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Solid-phase extraction of polar pesticides from environmental water samples on graphitized carbon and Empore-activated carbon disks and on-line coupling to octadecyl-bonded silica analytical columns

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Abstract

The suitability of Empore-activated carbon disks (EACD), Envi-Carb graphitized carbon black (GCB) and CPP-50 graphitized carbon for the trace enrichment of polar pesticides from water samples was studied by means of off-line and on-line solid-phase extraction (SPE). In the off-line procedure, 0.5–2 l samples spiked with a test mixture of oxamyl, methomyl and aldicarb sulfoxide were enriched on EnviCarb SPE cartridges or 47 mm diameter EACD and eluted with dichloromethane–methanol. After evaporation, a sample was injected onto a C_{18}-bonded silica column and analysed by liquid chromatography with ultraviolet (LC–UV) detection. EACD performed better than EnviCarb cartridges in terms of breakthrough volumes (>2 l for all test analytes), reproducibility (R.S.D. of recoveries, 4–8%, $n=3$) and sampling speed (100 ml/min); detection limits in drinking water were 0.05–0.16 μg/l. In the on-line experiments, 4.6 mm diameter pieces cut from original EACD and stacked onto each other in a 9 mm long precolumn, and EnviCarb and CPP-50 packed in 10×2.0 mm I.D. precolumn, were tested, and 50–200 ml spiked water samples were preconcentrated. Because of the peak broadening caused by the strong sorption of the analytes on carbon, the carbon-packed precolumns were eluted by a separate stream of 0.1 ml/min acetonitrile which was mixed with the gradient LC eluent in front of the C_{18} analytical column. The final on-line procedure was also applied for the less polar propoxur, carbaryl and methiocarb. EnviCarb could not be used due to its poor pressure resistance. CPP-50 provided less peak broadening than EACD: peak widths were 0.1–0.3 min and R.S.D. of peak heights 4–14% ($n=3$). In terms of analyte trapping efficiency on-line SPE–LC–UV with a CPP-50 precolumn also showed better performance than when Bondesil C_{18}/OH or polymeric PLRP-S was used, but chromatographic resolution was similar. With the CPP-50-based system, detection limits of the test compounds were 0.05–1 μg/l in surface water.

Keywords: Environmental analysis; Water analysis; Adsorbents; Sample preparation; Pesticides

1. Introduction

The trace-level determination of organic micropollutants in aqueous samples frequently requires enrichment of the analytes prior to liquid chromatography (LC) analysis. Today, solid-phase extraction (SPE) is the principal analyte concentration and clean-up technique in most areas of environmental analytical chemistry [1]. Major progress is related to the development of new sorbent materials and SPE devices. Numerous commercially available C_{18}-bonded silicas and poly(styrene–divinylbenzene) copolymers efficiently extract apolar and moderately polar analytes from environmental water samples and are used in both off-line and on-line procedures [2].

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A rather recent addition are particle-loaded membrane extraction disks (typically 0.5 mm thickness, 47 mm diameter) with which the sorbent is enmeshed in an inert net of PTFE. High sample flow-rates, the elimination of flow channelling, an improved capability for handling dirty samples, and a good potential for field sampling and sample storage are features which make the use of the extraction disks preferable [1]. Smaller-scale procedures which involve stacking of 3–7 mm diameter disks in, e.g. a small precolumn have also been published [3,4].

A major challenge in present day environmental analysis is the determination of polar analytes, whether industrial chemicals, pesticides or their degradation products, which cannot be efficiently retained by C_{18} or polymeric sorbents. Here, an interesting material is carbon. SPE cartridges packed with graphitized carbon black (GCB) were used successfully for multiresidue analysis of a large group of acidic, neutral and basic pesticides [5,6], phenols [7], chloroanilines [8], triazines [9] and organochlorine insecticides [10] in water. More recently, a new porous graphitic carbon (PGC), Hypercarb, was used for SPE of very polar polyhydroxybenzenes [11] and also naphthalene and several amino- and nitro- substituted benzenes [12]. Carbon materials are generally much stronger sorbents than C_{18}-bonded silicas, the basic difference being solute-stationary phase interactions which can be practically neglected with C_{18} silicas [13]. Despite promising results, difficulties with reproducibly manufacturing pressure-resistant carbon materials until recently prevented their widespread use in LC.

In on-line SPE–LC procedures the choice of a sorbent is determined not only by its trapping efficiency to the analytes of interest but also by its compatibility with the actual chromatographic system. Generally speaking the sorbent in the analytical column should have the same or higher retention capabilities than the precolumn material, and the precolumn should be as small as possible in order to prevent additional band broadening. Despite the obvious differences in retention characteristics of carbon and C_{18} materials, several researchers have attempted to combine pyrocarbon-modified silica, pyromodified carbon black [13,14], porous graphitic carbon [15] and graphitized carbon [16] to C_{18} analytical columns. A common conclusion was that polar compounds can be separated on C_{18} columns only with eluents containing such a high amount of water that desorption of polar analytes becomes inefficient and excessive band broadening occurs. A logical alternative, coupling a carbon precolumn to an analytical column containing the same material, was also tested [13,15]. However, the home-made and Hypercarb carbon columns used are not as efficient as C_{18} columns, thus the problem of broad peaks remains [15]. An elegant procedure to combine reversed-phase-type enrichment on a carbon precolumn and normal-phase separation on a C_{18} column was successfully used for the determination of nitrobenzene in surface water [13]. However, no follow-up was published, probably because normal-phase LC is a rather obsolete technique in environmental analysis.

In this study we first used an off-line set-up to compare breakthrough and related analytical characteristics of EnviCarb and EACD for a test mixture containing the carbamate pesticides oxamyl (OX) and methomyl (ME), and aldicarb sulfoxide (ASX). These highly polar analytes were selected because they are not easily preconcentrated on alkyl-bonded or polymeric sorbents. Next we tried to develop a set-up for the on-line coupling of a precolumn packed with a carbon material (Envi-Carb, EACD and CPP-50 graphitized carbon) and a C_{18} analytical column.

2. Experimental

2.1. Chemicals and procedures

ASX, OX, ME and carbaryl were obtained from Riedel-de Haën (Seelze, Germany), promecarb and methiocarb were from Promochem (Wesel, Germany). All compounds were at least 95% pure. HPLC-gradient grade acetonitrile was obtained from Biosolve (Barneveld, Netherlands). HPLC-grade methanol and water were from J.T. Baker (Deventer, Netherlands). Per-analysis grade ascorbic acid, ethyl acetate, tetrahydrofuran (THF) and hydrochloric acid were obtained from the same producer. Stock solutions of the test analytes were prepared at concentrations of 200 μg/ml in methanol. Amsterdam drinking water samples were taken after the water

had been kept running for 30 min. Surface water samples were filtered through a 0.45 μm acetylcellulose filter (Schleicher and Schuell, Dassel, Germany) prior to use. Prior to analysis, water samples were spiked with appropriate mixtures of the test analytes at concentration levels from 0.01 to 5 μg/l.

2.2. Instrumentation

2.2.1. Solid-phase extraction

SPE cartridges packed with 500 mg EnviCarb (non-porous GCB, 40–100 μm particle size, 100 m^2/g surface area; Supelco, Bellefonte, PA, USA) or 47 mm diameter EACD (ca. 1 mm thickness; 3M, Saint Paul, MN, USA), were used for off-line sample enrichment. In on-line experiments, two to six 4.6 mm diameter EACD were stacked on top of each other in a 9 mm×4.6 mm I.D. THF-resistant polypropylene precolumn placed in a home-made precolumn holder [3]. The CPP-50 graphitized carbon made by controlled pyrolysis of cellulose (Institute of Polymers, Bratislava, Slovakia Republic) was ground to ca. 10–20 μm particle size and dry-packed in a 10 mm×2.0 mm I.D. stainless-steel precolumn. No difference in performance was observed when the precolumn was packed with a methanolic carbon slurry instead. In comparative experiments, precolumns of the same geometry were slurry-packed with 20 μm, 100 Å PLRP-S (styrene–divinylbenzene copolymer; Polymer Laboratories, Church Stretton, UK) and 40 μm, 100 Å Bondesil-C_{18}/OH (Varian, Harbor City, CA, USA). The precolumns were mounted on a home-made six-port switching valve. In the on-line system two model 300 LC pumps (Separations, H.I. Ambacht, Netherlands) were used to deliver conditioning solvents and solutions, sample and acetonitrile.

Off-line procedures

For the SPE studies EnviCarb cartridges were placed in a Millipore (Bedford, MA, USA) SPE apparatus attached to a water aspirator via a pressure-metering valve. The cartridges were conditioned by slowly sucking through 5 ml dichloromethane–methanol (80:20, v/v) and, next, 2 ml methanol and 15 ml ascorbic acid solution (10 g/l, acidified to pH 2 with hydrochloric acid; for reduction of active oxidation sites on carbon surface [5]). Without letting the cartridge become dry, a 0.5–2 l drinking water sample was applied at a speed of ca. 5 ml/min. Next the cartridge was flushed with 7 ml HPLC-grade water and dried for 1 min under suction to remove traces of water. The vacuum was then interrupted and the analytes were eluted with 1 ml methanol and two times 5 ml of dichloromethane–methanol (80:20, v/v), all at a drop-by-drop rate. The eluate was evaporated at 38°C under a gentle stream of nitrogen to a final volume of 500 μl. A volume of 20 μl was injected into the LC system.

With EACD, the disk was placed in the standard all-glass Supelco filtration apparatus connected to a water aspirator. After optimization (see below), the same procedure for conditioning and elution was used as for the EnviCarb cartridges. The conditioning solvents were allowed to soak the disk for 3 min before applying the vacuum, the sampling speed was 100 ml/min.

On-line procedures

The precolumn (PR) mounted on a six-port valve (V1) was conditioned consecutively with 5 ml methanol and 10 ml acidified ascorbic acid (10 g/l, pH 2) followed by 50–200 ml sample. They were delivered by pump 2 at a flow-rate of 2 ml/min (Fig. 1). A flow of 0.1 ml/min acetonitrile which bypassed the precolumn, was delivered by pump 1 and mixed with 0.9–1 ml/min acetonitrile–water mixture (5: 95 v/v) in a T-piece (T) prior to entering the analytical column. Immediately after conditioning of the precolumn and sample loading, the LC gradient was started and valve V1 was switched to the elute position. As a consequence the flow of acetonitrile was directed through the precolumn and the trapped analytes were eluted and subjected to LC–UV analysis. Pulse-noise and pressure imbalance due to the connection of pump 1 and the gradient pump via the T-piece were suppressed by a combination of two pulse dampers (PD) and a restriction capillary (R, 20 mbar back-pressure). The introduction of a mixing coil in front of the column, the use of methanol instead of acetonitrile or using equal flow-rates for the LC gradient and acetonitrile (0.5 ml/min each) did not reduce the pulsing.

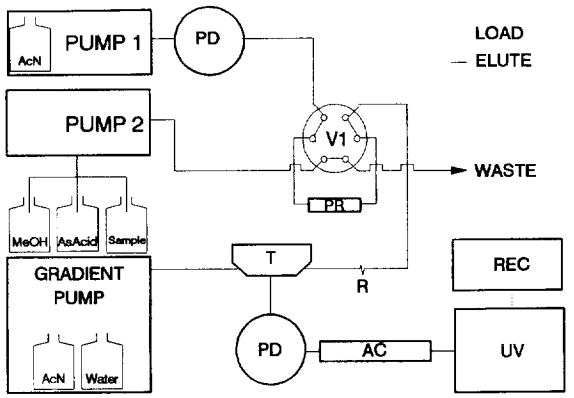

Fig. 1. Schematic of experimental set-up for on-line solid-phase extraction-LC–UV using carbon-packed precolumn. Pump 1 and 2, Separations model 300 LC pumps for delivery of acetonitrile (AcN), methanol (MeOH), acidified ascorbic acid solution (As-Acid) and sample; GRADIENT PUMP, L-6200 gradient system; V1, six-port switching valve; PR, precolumn; T, T-piece; R, restriction capillary; PD, pulse damper; AC, analytical column; UV, UV detector; REC, recorder; LOAD/ELUTE, positions of V1. For procedures, see Section 2.

2.3. Liquid chromatography

A Gilson (Villiers-le-Bel, France) LC gradient module system consisting of two Gilson 305 pumps, 811B Dynamic Mixer and 805 Manometric Module, was used for the off-line studies, and an L-6200A gradient pump (Merck-Hitachi, Darmstadt, Germany) for the on-line experiments. Separations were carried out on 250×4.6 mm I.D. analytical column packed with 5 μm, 100 Å Supelcosil C_{18} (Supelco, Bornem, Belgium) or a 250×4.0 mm I.D. Merck LiChroCART cartridge column packed with 5 μm LiChrospher 60. A specially designed T-piece and two pulse dampers were home-made. Detection was performed with a Spectroflow 757 UV absorbance detector (Kratos Analytical Instruments, Manchester, UK) operated at 254 nm or 220 nm. Signals were recorded on a Kipp and Zoonen BD 41 recorder (Delft, Netherlands).

In off-line experiments the eluent consisted of (A) methanol–water (5:95, v/v) and (B) methanol–water, (90:10, v/v). The gradient started at 100% A and decreased linearly to 70% A after 15 min, 30% A after 17 min and 0% A at 19 min, and then returned to 100% A in 2 min; the flow-rate was 1 ml/min. In the on-line experiments methanol was replaced by acetonitrile and the gradient went linearly from 100% A to 100% B in 30 min with a subsequent return to 100% A in 1 min; the flow-rate was 0.9–1.0 ml/min (see below).

3. Results and discussion

3.1. Off-line experiments

The performance of the LC part of the system (Supelco C_{18} analytical column) was checked daily with loop injections of the mixture of ASX, OX and ME. The UV detector was set at 254 nm to reduce interferences from matrix constituents present in the drinking water samples. No degradation of standard stock solutions or deterioration of the LC/UV system performance was observed during a 3-month period. Diluted stock solutions of each test compound were analysed regularly. R.S.D. of analyte peak heights were 6, 5 and 3% (n=11) for ASX, OX and ME, respectively; R.S.D. of retention times were less than 1%.

3.1.1. EnviCarb

A critical parameter in off-line SPE procedures is the volume of eluent (dichloromethane/methanol) required to elute the trapped analytes from the cartridge. Three subsequent analyses of 1 l drinking water spiked with 1 μg/l of each test analyte gave average recoveries of 47% (ASX), 80% (OX) and 95% (ME) with 6 ml eluent and essentially the same yields, viz. 42% (ASX) 79% (OX) and 100% (ME) with 10 ml eluent. However, for the most polar analyte, ASX, R.S.D. values improved dramatically from 25% with 6 ml eluent to 10% with 10 ml eluent; therefore the latter volume was used in further experiments.

In order to obtain an estimate of breakthrough volumes on the EnviCarb cartridge, 0.5–2 l drinking water samples spiked at the 1 μg/l level, were analysed. The data of Table 1 indicate that the least polar analyte, ME, does not show breakthrough even for the largest volume, while breakthrough of OX begins to occur between 1 and 2 l, and below 1 l for ASX. The data for OX are somewhat lower, but in the same range as those found in an earlier publication (68% recovery from 2-l sample on 250 mg of

Table 1
Recovery, R.S.D. ($n=3$) and limit of detection (LOD) of the three test analytes after enrichment of spiked drinking water samples on 500 mg EnviCarb solid-phase extraction cartridge

Compound	Recovery (R.S.D.) (%) of:							LOD[b] (μg/l)
	1 μg/l spike and sample vol. of:			1 l sample and spiking at:			0.5 μg	
	0.5 l	1 l	2 l	5 μg/l	0.5 μg/l	0.1 μg/l	Comp[a]	
Aldicarb sulfoxide	75 (5)	43 (11)	<15	42 (10)	35 (2)	n.d.	87 (4)	0.5
Oxamyl	77 (14)	71 (24)	54 (17)	79 (10)	69 (21)	83 (5)	98 (1)	0.05
Methomyl	84 (4)	99 (3)	91 (7)	100 (4)	101 (9)	93 (3)	92 (2)	0.1

[a] Comparative experiments without solid-phase extraction; 0.5 μg of each analyte in 1 ml methanol added to 10 ml dichloromethane–methanol (80:20, v/v), evaporated and volume of 20 μl analysed by LC–UV.
[b] For enriched volume of 1 l.
n.d., not detected.

sorbent [5]); the difference may well reflect the different characteristics of the two GCB carbon sorbents used. The rather low recovery (and high R.S.D.) of OX even at low sample volumes was earlier attributed to its high water solubility (280 mg/l against 58 mg/l for ME) which may well cause partial analyte losses irrespective of the sample volume. This may also explain the low recovery of ASX at 0.5 l sample volume, and the differences observed in comparative experiments with and without SPE (Table 1).

Further experiments carried out with 1-l samples spiked at various levels show an essentially constant recovery, as is to be expected, and fully satisfactory R.S.D. values for ME and ASX and, again, much less for OX. For a 1-l sample volume, the detection limits of OX, ME and ASX were 0.05, 0.1 and 0.5 μg/l, respectively (Table 1). The somewhat disappointing detection limit of ASX is mainly caused by its lower molar absorptivity.

3.1.2. Empore-activated carbon disks

In order to obtain a fair comparison of EnviCarb and EACD we tried to keep the SPE procedures as similar as possible. However, the use of carbon-loaded disk material has not been reported before. Therefore several parameters had to be studied.

Dichloromethane–methanol (80:20, v/v), acetonitrile–methanol (80:20, v/v), THF–methanol (80:20, v/v), THF and ethyl acetate, were used for the elution of EACDs loaded with 1 l drinking water samples spiked with 1 μg/l of each test analyte. As Table 2 shows, by far the best results were obtained with dichloromethane–methanol and this mixture was used in further studies. Rather poor results were obtained with both THF-containing eluents, especial-

Table 2
Recovery, relative standard deviation (R.S.D., $n=3$) and limit of detection (LOD) of the three test analytes after enrichment of drinking water samples on 47 mm diameter Empore-activated carbon disks[a]

Compound	Recovery (R.S.D.) (%) of:							LOD[b] (μg/l)
	DCM–MeOH (80:20) eluent for sample volume of:			1 l sample and elution with:				
	0.5 l	1 l	2 l	AcN–MeOH (80:20)	THF–MeOH (80:20)	THF	EtAc	
Aldicarb sulfoxide	72 (4)	75 (8)	75 (1)	47	75	70	43	0.16
Oxamyl	70 (7)	68 (7)	63 (5)	55	54	55	33	0.04
Methomyl	67 (4)	68 (5)	66 (4)	33	7	n.d.	23	0.05

[a] Analyte spikes, 1 μg/l; eluent volume, 10 ml; DCM, dichloromethane; MeOH, methanol; AcN, acetonitrile; EtAc, ethyl acetate.
[b] For enriched volume of 1 l; eluent, DCM–MeOH.
n.d., not detected.

ly for ME. Besides, with these eluents a dramatic increase of the background was observed. This may be due to enhanced extraction of impurities from the disk matrix, e.g. of plasticizers such as phthalate esters. Actually, after evaporation a yellow emulsion remained as was previously observed for C_{18} and C_8-loaded Empore disks [17,18]. Not surprisingly, the rather non-polar ethyl acetate was the weakest elution agent for the three polar analytes. On the other hand, the mixture of the more polar acetonitrile–methanol mixture gave only slightly higher recoveries. In future, the above explanations will have to be supported by more data considering, e.g. the high polarizability of the carbon surface, the formation of active oxidation sites on this surface and specific analyte-stationary phase interactions [5,13]. However, this is outside the scope of the present study.

In experiments with spiked 0.5, 1 and 2 l drinking water samples no breakthrough of the three analytes was observed and average recoveries were constant to within a few per cent, with highly satisfactory R.S.D. values of less than 8% (Table 2). No explanation can as yet be provided for the lower analyte recoveries observed with EACD compared with EnviCarb. The differences in recovery of e.g. ME with EnviCarb (84–101%) and EACD (66–68%) probably cannot be attributed to incomplete mass transfer due to the design of EACD (ca. 1 mm thickness) or sampling speed. The particle size of the carbon material in EACD should be much smaller than that of EnviCarb (40 μm) and particles in membranes should be evenly distributed (as is known from C_{18} and ST–DVB Empore disks) which provides sufficient mass transfer during SPE [1]. This was supported by an additional experiment, in which the sampling speed was reduced to 20 ml/min. This did not result in significantly higher recoveries.

The improved sorption efficiency of EACD compared with EnviCarb resulted in a much better detection limit of 0.16 μg/l for ASX. For OX and ME, the detection limits were about 0.05 μg/l.

3.1.3. Comparison of EnviCarb and EACD

Both of the above approaches proved to be suitable for the determination of the three polar analytes in drinking water (see Fig. 2). In actual practice, EACD will probably be preferred because a sampling speed of 100 ml/min can be used (2 l sample, 20 min) whereas with EnviCarb, the maximum sampling speed obtainable with water aspirator vacuum was ca. 5–7 ml/min which significantly prolonged the analysis (2 l sample, ca. 4.5–6.5 h). In addition, EACD apparently display better sorption strength (higher breakthrough) towards very polar analytes, and the precision of the experimental results is superior. On the other hand, the lower absolute recoveries observed with EACD, which cannot be explained as yet, detract from its overall performance with somewhat less polar analytes and analyte detectability became rather similar for EnviCarb and EACD. Finally, preliminary experiments with EACD show that the disks can be re-used for at least three consecutive analyses which was not possible with the EnviCarb cartridges.

3.2. On-line experiments

3.2.1. EnviCarb

A 10×2.0 mm I.D. precolumn was packed with EnviCarb material and subjected to on-line gradient elution by the LC eluent. An enormous increase of the background signal was observed which may be due to "collapsing" of the material under the operational pressure of the LC system [11]. Unfortunately, the material therefore had to be excluded from our further studies.

3.2.2. Empore-activated carbon disks

A combination of (i) a separate precolumn eluted with a suitable organic solvent and (ii) gradient LC (see Section 2) was used in the on-line experiments. Because of an intended comparison of the off-line and on-line approaches, we initially tried to keep the analytical conditions identical to those used in the off-line study. However, preliminary experiments showed that methanol had to be replaced by acetonitrile with its higher elution strength in LC eluent. Besides, the 19 min gradient was prolonged to 30 min (see Section 2) to avoid separation problems with ME.

100 ml HPLC-grade water spiked with 5 μg/l of the three test analytes were analysed first by direct on-line SPE–LC–UV with the 1 ml/min acetonitrile–water gradient (Fig. 3A). As expected, dramatic

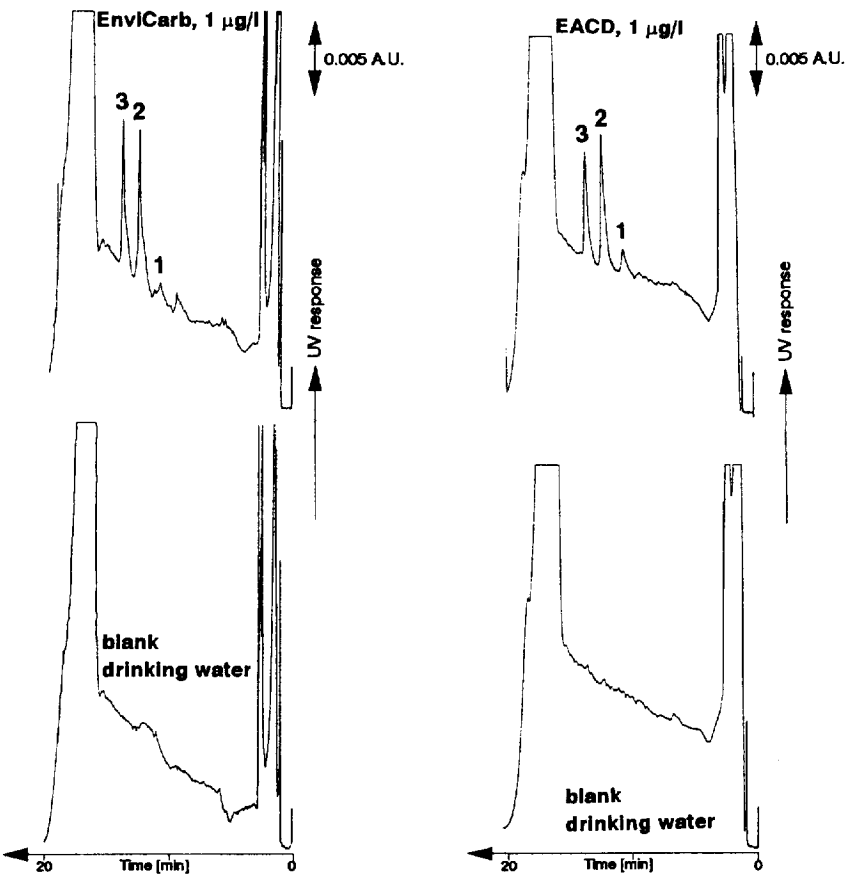

Fig. 2. LC–UV chromatograms of spiked drinking water obtained after off-line solid-phase extraction with 500 mg EnviCarb cartridges and 47 mm diameter Empore-activated carbon disk (EACD). Sample volume, 1 l; analytical column, 250×4.6 mm I.D. 5 µm C_{18} Supelco; UV detection, 254 nm; A.U., arbitrary units. Compounds, (1) aldicarb sulfoxide, (2) oxamyl and (3) methomyl; spiking level, 1 µg/l each. For other conditions, see Section 2.

peak broadening was observed. The number of disks in the EACD-packed precolumn was five to achieve as much analyte retention as possible. With six disks, back-pressure during sampling became too high.

In the next step, mixtures of acetonitrile–methanol (80:20 or 50:50, v/v), acetonitrile–water (95:5 or 80:20, v/v), acetonitrile and THF were used to elute the precolumn, using flow-rates of 0.1, 0.3 or 0.5 ml/min, while the total flow delivered on-column was maintained at 1 ml/min. Elution with THF released large amounts of impurities from the disks and this solvent was therefore rejected. Acceptable results were obtained with all other solvents. Optimum peak shapes were found with acetonitrile–methanol (80:20, v/v) (Fig. 3B) and pure acetonitrile, at flow-rates of 0.1 ml/min. Additional peak broadening was largely suppressed (cf. Figs. 1 and 3B). The peak width of e.g. OX was reduced from 1.3 min to 0.4 min; ASX and ME gave peak widths of ca. 0.4 and 0.6 min, respectively. With this set-up ASX could be detected at the 0.3 µg/l level when using a 100 ml sample.

However, all the peaks of Fig. 3B are tailing which, of course, detracts from the detectability of the analytes. One explanation is that the sorption strength of EACD is too high for the present set-up. Another carbon material was therefore tested as an alternative.

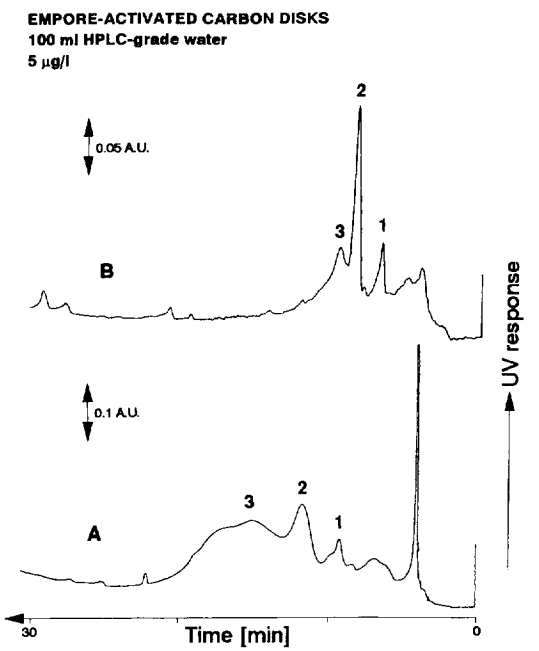

Fig. 3. Chromatograms of spiked 100 ml HPLC-grade water obtained by direct on-line SPE–LC–UV (A) without separate elution and (B) with separate elution by 0.1 ml/min acetonitrile–methanol (80:20 v/v). Precolumn, 9×4.6 mm I.D. packed with five Empore-activated carbon disks; flow-rate of acetonitrile–water gradient, 1.0 ml/min in A and 0.9 ml/min in B. Analytical column, 250×4.6 mm I.D. 5 µm C_{18} Supelco; UV detection, 254 nm. Compounds, (1) aldicarb sulfoxide, (2) oxamyl and (3) methomyl; concentration, 5 µg/l each. For other conditions, see Section 2.

3.2.3. CPP-50 graphitized carbon

A limited amount of an experimental 10–20 µm graphitized carbon material was obtained while the present study was in progress. The material was packed in 10×2.0 mm I.D. precolumns, and tested using the set-up developed for EACD. All optimization steps were performed with 100 ml HPLC-grade water spiked with 5 µg/l of each test analyte. With this material, a flow of 0.1 ml/min of acetonitrile provided better recoveries and peak shapes than the acetonitrile–methanol mixture. As with the EACD, desorption with THF released a huge amount of impurities from the CPP-50 material. Rather surprisingly, backflush elution of the cartridge resulted in essentially the same peak shape and retention times as did the forward-flush mode. This indicates symmetrical distribution of the analytes over the carbon surface in the precolumn or a well-balanced sorption/desorption set-up. The enhanced performance of CPP-50 compared with EACD is evident from Fig. 4. The strong tailing of the ME peak has essentially disappeared and peak widths have improved (also see below).

In order to find out whether the present set-up can also be used in the presence of less polar analytes (the potential problem being too high retention), the carbamates propoxur, carbaryl and methiocarb were added to the test set. Because the absorption maxima of these compounds are close to 220 nm, the wavelength was adjusted accordingly. Unfortunately, this resulted in high detection limits for ASX due to matrix interferences. Because of high molecular absorptivity, carbaryl was spiked at 10-fold lower concentration than the other five analytes.

Experiments with 20–200 ml drinking water sample spiked with 5 µg/l of each of the five remaining test analytes showed a continuous increase of the peak heights with sample volume up to 200 ml.

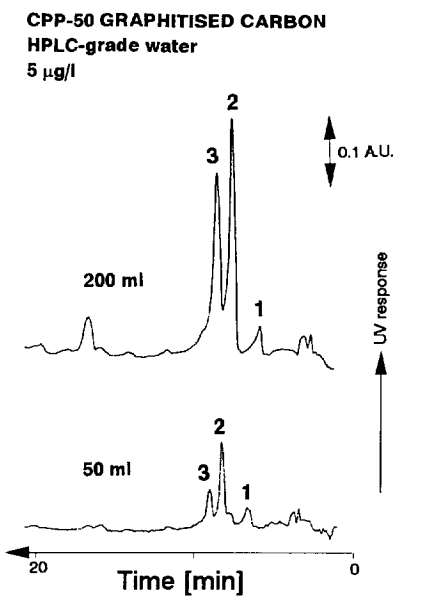

Fig. 4. On-line SPE–LC–UV chromatograms of HPLC-grade water spiked with 5 µg/l of (1) aldicarb sulfoxide, (2) oxamyl and (3) methomyl. For set-up, see Fig. 1. Precolumn, 10×2.0 mm I.D. packed with CPP-50 carbon material; eluent, separate flow of 0.1 ml/min acetonitrile mixed with 1 ml/min acetonitrile–water gradient; sample volumes, 50 and 200 ml; analytical column, 250×4.6 mm I.D. 5 µm C_{18} Supelco; UV detection, 254 nm.

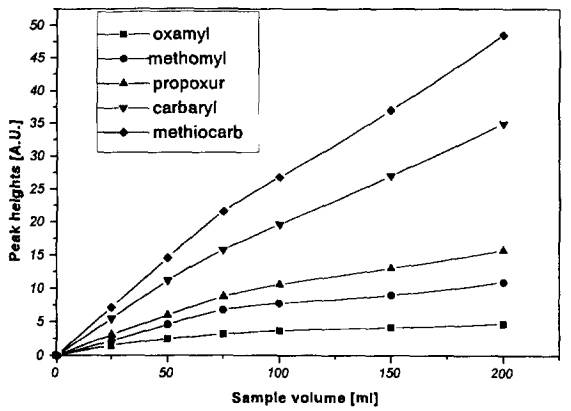

Fig. 5. Dependence of peak heights of five test analytes upon enriched drinking water sample volumes. Values obtained in on-line SPE–LC–UV; precolumn, 10×2.0 mm I.D. packed with CPP-50 carbon material; analytical column, 250×4.0 mm 5 μm C_{18} LiChroCart; UV detection, 220 nm; spiking level, 5 μg/l each. For other conditions, see Section 2.

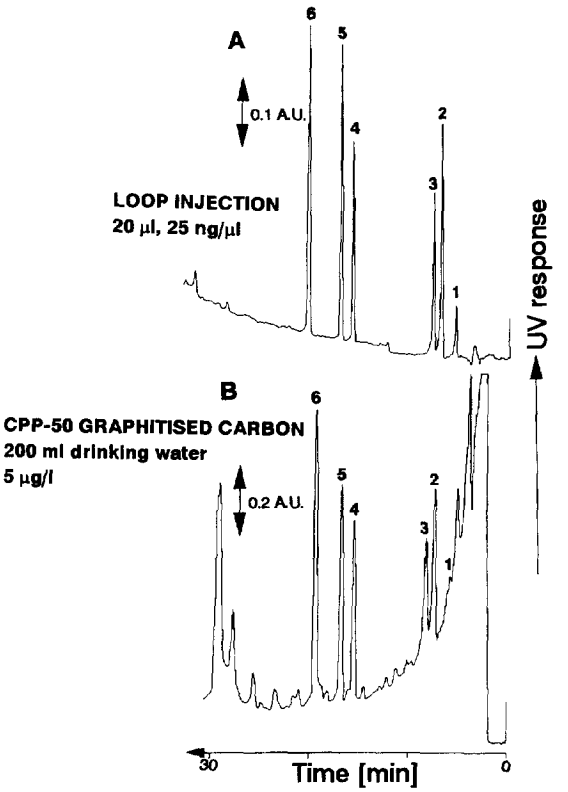

Fig. 6. (A) Loop injection of six compounds and (B) on-line SPE–LC–UV of 200 ml spiked drinking water. Injected amount of each analyte, 500 ng (20 μl/25 ng/μl); spiking level, 5 μg/l; precolumn, 10×2.0 mm I.D. packed with CPP-50 carbon material (B); analytical column, 250×4.0 mm 5 μm C_{18} LiChroCart; UV detection, 220 nm. Compounds, (1) aldicarb sulfoxide, (2) oxamyl, (3) methomyl, (4) propoxur, (5) carbaryl and (6) methiocarb. For other conditions, see Section 2.

Rather unexpectedly, however, the plots are not linear, but consist of two linear portions with a change in slope occurring after 25 ml for OX, and after 50–75 ml for the other four compounds (Fig. 5). This behaviour which has also been observed for metal-loaded phases [19] strongly suggests that more than one retention mechanism is involved; possibly, both hydrophobic interaction and adsorption processes take place on the carbon surface [11,13,15]. It should be stressed that the quoted behaviour does not detract from the practicality (inclusive of the quantification steps) of the final method ([11,19], cf. below).

Table 3 summarizes relevant analytical data on the trace-level determination of the test analytes in spiked drinking water. Typical chromatograms are shown in Fig. 6. The recovery data which were calculated by comparing the results with loop injections, satisfactorily reflect the earlier findings regarding breakthrough (cf. Fig. 5). Actually, with on-line methods, repeatability is of primary importance [11]. The present R.S.D. values of 4–8% are fully satisfactory in this respect. The higher value found for OX is presumably caused by the same effects as discussed in the off-line section above. R.S.D. values of retention times were less than 2%.

Table 3
Peak heights obtained with the carbon material taken as reference

Sorbent	ASX	OX	ME	Propoxur	Carbaryl	Methiocarb
CPP-50	100	100	100	100	100	100
PLRP-S	–	40	15	130	115	100
Bondesil	–	–	–	35	50	100

A similarly satisfactory picture is provided when comparing peak widths recorded in the on-line studies and for loop injections. As regards robustness, each CPP-50 precolumn was re-used 5 or 6 times before repacking. Control runs without sample enrichment, performed after every third analysis, showed the absence of memory effects.

Direct elution of the CPP-50-packed precolumn with the LC gradient eluent, resulted in a ca. 1 min shift in retention times, tailing peaks and low recoveries of 25% for propoxur and 50% for carbaryl and methiocarb.

As a final demonstration of the good performance of the CPP-50 precolumns, a comparison was made with copolymer PLRP-S and mixed-mode (hydrophobic/hydroxyl) Bondesil C_{18}/OH. With all three sorbents packed in precolumns of the same geometry, and 100 ml samples spiked at the 5 μg/l (carbaryl, 0.5 μg/l) level, on-line SPE–LC–UV showed striking differences.

Although it can be of course argued that with the C_{18}-type Bondesil material, on-line combination with a C_{18}-bonded silica analytical column allows the use of a precolumn somewhat larger than the present one (to compensate for the lower sorption), this will never make up for the hugely different results for the highly polar analytes.

The detection limits (S/N 3) of the five test compounds in surface water were calculated from five-level calibration curves. Despite strong interferences from co-extracted compounds (Fig. 7), they ranged from 0.05 μg/l (carbaryl, No. 5) to 1 μg/l (OX, ME, Nos.: 2, 3) (Table 4). It can be assumed

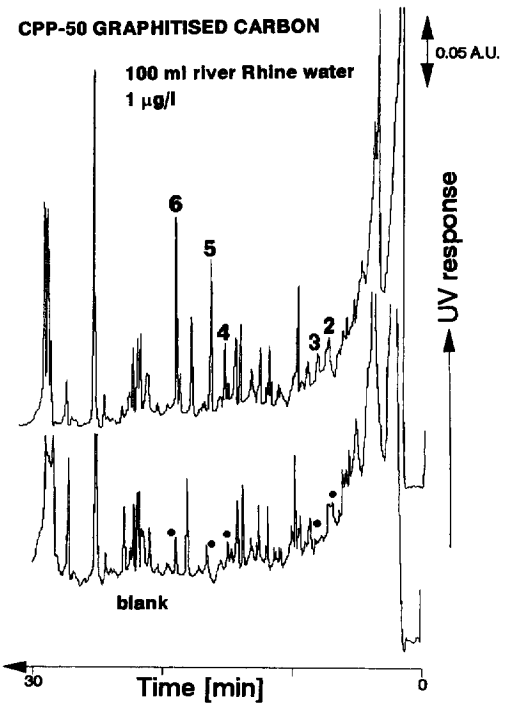

Fig. 7. On-line SPE–LC–UV chromatograms of 100 ml of (A) Rhine river water (blank) and (B) Rhine river water, both spiked with 1 μg/l of (1) aldicarb sulfoxide, (2) oxamyl, (3) methomyl, (4) propoxur, (5) carbaryl and (6) methiocarb. For set-up, see Fig. 1.; precolumn, 10×2.0 mm I.D. packed with CPP-50 carbon material; eluent, separate flow of 0.1 ml/min acetonitrile mixed with 1 ml/min acetonitrile–water gradient; analytical column, 250×4.0 mm 5 μm C_{18} LiChroCart; UV detection, 220 nm. Black dots indicate expected positions of spiked analytes. For details, see Section 2.

Table 4
Relevant analytical data on five carbamates obtained by on-line solid-phase extraction–LC–UV of 100 ml spiked drinking water[a]

Compound[a]	On-line SPE			Loop inj. PW (min)[b]	LOD_{sw} (μg/l)
	t_{ret} (min) (R.S.D.)	Recovery (%) (R.S.D.)	PW (min)[b]		
Oxamyl	7.2 (2)	40 (14)	0.30	0.21	1
Methomyl	7.9 (1)	56 (6)	0.30	0.27	1
Propoxur	15.2 (1)	72 (8)	0.21	0.15	0.75
Carbaryl	16.5 (1)	78 (6)	0.15	0.15	0.05
Methiocarb	19.1 (1)	88 (4)	0.15	0.15	0.5

[a] n=3; loop inj., loop injection of 500 ng (in 20 μl) on-column; LOD_{sw}; detection limits calculated from calibration curve (levels 0.1–5 μg/l) in 100 ml river Rhine water. Concentration of each analyte, 5 μg/l, carbaryl 0.5 μg/l; precolumn, 10×2.0 mm I.D. packed with CPP-50 carbon material; PW, peak width at 33% peak height.

[b] Relative standard deviations (R.S.D.) less than 0.5%, n=3.

that with a more selective detection mode than UV detection at 220 nm detectability will certainly improve.

4. Conclusions

Three carbon materials, EnviCarb, the experimental Empore-activated carbon disks (EACD) and CPP-50 graphitized carbon, were studied for their suitability to extract very polar analytes from environmental water matrices in both off-line and on-line modes, with subsequent analysis on ordinary C_{18}-bonded silica columns.

Off-line studies on Envicarb and EACD showed that the latter material should especially be valued because of the high sampling speed allowed (100 ml/min in present study vs. maximum of 5–7 ml/min for EnviCarb). In addition, the precision of recovery data collected for EACD was better than for EnviCarb (R.S.D., 4–8% vs. 2–24%) and breakthrough volumes for ASX and OX were above 2 l for EACD as against 0.5–1 l for EnviCarb. Even though EnviCarb gave higher absolute recoveries for ME and OX and detection limits, consequently, were not too far apart (0.04–0.16 μg/l in 1 l drinking water for EACD vs. 0.05–0.5 μg/l for EnviCarb), EACD seems to be the material of choice in environmental analysis of polar analytes.

In further studies, a successful experimental set-up was developed for the first time to couple carbon-packed precolumns with a C_{18} analytical column. Excessive peak broadening was effectively suppressed by eluting the precolumn with a separate stream of 0.1 ml/min of organic solvent which was mixed with the LC gradient (0.9–1.0 ml/min) in front of the analytical column. EnviCarb showed too little pressure resistance. Good results were obtained with up to five small disks of EACD packed into a 9×4.6 mm I.D. precolumn; the peak widths of the three test analytes diminished from 1.3–3 min (direct on-line coupling) to ca. 0.5 min (separate elution). Peak widths obtained with CPP-50 graphitized carbon packed in 10×2.0 mm I.D. were even better, i.e. <0.3 min which is comparable with those obtained by loop injection, even for more hydrophobic analytes such as propoxur, carbaryl and methiocarb. R.S.D. values of peak heights were 4–14% and no memory effects were observed. The on-line procedure significantly reduces the overall analysis time because off-line evaporation is circumvented and will enable future automation. Although CPP-50 graphitized carbon is not commercially available, the present results indicate that further work in this direction is justified and should be stimulated. In such work, attention should also be devoted to using optimized detection conditions rather than the single wavelength procedure which was adopted to simplify this first study of the several off-line and on-line carbon-SPE–C_{18}-LC options.

Acknowledgments

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