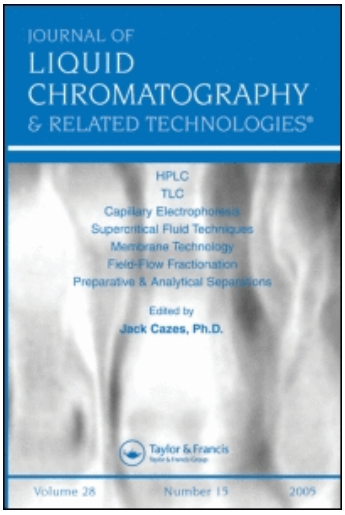

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BEHAVIOUR OF GRAPHITIZED CARBON BLACK IN THE EXTRACTION OF POLAR NON-IONIC NITROGEN-CONTAINING PESTICIDES. A CHECKING OF HYPOTHESES

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ABSTRACT

Graphitized Carbon Black (GCB) extractive cartridges are evaluated for on-line coupling with a C8 analytical column to determine eleven carbamates and one carboximide pesticide from spiked deionized water at the 1.2 μg/L level. Several experiments were carried out to ascertain whether GCB saturation, pesticide degradation on the surface, existence of by-pass channels, mobility among the bulk cartridge, or strong retention on the surface interfere with the determination of pesticides.

Problems in on-line CGB elution are partially solved by modifying the acetonitrile/water gradient to contain a front of 100% acetonitrile for a few seconds. Eluting the same GCB cartridges off-line with dichloromethane/methanol gives recoveries higher than 77% for the selected pesticides.

INTRODUCTION

Graphitized carbon black (GCB) has been used as stationary phase in gas-solid chromatography,[1] as reversed phase in high performance liquid chromatography (HPLC),[2] as fibers for solid-phase microextraction (SPME),[3] and,

as adsorbent in solid phase extraction (SPE) for the analysis of several polar compounds in different matrices.[4-8] Some authors have used the GCB in the on-line procedures.[8,9]

The active surface sites retaining analytes on GCB are mainly non-polar, presenting a graphite-like structure of carbon atoms. Nevertheless, it is also possible to find polar adsorption sites. Some of these polar sites in the surface are oxygen chemical complexes whose structures are similar to benzpyrilium salts, chromene, quinones, and hydroquinones.[4,10-13]

The GCB adsorption and desorption mechanisms are still not completely understood,[7] thus, GCB behavior seems sometimes contradictory. The literature presents several justifications to explain analyte retention on GCB. The dominant factor in the adsorption and retention process could be dispersion forces,[2] or a double nature of reversed-phase and anion exchanger characteristics.[13-16]

The purpose of this work is the study of hypotheses to justify the behaviour of GCB as extractant of polar non-ionic N-containing pesticides in an on line SPE-HPLC system. For this study, eleven carbamates and a carboximide pesticide were selected.

EXPERIMENTAL

Reagents

All solvents were HPLC grade and degassed before use. Acetonitrile was obtained from Scharlau (Barcelona, Spain), methanol and dichloromethane were obtained from Merck (Darmstadt, Germany), water was prepared by filtering deionized water through a 0.45 μm filter with a Waters-Millipore system (Milford, MA, USA). Ascorbic acid was purchased from Merck.

Carbaryl, carbendazim, carbofuran, diethofencarb, dioxacarb, fenothiocarb, iprodione, methomyl, methylthiophanate, molinate, oxamyl, and thiobencarb were purchased from Promochem (Wesel, Germany). All pesticides were at least 98% pure. Stock solutions (500 μg/mL) were prepared in acetonitrile. A composite working solution was made up daily, by diluting with acetonitrile to obtain a 1.2 μg/mL of each pesticide. Stock and working solutions were stored at -20°C, for a maximum of 1 year.

Apparatus

Two LaChrom L-7100 pumps, an OSP-2A automatic sample preparation device, a LaChrom L-7400 programmable wavelength detector, and a D-2500 integrator from Merck-Hitachi were used. The extractive cartridges (10.0 x 4.6

mm i.d.) were handily filled with Carbograph (37-150 μm particle size, 100 m^2/g surface area) (Alltech Associates, Carnforth, UK) and immobilized by appropriated LiChrocart frits (Merck). LiChrospher RP-18 (Merck) extractive cartridges (10 μm particle size, total carbon coverage about 18%) were also required. Analytes were separated on an 150 x 4.6 mm I.D. analytical column packed with 3 μm Spherisorb C_8 (Phase Separations, Waddinxveen, Netherlands) using a water-acetonitrile gradient at 0.7 mL/min.

Analytical Procedure

Following the scheme detailed in Figure 1, the cartridge was activated with 5 mL of acetonitrile and 5 mL of HPLC grade water. After that, water samples were forced through the cartridge at 5 mL/min flow rate. Then, the flow was stopped, backflushed, and a gradient to elute the cartridge and to separate analytes into the analytical column was started at 0.7 mL/min with 23% acetonitrile for 0.1 min, followed by a linear gradient to 45% acetonitrile in 14.9 min, and another linear gradient to 75% acetonitrile in 25 min.

At the end of the run, a 23% acetonitrile in water mixture was pumped directly to the analytical column. Detection was done at 210 nm.

RESULTS AND DISCUSSION

A chromatogram from the extraction with GCB of 50 mL of spiked water (1.2 μg/mL) is shown in Figure 2A. Diethofencarb/molinate and iprodione/thiobencarb pairs are not resolved. Therefore, to quantify them, new runs were performed with a wavelength program in which dietofencarb was monitored at 240 nm and iprodione at 250 nm. In such conditions, molinate and thiobencarb did not adsorb.

Table 1(a) shows the Limits of Detection (LODs, ng/L) and the recoveries corresponding to the on-line extraction of 50 mL of spiked water samples. Relative standard deviations (RSD%, n=4) were lower than 11%. These rather poor results were not *a priori* expected. To know why recoveries were low for most selected pesticides, several hypotheses were proposed and assays to support or discard them were carried out.

The GCB Extractive Surface Is Saturated

Saturation of the extractive surface has been argued to explain low recoveries obtained with carbon.[14,15] This happened when natural waters with high organic matter content were extracted.

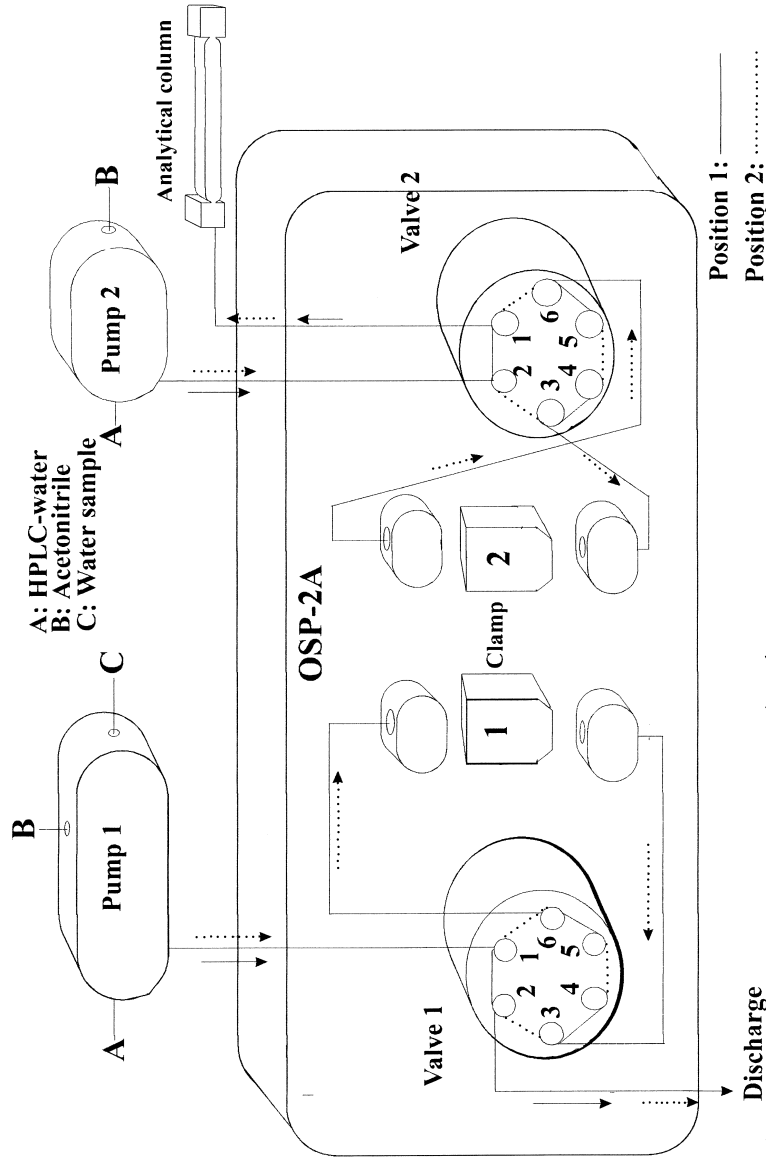

Figure 1. Scheme of the OSP-2A system.

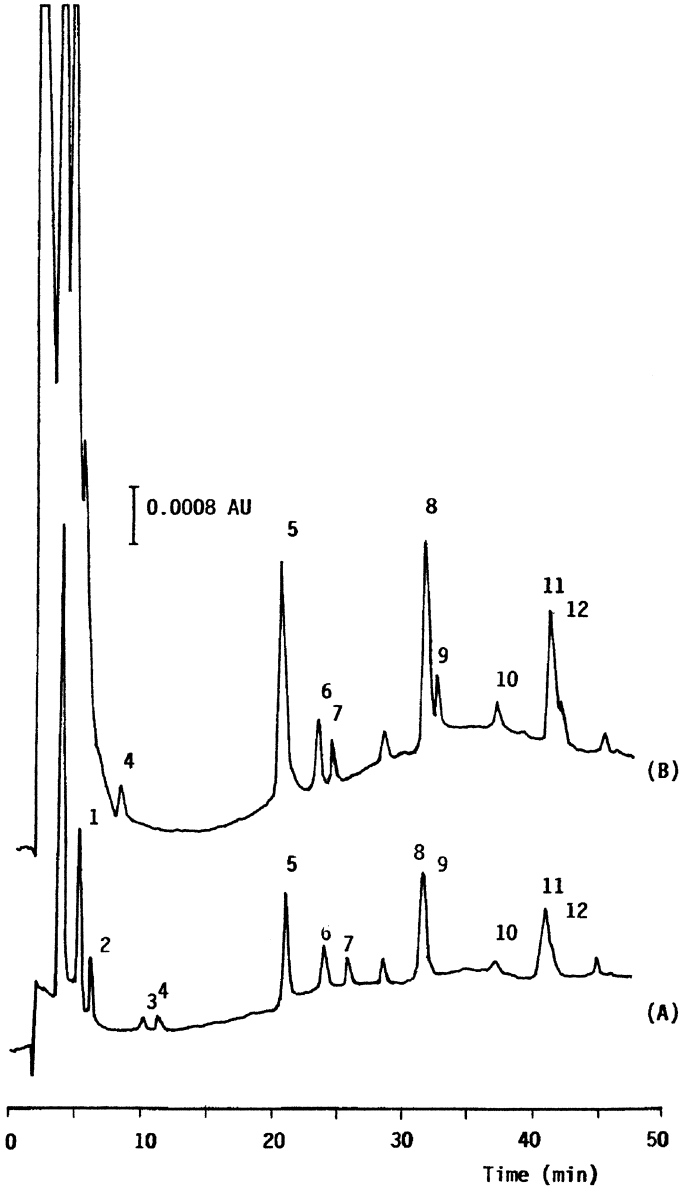

Figure 2. HPLC-UV (210 nm) chromatograms obtained after on-line preconcentration of 50 mL of spiked deionized water samples (1.2 μg/L level). Backflush elution of GCB cartridges as described in analytical procedure (A). Backflush elution of GCB cartridges pumping 100% of acetonitrile for 0.2 minutes, and then, the acetonitrile/water gradient described in analytical procedure (B). Peaks: oxamyl (1), methomyl (2), dioxacarb (3), carbendazim (4), methylthiophanate (5), carbofuran (6), carbaryl (7), dietofencarb (8), molinate (9), fenothiocarb (10), iprodione (11), and thiobencarb (12).

Table 1

Recoveries, Relative Standard Deviation, and Limits of Detection for the Extraction of 50 mL of Spiked Deionized Water Samples*

Pesticide	LODs[a]	On-Line R (RSD)[a]	On-Line R (RSD)[b]	Off-Line R (RSD)[c]	Off-Line R (RSD)[d]
Oxamyl	26	93 (7)	91 (6)	-	97 (5)
Methomyl	38	99 (6)	97 (6)	-	95 (8)
Dioxacarb	93	23 (11)	28 (9)	-	91 (6)
Carbendazim	260	20 (11)	25 (11)	65 (13)	95 (6)
Methylthiophanate	172	71 (6)	74 (7)	91 (10)	91 (5)
Carbofuran	74	55 (7)	55 (8)	72 (10)	86 (7)
Carbyl	107	42 (8)	47 (7)	63 (11)	85 (8)
Dietofencarb	55	19 (11)	24 (10)	70 (14)	79 (9)
Molinate	100	66 (6)	68 (7)	89 (10)	81 (8)
Fenothiocarb	91	18 (11)	23 (10)	76 (12)	77 (10)
Iprodione	80	23 (11)	23 (12)	57 (14)	78 (9)
Thiobencarb	132	42 (11)	45 (9)	67 (10)	93 (6)

* Recoveries = (R%); Relative Standard Deviation: (RSD%, n=4); Limits of Detection: (LODs in ng/L); Spiked Deionized Water Samples (1.2 μg/L).
[a] Elution conditions as described in analytical procedure. [b] GCB cartridge treated before extraction with 10 mL ascorbic acid (10 g/L) in HCl-acidified water (pH=2) and then, as in analytical procedure. [c] Elution started with 100% AcN for 0.2 min followed by the same gradient described in analytical procedure. [d] GCB cartridge eluted off-line with 2 mL methanol plus 6 mL dichloromethane/methanol (80:20). - Peak interfered.

Such supposition did not take place on our GCB cartridge conditions because we deal with deionized water, and, extracting 50 mL of 2.4 μg/L spiked samples instead of 50 mL of 1.2 μg/L, the absolute quantities of retained pesticides increased nearly twice.

Degradation of Pesticides Occurs on the GCB Surface

Some complex mechanisms for oxidative and/or hydrolytic reactions occurring on the surface of carbon have already been described.[4,11,12] According to studies by Di Corcia et al.,[4,15] the surface quinone groups are mainly responsible for the degradation. Washing the carbon with an aqueous solution of ascorbic acid[4,15] is a way to deactivate such groups. This procedure has been used to re-extract acidic and basic-neutral compounds.[4,12]

To verify this hypothesis, after activating the cartridge and preceding the sample extraction, 10 mL of ascorbic acid (10 g/L) in HCl-acidified water (pH 2) was passed through it. As can be seen in Table 1(b), such actuation improved most recoveries by 2 to 5%; this tendency had no statistical significance (α=0.05, n=4). This indicates that the active surface groups of the GCB had little relevance, but it should not be ignored in degradation processes involving selected pesticides.

Analytes Crossing Through Bypass Channels

Such a situation was suggested by Schülein et al[7] when authors emphasized the importance of GCB activation. An insufficient wetting with water could cause shrinking of the sorbent creating the bypass channels.

To corroborate this hypothesis, 50 mL of spiked deionized water sample (1.2 μg/L level) was extracted by connecting a second RP-18 extractive cartridge in series to the first GCB cartridge. The octadecylsilica sorbent was used because it reached high recoveries in a previous work.[8] Pesticides were not detected from the elution of this second RP-18 cartridge. Therefore, the non-retention hypothesis was discharged as the main cause of the low recoveries. If any pesticide would pass through the GCB cartridge, they would be retained on the second one.

Mobility of Analytes Among the Bulk GCB

Most authors elute the GCB extractive cartridge by backflushing it, either in off-line[5,11,12] or on-line[5,6,8] procedures. It can be a sign of pesticide retention on the extractive cartridge head, consequently having a poor mobility within the bulk of the carbon. Otherwise, it has been also reported that backflush and forward elution of oxamyl and methomyl generated the same peak shapes and retention times[6] in an on-line procedure.

Extractions of 50 mL of spiked water samples with two different ways of elution (forward and backflush) were accomplished. By eluting the GCB cartridge forward, oxamyl and methomyl were quantitatively recovered, but, only 15% methylthiophanate, 17% molinate, 7% fenothiocarb, and 48% thiobencarb were quantified. The other selected pesticides did not elute. Recoveries for backflush elution are shown in Table 1(a). Obtained results in backward or forward elution show that oxamyl and methomyl moved easily within the carbon, and their distribution among the bulk of the carbon is homogeneous.

Thiobencarb distribution was similar to those of oxamyl or methomyl, anyway, its elution was incomplete. The rest of pesticides distributed asymmetrically and were mainly retained at the head of the cartridge being eluted by back-

flushing. Distribution and mobility behaviour of chemically close pesticides onto the GCB was divergent, and no structure/behaviour relationship was found.

Strongly Retained Compounds on the GBC Surface

Hydroquinones,[4,14] or other unknown active sites present on the GCB surface,[13] have been reported as responsible groups of partial irreversible adsorption. Furthermore, the use of acetonitrile reduced the eluting efficiency due to the forming hydrogen bond.[4] Strong eluting solvents such as dichloromethane can not be used in on-line procedures because it is not soluble with the aqueous mobile phase.

The following assays were carried out to ascertain if elution was incomplete. Samples of 50 mL of spiked water were forced through a GCB cartridge. Then, it was inverted and off-line eluted with 2 mL methanol plus 6 mL dichloromethane/methanol (80:20). The extract was concentrated to 0.2 mL at 45°C under a gentle stream of helium and 20 μL of it was analyzed.

Recoveries were, at that time, quantitative for oxamyl, methomyl, dioxacarb, carbendazim, methylthiophanate, and thiobencarb, but they were only near 80% for carbofuran, carbaryl, dietofencarb, molinate, fenothiocarb, and iprodione. Results are shown in Table 1(d).

To facilitate on-line backflush elution, an assay was performed in which the elution gradient described in the analytical procedure was modified to pump 100% of acetonitrile during 0.2 min just before starting it. Results are reported in Table 1(c). Recoveries for most of the selected pesticides increased by 20 to 50%; the peaks from dietofencarb and molinate were separated and quantified, but oxamyl, methomyl, and dioxacarb eluted together with the front solvent as can be seen in Figure 2B.

These results testify that some analytes were intensely retained by the carbon and were not completely eluted by the mobile phase, attesting that on-line elution with the acetonitrile/water gradient was insufficient. The substitution of acetonitrile for methanol did not improve recoveries. Other water-miscible solvents such as tetrahidrofuran or dimethylformamide absorb at usual determination wavelengths (210-230 nm).

CONCLUSIONS

Of the formulated different hypotheses in the literature, two of them explained the behaviour of GCB as extractant of polar non-ionic N-containing

pesticides. The first, is based on the strong retention of the analytes over the GCB surface, and the other hypotheses, is that the active surface groups of the GCB had little relevance in degradation processes of the selected pesticides. The use of other solvents instead of acetonitrile, does not improve results or is not possible in an on-line procedure.

Results can be improved by backflushing the elution gradient and modifying it to contain a 100% acetonitrile wave for 12 seconds. In this way, resulting peaks are narrow and the dietofencarb/molinate pair is resolved, but it deteriorates reproducibility and oxamyl, methomyl, and dioxacarb elute with the front solvent. Elution of the GCB is almost complete when dichloromethane/methanol is used in an off-line procedure.

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