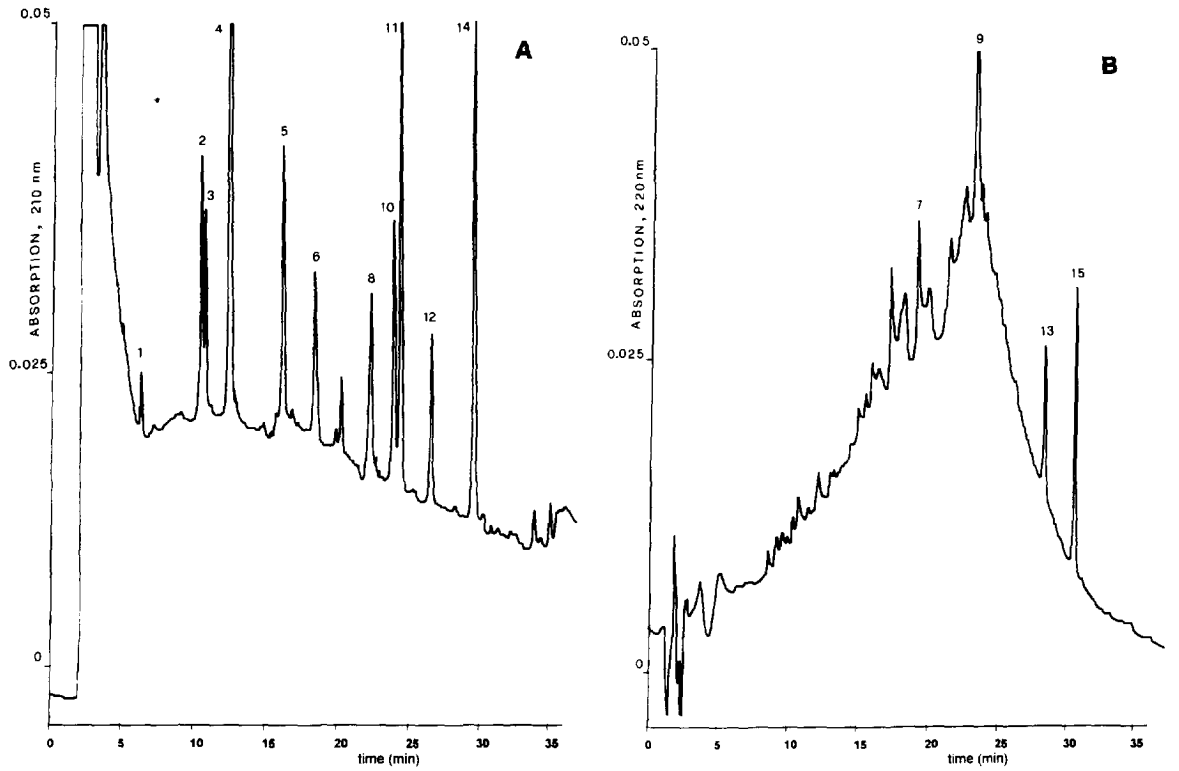

Fig. 3. LC–UV chromatograms obtained by analyzing 1 l of Aldrich humic acid-spiked drinking water (20 mg/l DOC) spiked with selected non-acidic (A) and acidic (B) polar pesticides at 2 μg/l. Sample extraction and acid–neutral class fractionation was performed by a 0.5-g Carbograph 4 cartridge. Chromatographic conditions for non-acidic pesticides: solvent A: H_2O; solvent B: CH_3CN. Initially, solvent B was 10%, and was increased to 48% after 35 min. Wavelength of the UV detector: 210 nm. Chromatographic conditions for acidic pesticides were the same as those reported in the caption of Fig. 2. Peak numbering is the same as in Fig. 2.

Table 6
Recovery (%) of selected surfactant biointermediates with four different adsorbing media and two spiking levels

Compound	Sorbent material							
	Envichrom P		LiChrolut		Carbograph 4		Carbograph 5	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
SPP	ND	ND	8	6	101	40	98	93
SPB	7	14	18	28	94	65	95	96
SPV	34	55	47	60	93	94	98	97
NP1EC	96	97	96	95	98	96	95	98
NP2EC	96	93	97	98	99	102	95	98

Extraction from 4 l of drinking water (sample A, spike level = 100 ng/l) and 0.5 l of Aldrich humic acid-spiked drinking water (sample B, spike level = 10 μg/l). Mean recovery values obtained from three measurements.

least, analysis of low amounts of polar pollutants in surface waters with an abnormally large content of humic materials could still be performed.

Surfactant biointermediates

For several reasons, monitoring of surfactant biointermediates in aqueous environmental compartments, including municipal waters, is becoming increasingly relevant. The performances of the four adsorbing media under study were comparatively evaluated by analyzing 4 l of drinking and 0.5 l of simulated river water samples spiked with three selected very polar LAS biointermediates (SPCs), i.e. sulphophenylpropionate (SPP), sulphophenylbutyrate (SPB) and sulphophenylvalerate (SPV), and two biointermediates of nonylphenolpolyethoxylate (NPEO) surfactants, that is nonylphenoxy carboxylic (NP1EC) and nonylphenolethoxycarboxylic acids (NP2EC). Before extracting with the two PS–DVB-based materials, water samples were acidified to pH 2. Recovery data averaged from three measurements (Table 6) showed that, among the four sorbent materials used, Carbograph 4 and, to a larger extent, Carbograph 5 were by far the most efficient in extracting SPCs from the two aqueous matrices considered. These results can be explained by considering that, although the water samples were acidified, the ionization of the sulphonic group of SPCs could not be repressed so that low-molecular-mass SPCs had high mobilities on pure reversed-phase sorbent columns. This did not occur with GCBs, as strongly acidic species have a large affinity for the positively charged adsorption sites present on their surfaces.

By the use of a single GCB extraction cartridge, in addition to the neutral–acid class fractionation, subfractionation of co-extracted acidic species based on their different acid strengths was shown to be possible by a multistage desorption process [17]. As an example of the effectiveness in terms of sensitivity and selectivity of an analytical scheme involving the use of a GCB cartridge for analyzing surfactant biointermediates, in Fig. 4 is shown a chromatogram obtained by analyzing 1 l of a river (Tiber) water sample. Extraction of the sample was performed by the use of a 0.5-g Carbograph 4 cartridge. As can be seen, well-defined peaks for trace amounts of the biodegradation products of NPEO surfactants were realised without the presence of interfering peaks. This result was obtained by first passing a neutral solvent mix-

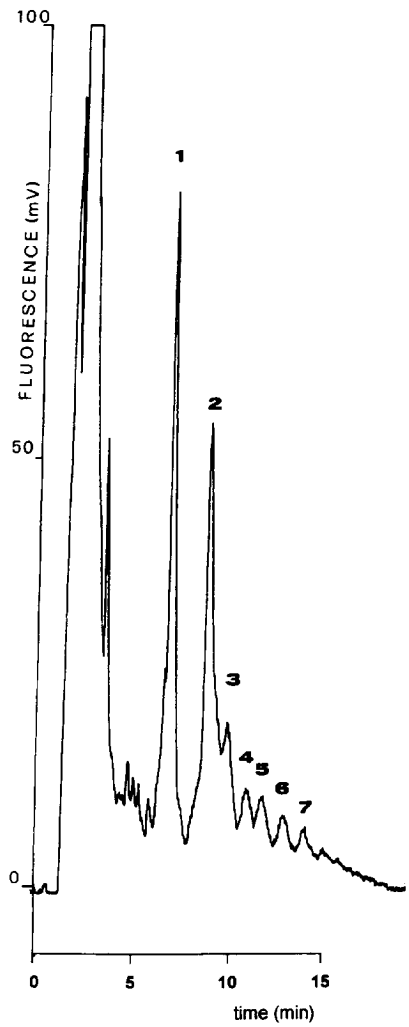

Fig. 4. LC–FL chromatogram obtained by analyzing 1 l of a river (Tiber) water sample contaminated by biointermediates of NPEO surfactants. Sample extraction was performed by a 0.5-g Carbograph 4 cartridge. As measured by us, the concentrations in ng/l of the various biointermediates were as follows: NP1EC, 300; NP2EC, 170; NP3EC, 45; NP4EC–NP7EC, 50 (as sum). Peaks: 1 = NPE1C; 2 = NP2EC; 3 = NP3EC; 4 = NP4EC; 5 = NP5EC; 6 = NP6EC; 7 = NP7EC.

ture through the cartridge (see Section 2) for eliminating co-extracted neutral species and then passing a moderately acidified eluent phase, CH_2Cl_2–CH_3OH containing formic acid 25 mmol/l [15]. In this way, weakly acidic species, such as NPEC, were isolated not only from base/neutral ones but also from strongly acidic compounds, such as LAS and their biointermediates, as the weakly acidified eluent phase was unable to remove the latter compounds from the GCB surface. In a previous paper [24], LAS was found to interfere with the analysis of NPEC.

4. Conclusion

This study has shown that, for extracting very polar compounds from water, two new types of GCBs, namely Carbographs 4 and 5, are more effective than the older GCB, Carbograph 1, and two recently introduced PS–DVB-based sorbents. In particular, Carbograph 5 has an extraction efficiency better than that of Carbograph 4, as expected considering that the former has a surface area more than two times higher than that of the latter. On the other hand, the surface of the latter adsorbent is less affected than that of the former one by the presence of active sites capable of binding particular adsorbates irreversibly. Moreover, compared with Carbograph 5, Carbograph 4 material is more suitable to acid–neutral class fractionation. Thus, Carbograph 4 could be the best candidate to advantageously replace Carbograph 1 in extraction cartridges.

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