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Comparison of the performance of graphitized carbon black and poly(styrene–divinylbenzene) cartridges for the determination of pesticides and industrial phosphates in environmental waters

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Abstract

The determination of polar and nonpolar organophosphorus compounds, triazines and their metabolites, molinate and chlorothalonil in 1 l water samples was investigated using off-line solid-phase extraction followed by gas chromatography with nitrogen–phosphorus and flame photometric detection. The ethylvinylbenzene–divinylbenzene copolymer (LiChrolut EN) and the commercial graphitized carbon black (GCB) of Envi-Carb were tested as solid-phase sorbents. The matrix effect was studied by extracting the compounds spiked in water samples of different types (Milli-Q, tap, salted tap water, river and sea water). The polymeric sorbent LiChrolut EN allowed the determination at low ng/l of all 40 compounds tested, except the very polar atrazine-desethyl-deisopropyl (DDA). Recoveries of compounds from the Envi-Carb sorbent are comparable to those obtained for LiChrolut EN with the exception of chlorothalonil and the more hydrophobic organophosphorus compounds (coumaphos, leptophos), which were strongly sorbed in the Envi-Carb cartridges. Envi-Carb, however, enabled the determination of DDA with a limit of detection of 14 ng/l.

Keywords: Solid-phase extraction; Extraction methods; Water analysis; Environmental analysis; Pesticides; Phosphates; Organophosphorus compounds; Triazines

1. Introduction

Solid-phase extraction (SPE) has become a very important technique for sample preparation in environmental investigations. The advantages of this technique over the liquid–liquid extraction (LLE) technique have been widely recognized [1,2]. Of the sorbents available for solid-phase extraction of contaminants from water, C_{18} and C_8 bonded to porous silica have become very popular. Recently their use was proposed by the US Environmental Protection Agency (EPA) in the analysis of basic and neutral organics in drinking water (Method 525) [3]. These sorbents, which are now available in cartridges and disks, can successfully preconcentrate nonpolar compounds but they fail for the more polar compounds due to their small breakthrough volumes [4–13]. The nonpolar poly(styrene–divinylbenzene) (PS–DVB) co-polymer disk also provides comparable results to

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the C_{18} disks only achieving good recoveries for compounds with log K_{ow} (octanol–water partition coefficient) greater than 2 [14]. Other materials based on highly cross-linked PS–DVB copolymers or graphitized carbon black (GCB) have recently been prepared in commercial cartridge formats. Another new polymeric sorbent chemically modified with an acetyl group has also been synthesized [15]. All these sorbents are claimed to have a high sorption capacity for different kinds of environmental contaminants, including highly polar compounds such as phenols [15–17].

The aim of the present paper is to evaluate the abilities of the sorbents with a high specific surface area for the determination of a variety of compounds of differing hydrophobicity, including organophosphorus, triazines, carbamates and phtalamides and to establish a method for water analysis using gas chromatography with nitrogen–phosphorus detection (GC–NPD) and flame photometric detection (GC–FPD). For this purpose, the ethylvinylbenzene–divinylbenzene copolymer (sold as LiChrolut EN) and the commercial GCB of Envi-Carb were selected. Special attention was paid to the extractability from large water volumes of those pesticides and pesticide metabolites that are supposed to be difficult to extract by LLE and SPE techniques, such as monocrotophos, dimethoate, atrazine-desethyl (DEA), atrazine-deisopropyl (DIA) and atrazine-desethyl-deisopropyl (DDA). The influence of the salt and the water matrix on the extraction efficiency was investigated. Emphasis was also placed on the analysis of the recently new antifouling triazine, Irgarol 1051, for which at present, among the analytical methods reported [18–24], there are no studies using these two sorbents.

LiChrolut EN has already been successfully used to preconcentrate 33 pesticide components, including phenylureas, carbamates, triazines and their metabolites, from 1 l samples of drinking water [25]. However, other studies using LiChrolut EN [26] for the analysis of organochlorine compounds, triazines, malathion, molinate and bentazone have reported a considerable decrease in the recoveries of organochlorine compounds and bentazone from 1 l Milli-Q water.

GCB cartridges has also been shown to recover quantitatively the polar metabolites of atrazine [17,27–29], chlorinated pesticides [30], organophosphorus pesticides, phenylureas, carbamates and phenoxiacids in various environmental waters [16,31]. Indeed, they allowed the complete separation of base-neutral pesticides from acidic ones by a stepwise elution system [16].

2. Experimental

2.1. Materials and reagents

Disposable 3-ml cartridge columns packed with 200 mg PS–DVB copolymer (trademark LiChrolut EN) were obtained from Merck (France). The PS–DVB particles have diameters from 40 to 120 μm, with a pore volume of 0.75 mg/l and 1200 m^2/g surface area.

SPE cartridges (trademark Envi-Carb) packed with 500 mg non-porous GCB, 40–100 μm particle size, 100 m^2/g surface area, 120–400 mesh, were provided by Supelco (France).

Off-line trace enrichment was carried out using the 12-port SPE Visiprep DL system (Supelco). This extraction unit is connected to the samples with PTFE tubing (Visiprep Large Volume Sampler), which are fitted to the cartridges via appropriate adapters.

Solvents used were of high purity pesticide quality (Burdick and Jackson Labs., Muskegon, MI, USA). Analysis-grade ascorbic acid, anhydrous sodium sulfate and 32% hydrochloric acid were supplied by Merck (France). Anhydrous sodium sulfite was obtained from Riedel-de Haën (Seelze, Germany) and sodium chloride from Prolabo (France). Sodium sulfate used for drying organic extracts and Whatman glass-fiber filters (GFFs) were baked to 450°C overnight before use in order to remove any traces of organic contaminants.

Authentic standards [ametryne, atrazine, DEA, DIA, DDA, azinphos-ethyl, azinphos-methyl, chlorothalonil, chlorpyrifos, chlorpyrifos-methyl, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, *O*-ethyl *O*-4-nitrophenyl phenylphosphonothionate (EPN), ethion, fenamiphos, fenitrothion, fenthion, Irgarol 1051, leptophos, malathion, methidathion, molinate, monocrotophos, parathion, parathion-methyl, prometon, prometryn, propazine, simazine,

sulfotep, symethryne, tetrachlorvinphos, tributoxiethylphosphate, tributylphosphate (TBP), triisobutylphosphate (TiBP), tris(2-ethylhexyl)phosphate, triphenylphosphate] were purchased from Riedel-de Haën and stock solutions of the target compounds were prepared in ethyl acetate and diluted further with acetone for spiking aqueous samples. Ethyl acetate was the diluent used for the GC standards.

2.2. Solid-phase extraction

The extraction efficiency of the LiChrolut EN and Envi-Carb cartridges was investigated by spiking 1 l of Milli-Q (pH 7), tap (pH 7), tap water salted with 60 g of NaCl (pH 7), river (pH 7) and sea water (pH 8, salinity of 38) with a solution containing a mixture of each compound, which provided concentrations between 150 and 400 ng/l for each pesticide. No pH adjustment was done since the majority of the studied compounds are stable in neutral media and under the pH of natural waters (pH 5 to 8). Only at pH greater than 8, the hydrolysis rate of organophosphorus compounds increases steeply [32].

The tap water used was from the municipal water supply of Monaco, the river water from the River Var (south France) and the sea water from the Mediteranean Sea, near Monaco.

River water was filtered through precombusted Whatman GF/F glass-fiber filters to remove the suspended particles. Some tap water was also prefiltered to assess whether low recoveries of some hydrophobic organophosphorus compounds in tap water were caused by adsorption on particles.

None of the water matrices contained the compounds under investigation, with the exception of the industrial phosphate TBP, which was present in the tap and river waters.

2.2.1. LiChrolut EN cartridges

Cartridges were first activated by wetting with 6 ml methanol. Then they were washed with 3×3 ml ethyl acetate and were vacuum dried. Methanol (6 ml) and Milli-Q water (6 ml) were then percolated through the cartridges prior to use. The 1 l spiked water sample was extracted at a flow-rate of approximately 20 ml/min (no differences on recovery yields were observed using flow-rates between 7 to 20 ml/min). Then the cartridges were dried for 3 min under vacuum. Compounds were sequentially eluted with 2×3 ml ethyl acetate. During the initial elution phase, no vacuum was used to allow the process to proceed optimally. Finally, the extract was dried over anhydrous sodium sulfate. Extracts were concentrated to a final volume of 500 μl under a gentle stream of nitrogen and were then analyzed by GC.

2.2.2. Envi-Carb cartridges

Cartridges were first activated by wetting with 6 ml methanol. Then they were washed 3×6 ml dichloromethane and vacuum dried. Methanol (6 ml) and Milli-Q water (6 ml) were then percolated through the cartridges prior to use. The 1 l spiked water sample was extracted at a flow-rate of approximately 20 ml/min (no differences on recovery yields were observed using flow-rates between 7 to 20 ml/min). The cartridges were then dried for 3 min under vacuum. The residual water was removed by flushing with 1 ml of methanol, which was discarded and the compounds were collected with the elution of 2×6 ml of dichloromethane. During the initial elution phase, no vacuum was used to allow the process to proceed optimally. Finally, the extract was dried over anhydrous sodium sulfate and the dichloromethane solvent exchanged to ethyl acetate. Extracts were concentrated to a final volume of 500 μl under a gentle stream of nitrogen gas prior to analysis by GC.

2.3. Chromatographic conditions

The 40 compounds investigated in this paper include several types of compounds: 20 organophosphorus insecticides (azinphos-ethyl, azinphos-methyl, chlorpyrifos, chlorpyrifos-methyl, chlorthion, coumaphos, diazinon, dichlorvos, dimethoate, EPN, ethion, fenamiphos, fenitrothion, fenthion, leptophos, malathion, methidathion, monocrotophos, parathion, parathion-methyl, sulfotep, tetrachlorvinphos), five industrial organophosphorus compounds (tributoxiethylphosphate, TBP, TiBP, tris(2-ethylhexyl)phosphate, triphenylphosphate), seven triazine herbicides (ametryne, atrazine, prometon, prometryn, propazine, simazine, symethryne), one triazine antifouling agent (Irgarol 1051), three metabolites of atrazine (DEA, DIA and DDA), one thiocarbamate (molinate) and one phtalamide fungicide (chloro-

thalonil). Recovery rates and limits of detection (LODs) of the organophosphorus compounds were carried out by GC–FPD using the OV-1701 column due to a better chromatographic resolution of these 27 compounds compared to the PTE-5 column, where some organophosphorus insecticides coelute. The other target compounds (triazines, molinate and chlorothalonil), including the respective recovery rates and LODs, were determined by GC–NPD.

2.3.1. GC–FPD

Organophosphorus compounds were analyzed using an HP 5890 gas chromatograph with a FPD system equipped with a phosphorus filter (526 nm) (Palo Alto, CA, USA), as described elsewhere [14]. A 25 m×0.25 mm I.D., 0.20 μm Chrompack OV-1701 was used for the analyses. The GC system conditions were as follows. Carrier gas: helium at a flow-rate of 1.5 ml/min, temperature programme: 60°C for 1 min; 60°C to 190°C at 25°C/min, 190°C to 225°C at 2°C/min, 225°C to 280°C at 5°C/min, 280°C isothermal for 10 min; injector temperature: 250°C; detector temperature: 225°C. Dibenzothiophene was coinjected with each analysis to monitor variations in FPD response.

Aliquots of 1–2 μl were injected in the splitless mode using a ''hot needle technique''.

2.3.2. GC–NPD

Nitrogen and phosphorus containing herbicides were analyzed using a Hewlett-Packard 6890 gas chromatograph equipped with a NPD system. GC conditions were as described elsewhere [18]: 30 m×0.25 mm I.D., 0.25 μm (film thickness) fused-silica capillary column PTE-5 (Supelco); He carrier gas at 1.9 ml/min; GC temperature programme, 60°C for 1 min, 60–120°C at 10°C/min, 120–200°C at 3°C/min, 200–280°C at 6°C/min and 280°C isothermal for 10 min; injector temperature, 250°C; detector temperature, 300°C. Desmetryn was coinjected with each analysis to monitor variations in NPD response. Aliquots of 1 μl were injected in the pulsed splitless mode (pulse pressure of 80 p.s.i. for 1 min) using a ''hot needle technique'' (1 p.s.i.= 6894.76 Pa).

3. Results and discussion

3.1. Selection and optimization of the extraction solvents

Since ethyl acetate was the solvent used for the GC injections and evaporation to dryness should be avoided to minimize losses of the more volatile compounds, e.g., dichlorvos, this solvent was the one chosen to start the elution of cartridges. Dichloromethane was also selected because of its relatively high polarity and its low boiling point, which allowed it to be easily exchanged by ethyl acetate.

After passing 100 ml of spiked Milli-Q water through the LiChrolut EN cartridges, good recoveries (>90%) were achieved for all target compounds, with the exception of the very polar DDA, using a total volume of 6 ml ethyl acetate. Losses of DDA indicates a breakthrough volume lower than 100 ml.

A critical parameter in Envi-Carb cartridges is the volume of eluent required to desorb the trapped analytes. Table 1 illustrates the recovery rates obtained by using sequential eluents after passing 100 ml of spiked Milli-Q water through the cartridge. A 12 ml (2×6 ml) volume of ethyl acetate did not recover chlorothalonil and Irgarol 1051, and the last GC-eluting organophosphorus compounds (azinphos-methyl, leptophos, azinphos-ethyl and coumaphos) were also poorly desorbed. An additional volume of 12 ml (2×6 ml) dichloromethane only allowed recovery of azinphos-methyl, azinphos-ethyl, leptophos and coumaphos at levels of 35 to 70%. Using a greater volume of dichloromethane or a more polar solvent such as methanol, chlorothalonil and Irgarol 1051 were still not desorbed.

Similar recoveries were also obtained by using only 12 ml of dichloromethane, the exception being the very polar DDA, which was not recovered.

Other solvent mixtures that have proved to be effective by other authors were also tested [16,28]. Good recoveries were achieved for Irgarol 1051 when desorption of the analytes from the cartridge was preceded by the percolation of 1 ml methanol followed by 6 ml of CH_2Cl_2–CH_3OH (80:20). However, DDA, chlorothalonil, leptophos and coumaphos were still not eluted quantitatively by passing an additional volume of 6 ml CH_2Cl_2–

Table 1
Percent recovery rates (R_t, total recovery and R_2, second fraction only) and relative standard deviations (RSDs, %, $n=3$) of the compounds after percolation of 100 ml Milli-Q water on Envi-Carb cartridges and sequential elution with different volumes of solvents

	Peak No.	$R_t=R_1+R_2$							
						1 ml CH_3OH (discard)			
		R_1=12 ml ethyl acetate		R_1=6 ml CH_2Cl_2		R_1=6 ml CH_2Cl_2–CH_3OH (80:20)		R_1=12 ml CH_2Cl_2	
		R_2=12 ml CH_2Cl_2		R_2=6 ml CH_2Cl_2		R_2=6 ml CH_2Cl_2–CH_3OH (80:20)		R_2=12 ml CH_2Cl_2	
		R_t (R_2)[a]	RSD (%)	R_t (R_2)[a]	RSD (%)	R_t (R_2)[a]	RSD (%)	R_t (R_2)[a]	RSD (%)
Dichlorvos	1	96	2	81	7	65	16	84	6
TiBP	2	105	6	84	6	79	5	88	6
Molinate	3	103	11	96	8	60	12	98	7
Atrazine desethyl desisopropyl	4	59	16	0		29	11	66	15
Atrazine desisopropyl	5	107	15	84	8	64	21	88	6
TBP	6	104 (2)	5	111	2	88	2	99	4
Atrazine desethyl	7	105	13	98	3	74	3	96	5
Monocrotophos	8	80 (2)	6	86	10	82	9	90	8
Sulfotep	9	95	4	69	11	82	9	90	7
Dimethoate	10	80	3	83	12	82	2	92	8
Simazine	11	106	16	103	6	83	4	99	7
Prometon	12	106	17	96	11	80	5	95	9
Atrazine	13	106	15	99	7	84	6	98	8
Propazine	14	105	17	103	9	81	2	99	7
Diazinon	15	105	3	97	4	94	9	98	5
Chlorothalonil	16	0		0		0		46 (46)	15
Parathion-methyl	17	105 (5)	2	87	4	90	12	97	6
Chlorpyriphos-methyl	18	100 (20)	2	79	3	96	14	98	5
Symetryne	19	107	19	97	12	82	1	96	9
Ametryne	20	106	13	95	6	84	3	97	8
Prometryne	21	107	13	98	8	83	2	97	8
Fenitrothion	22	106	1	100	6	85	5	99	7
Malathion	23	100	5	100	8	86	3	101	8
Fenthion	24	109	2	96	9	84	9	99	9
Parathion	25	103	2	104	7	99	15	99	8
Chlorpyriphos	26	100 (15)	2	83	2	99	15	95	5
Chlorthion	27	104	1	101	5	95	4	98	6
Irgarol 1051	28	0		31	22	89	6	96	7
Methidathion	29	109	4	105	7	86	3	98	8
Tetrachlorvinphos	30	110	3	102	10	89	3	96	9
Fenamiphos	31	114	9	82	6	91	9	92	8
Ethion	32	107	6	101	10	77	7	90	7
TPP	33	102 (21)	16	100 (4)	12	84	3	98	8
Tributoxyethylphosphate	34	104	15	88	28	71	10	90	12
EPN	35	89	23	91	12	88	7	92	10
Tris(2-ethylhexyl)phosphate	36	72 (5)	15	70	14	73	4	86	9
Azinphos methyl	37	56 (45)	2	94	5	91	7	95	8
Leptophos	38	50 (50)	7	51 (26)	9	50 (50)	13	52	10
Azinphos ethyl	39	88 (70)	10	93	2	93	9	94	5
Coumaphos	40	35 (35)	18	40 (32)	13	52 (52)	1	66	10

[a] Unless otherwise indicated, no compound was extracted in R_2.

CH_3OH (80:20). When the elution was carried out as described by Cai et al. [28], who quantitatively recovered DDA from 250 mg of GCB using 0.5 ml ethyl acetate and 5 ml of CH_2Cl_2–CH_3OH (60:40), this compound was only recovered at a 50% efficiency using twice the eluent volume. Moreover, the more volatile compounds (e.g., dichlorvos) were lost and poor recoveries were obtained for most of the compounds after removing the methanol to dryness for GC analyses (results not reported).

In view of the results above, the extraction efficiency of pure dichloromethane after the methanol washing was also tested. Recoveries proved not to be notably different from the mixture CH_2Cl_2–CH_3OH (80:20) with the exception of DDA, which showed a considerable improvement.

Interestingly, the 1 ml methanol washing resulted in quantitative recovery of Irgarol 1051, which showed the tendency to be strongly adsorbed onto the GCB surface. From a practical point of view, this methanol was discarded since it did not contain any of the analytes studied and a final volume of 12 ml of dichloromethane was used in further experiments, although DDA, leptophos, coumaphos and chlorothalonil were not quantitatively recovered.

For the nonpolar chlorothalonil, a strongly adsorption of this compound is likely to occur onto the Envi-Carb sorbent. It is well known that quinone groups, if present on graphitized carbon black sorbents, can provoke effects of chemisorption for particular adsorbates, probably via addition reactions [16]. In order to eliminate this undesirable effect, some experiments previously described in the literature [16] were performed without success for the target compounds. Quinones present in the Envi-Carb were converted to the less reactive hydroquinones by washing the Envi-Carb cartridge with 15 ml of ascorbic acid (10 g/l acidified to pH 2 with hydrochloric acid). As this experiment resulted in only 20% recovery of chlorothalonil, no pretreatment of the Envi-Carb cartridges with ascorbic acid was applied for studying its performance and no more attempts were performed to recover chlorothalonil. Although re-extraction by back-flushing on GCB reversible cartridges has been shown to improve considerably the recovery of two triazinones [17] by reducing the excessive time of contact between the eluates and quinone groups, this alternative could not been considered because only forward-flushing cartridges were available.

3.2. Performance of the LiChrolut EN cartridges

Table 2 shows the percentage recoveries (*R*) and relative standard deviations (RSDs) obtained for the compounds under investigation extracted from 1 l of different water matrices spiked at concentration levels of 100–600 ng/l onto LiChrolut EN cartridges.

Recoveries of molinate, triazines and metabolites from ultra-pure Milli-Q water compared well with those obtained from environmental waters. Extraction efficiencies were higher than 78% and the RSDs were lower than 18%, except for DDA, which was not extracted. Very low recoveries for the completely dealkylated and very polar didealkylterbuthylazine were also reported in the analyses of 1 l of tap water using the LiChrolut sorbent [33].

Lower recoveries were obtained for some organophosphorus compounds (dichlorvos, sulfotep, parathion-methyl, chlorpyriphos-methyl, chlorpyriphos, chlorthion, EPN, leptophos) and chlorothalonil from tap water (25 to 54%) compared to Milli-Q water (82 to 94%). This was firstly attributed to possible oxidation of the compounds by hipochlorite and other potential oxidants presents in the tap water. However the addition of a reducing agent (0.4 g/l of sodium sulfite) to the tap water sample did not improve the recoveries (results not reported). Tap water that was previously extracted through the LiChrolut EN cartridge was passed through the Envi-Carb cartridge and none of the compounds under investigation was found on the later sorbent. Recoveries from pre-filtered tap water were not notably different for those without filtration (results no reported) indicating that the losses were not caused by adsorption onto suspended particles. Therefore, all these experiments suggest that the low recoveries of some organophosphorus compounds did not result from poor extraction efficiencies and it is suspected that a partial degradation of these compounds occurred during the preconcentration of the tap water samples. Other authors have also noticed the degradation of organophosphorus compounds after spiking into water and during the extraction of water [34]. These compounds in waters were shown to be

Table 2
Recovery efficiencies (R, %), RSD (%; in parentheses; $n=3$) and limits of detection (LODs) of selected pesticides and industrial compounds extracted from 1 l of different water samples after SPE on LiChrolut EN cartridges

	Spike level	R (RSD)					LOD[a]
	(ng/l)	Milli-Q water	Tap water	River water	Salted tap water	Sea water	(ng/l)
Dichlorvos	90	88 (15)	13 (13)	7 (11)	85 (6)	83 (8)	0.5–6.5
TiBP	90	76 (14)	74 (10)	58 (12)	85 (5)	75 (20)	0.8
Molinate	72	82 (11)	80 (6)	97 (12)	78 (14)	84(7)	2.6
Atrazine desethyl desisopropyl	127	0 (n.d.)	0 (n.d.)	0 (n.d.)	0 (n.d.)	0 (n.d.)	n.d.
Atrazine desisopropyl	174	93 (8)	84 (9)	106 (18)	86 (10)	88 (11)	2.5
TBP	96	88 (12)	77 (7)	76 (10)	74(15)	82 (16)	0.6
Atrazine desethyl	198	96 (10)	96 (6)	100 (13)	89 (10)	95 (5)	2.1
Monocrotophos	202	79 (12)	75 (11)	98 (7)	91 (4)	98 (5)	2.7
Sulfotep	90	88 (4)	34 (24)	85 (7)	50 (13)	74 (7)	0.5
Dimethoate	101	83 (13)	72 (6)	99 (4)	94 (3)	95 (5)	0.6
Simazine	125	94 (11)	83 (5)	98 (14)	87 (16)	93 (5)	1.4
Prometon	93	103 (7)	99 (6)	95 (15)	95 (15)	94 (8)	1.8
Atrazine	128	103 (10)	80 (4)	97 (13)	81 (13)	93 (8)	1.4
Propazine	109	94 (9)	92 (4)	99 (12)	89 (14)	93 (6)	1.9
Diazinon	90	90 (13)	62 (10)	86 (8)	79 (11)	82 (7)	0.5
Chlorothalonil	198	81 (9)	39 (8)	31 (11)	70 (7)	81 (10)	3.3–9
Parathion-methyl	90	90 (7)	54 (12)	91 (4)	70 (6)	84 (3)	0.6
Chlorpyriphos-methyl	95	92 (8)	31 (15)	93 (5)	62 (15)	86 (12)	0.5–1.5
Symetryne	93	106 (2)	81 (7)	99 (18)	96 (18)	89 (4)	2
Ametryne	109	86 (6)	85 (7)	95 (12)	88 (14)	92 (4)	1.6
Prometryne	80	95 (13)	87 (6)	98 (14)	84 (14)	93 (3)	1.9
Fenitrothion	100	115 (10)	72 (12)	92 (5)	78 (2)	91 (2)	0.5
Malathion	103	94 (12)	60 (13)	89 (6)	79 (4)	86 (5)	0.8
Fenthion	101	71 (6)	79 (7)	82 (6)	80 (4)	79 (7)	0.6
Parathion	102	89 (9)	61 (10)	93 (8)	76 (6)	82 (10)	0.7
Chlorpyriphos	101	88 (8)	36 (15)	85 (9)	54 (15)	75 (12)	0.5–1.2
Chlorthion	100	94 (7)	41 (16)	93 (10)	80 (9)	91 (2)	0.7–1.5
Irgarol 1051	87	94 (5)	85 (5)	97 (12)	81 (13)	92 (3)	1.8
Methidathion	181	101 (12)	80 (16)	97 (6)	81 (5)	94 (4)	0.8
Tetrachlorvinphos	181	98 (16)	75 (6)	83 (11)	86 (5)	90 (1)	1.2
Fenamiphos	326	70 (6)	82 (7)	74 (9)	73 (5)	80 (4)	1.3
Ethion	100	87 (4)	65 (11)	79 (5)	44 (5)	64 (23)	0.7
TPP	358	100 (6)	98 (5)	88 (9)	82 (10)	84 (6)	1.6
Tributoxyethylphosphate	595	85 (12)	81 (8)	70 (12)	46 (13)	55 (26)	3
EPN	208	105 (5)	22 (40)	93 (8)	12 (5)	80 (6)	6.7
Tris(2-ethylhexyl)phosphate	499	47 (12)	50 (10)	32 (14)	37 (9)	34 (15)	4.6
Azinphos-methyl	398	109 (12)	74 (12)	106 (12)	82 (14)	98 (2)	3
Leptophos	204	82 (14)	23 (18)	75 (10)	12 (37)	52 (21)	1.4–9.5
Azinphos-ethyl	406	100 (8)	70 (11)	97 (13)	81 (15)	92 (2)	2.4
Coumaphos	398	95 (11)	74 (12)	90 (9)	79 (10)	96 (3)	3

[a] It was estimated from a typical instrumental detection limit at a signal-to-noise ratio of 3:1, taking into account the lowest recovery yield obtained for the different water matrix, using a sample volume of 1 l and injecting 1 μl into the GC system from a final extract volume of 50 μl. For those compounds in which a data range is given, the values account for the lowest and higher recovery yield which are very different and dependent on the matrix water.

mainly degraded by chemical hydrolysis and biodegradation for which photolysis played a minor role in the breakdown [35], with the exception of fenitrothion where photolysis and microbial processes seems to be the main degradation pathways [36]. Some studies have indicated the importance of biological hydrolysis on the degradation of parathion, whereas chemical degradation appeared to

play a major role in the degradation of chlorpyriphos, diazinon and EPN [37,38]. The higher losses observed in natural waters compared to pure water could not result from a difference on the pH (all samples had pH 7, except sea water, pH 8), but could be due to the presence of inorganic ions (e.g., copper, iron) that are known to catalyse the rate of hydrolysis of some organophosphorus compounds, such as chlorpyriphos and diazinon [39–41]. Alternatively, when using samples of high ionic strength (tap water with NaCl and sea water), higher recoveries were obtained for chlorothalonil and some of the organophosphorus compounds, such as dichlorvos, sulfotep, parathion-methyl, parathion, chlorpyriphos-methyl, chlorpyriphos and chlorthion. A different behavior was observed for EPN and leptophos, for which higher recoveries were obtained in sea and river water compared to tap and salted tap water. In the case of tributoxiethylphosphate, lower recoveries were achieved in sea and salted tap water. These results indicate that some organophosphorus compounds might suffer less degradation on the LiChrolut EN cartridge under the presence of an electrolyte (e.g., NaCl), which probably reduces the hydrolysis rates of these compounds, whereas for others sodium chloride might have or not an apparent catalytic effect on degradation. The results are in agreement with the marked increase in the persistence of parathion and chlorpyriphos moving from fresh water to sea water under abiotic conditions [35]. Similar observations have been reported for carbamate insecticides, where the salt content of natural waters affected the rate of hydrolysis of the carbamates, possibly resulting from decreasing the activity of the hydroxyl ions and the insecticide [42]. Other studies have also shown an improvement in the recovery of some organochlorine pesticides under LiChrolut EN sorbent when NaCl was added to the aqueous sample [26]. On the other hand, the recovery yields for malathion agree also with the reported aqueous hydrolysis half-lives, which are not affected by salt concentration [43].

The detection method for each compound is also shown in Table 2. It was estimated from a typical instrumental detection limit at a signal-to-noise ratio of 3:1, taking into account the lowest recovery yield obtained for the different water matrix, using a sample volume of 1 l and injecting 1 μl into the GC from a final extract volume of 50 μl. They range between 0.5 to 10 ng/l for the organophosphorus compounds, between 1.4 and 2.5 ng/l for triazines and the two recovered metabolites, 2.6 ng/l for molinate and 9 ng/l for chlorothalonil.

The recoveries reported here using LiChrolut EN agree with those reported by Aguilar et al. [26] for triazines and molinate in 500 ml of tap and river water, but are better for malathion. They are also similar to those obtained by Junker-Buchheit and Witzenbacher [25], who successfully preconcentrated DIA and DEA in the low ppb range from 1 l of drinking water at a flow-rate of 5 ml/min. From findings here, a flow-rate of 20 ml/min can also be used to preconcentrate pesticides onto LiChrolut EN without loss of efficiency. An additional benefit is a noticeable reduction of the extraction time.

3.3. Performance of the Envi-Carb cartridges

Table 3 shows the percentage recoveries and RSDs obtained for the compounds extracted from 1 l of different water samples spiked at concentrations of 100–600 ng/l onto Envi-Carb cartridges.

Analyte recoveries of molinate, triazines and metabolites were invariably greater than 80%, with the exception of DDA, and were unaffected by the nature of the aqueous matrices in which the analytes were dissolved. Precision (RSD) for the above compounds was lower than 21%. For DDA, which is the most polar compound studied, recoveries ranged from 20% in salted tap water to 55% in river water.

Partial losses of some organophosphorus compounds, especially for sulfotep, EPN and leptophos, were observed in the tap water matrix, and attributed to the low stability of these compounds in the matrix. The addition of sodium chloride did not improve the extraction efficiency of these compounds.

Results reported for the strongly adsorbed chlorothalonil and coumaphos show that when samples with a high ionic strength (salted tap water and sea water) are passed through the Envi-Carb bed, recovery is improved. This suggests that the adsorption sites able to establish strong interaction with particular compounds are minimized or reduced by the addition of a certain amount of electrolyte to the aqueous sample.

The LOD for each compound is shown in Table 3.

Table 3
Recovery efficiencies (R, %), RSD (%; in parentheses; $n=3$) and limits of detection (LOD) of selected pesticides and industrial compounds extracted from 1 l of different water samples after SPE on Envi-Carb cartridges

	Spike level	R (RSD)					LOD[a]
	(ng/l)	Milli-Q water	Tap water	River water	Salted tap water	Sea water	(ng/l)
Dichlorvos	90	96 (2)	71 (9)	76 (11)	79 (16)	72 (17)	0.6
TiBP	90	80 (6)	77 (15)	64 (16)	71 (7)	64 (5)	0.7
Molinate	72	89 (11)	92 (19)	95 (21)	80 (11)	60 (18)	3.5
Atrazine desethyl desisopropyl	127	39 (4)	34 (27)	55 (18)	20(20)	41 (18)	14
Atrazine desisopropyl	174	95 (15)	101 (5)	96 (6)	90 (10)	104 (9)	2.3
TBP	96	88 (5)	71(12)	82 (13)	73 (11)	63 (9)	0.7
Atrazine desethyl	198	97(13)	103 (8)	100 (3)	92 (13)	93 (4)	2
Monocrotophos	202	96(6)	115 (3)	110 (6)	99 (8)	93 (10)	1.7
Sulfotep	90	95(4)	59 (10)	82 (12)	55 (7)	64 (3)	0.3
Dimethoate	101	91(3)	88 (4)	89 (13)	83 (8)	71 (9)	0.7
Simazine	125	93(16)	99 (8)	103 (4)	112 (12)	91 (4)	1.3
Prometon	93	88(17)	97 (8)	95 (4)	107 (12)	90 (4)	1.9
Atrazine	128	93(15)	97 (9)	101 (4)	112 (12)	89 (3)	1.3
Propazine	109	95(17)	99 (9)	102 (4)	115 (11)	94 (5)	1.8
Diazinon	90	98(3)	81 (8)	71 (2)	82 (9)	68 (5)	2
Chlorothalonil	198	0(n.d.)	29 (12)	35 (14)	80 (9)	58 (17)	3–n.d.
Parathion-methyl	90	98(2)	60 (10)	90 (10)	61(13)	74 (5)	0.6
Chlorpyriphos-methyl	95	101(2)	62 (11)	83 (11)	62 (12)	67 (6)	0.7
Symetryne	93	78(19)	94 (8)	91 (1)	86 (10)	88 (3)	2
Ametryne	109	86(13)	92 (8)	88 (3)	92 (14)	83 (3)	1.6
Prometryne	80	84(13)	95 (8)	88 (3)	94 (12)	84 (4)	1.9
Fenitrothion	100	100(4)	82(3)	87 (10)	75 (12)	67 (5)	0.5
Malathion	103	102(5)	80 (4)	87 (11)	74 (15)	69 (5)	0.7
Fenthion	101	117(2)	86(6)	88 (10)	64 (12)	68 (7)	0.7
Parathion	102	104(2)	79 (6)	89 (11)	77 (9)	72 (6)	0.6
Chlorpyriphos	101	94(2)	83 (6)	85 (11)	84 (9)	66 (8)	0.7
Chlorthion	100	101(5)	65 (10)	81 (2)	75 (10)	77 (5)	1.0
Irgarol 1051	87	80(7)	90 (6)	87 (1)	90 (17)	82 (1)	1.8
Methidathion	181	108(4)	84 (5)	76 (1)	79 (11)	72 (4)	0.8
Tetrachlorvinphos	181	90(3)	87 (4)	71 (2)	81 (10)	83 (5)	1.2
Fenamiphos	326	85(9)	83 (6)	70 (2)	70 (10)	77 (6)	1.3
Ethion	100	63(6)	59 (12)	59 (6)	54 (12)	52 (8)	0.6
TPP	358	79(16)	79 (8)	68 (3)	68 (10)	62 (7)	2.5
Tributoxyethylphosphate	595	62(12)	53 (18)	51 (9)	48 (15)	50 (12)	2.7
EPN	208	75(15)	35 (5)	70 (3)	21 (36)	63 (7)	3.8
Tris(2-ethylhexyl)phosphate	499	40(15)	53 (10)	35 (11)	44 (15)	43 (11)	4.2
Azinphos-methyl	398	66(2)	83 (3)	80 (1)	83 (15)	72 (5)	3
Leptophos	204	51(7)	20 (11)	56 (7)	25 (29)	44 (9)	6
Azinphos-ethyl	406	76(10)	79 (5)	73 (1)	72 (15)	66 (6)	2.6
Coumaphos	398	45(18)	55 (13)	57 (10)	69 (15)	61 (7)	5.5

[a] It was estimated from a typical instrumental detection limit at a signal-to-noise ratio of 3:1, taking into account the lowest recovery yield obtained for the different water matrix, using a sample volume of 1 l and injecting 1 μl into the GC system from a final extract volume of 50 μl. For those compounds in which a data range is given, the values account for the lowest and higher recovery yield which are very different and dependent on the matrix water.

They range between 0.3 and 5.5 ng/l for the organophosphorus compounds, between 1.3 and 1.9 ng/l for triazines, between 2.0 and 14.0 ng/l for triazine metabolites including DDA and 3.5 ng/l for molinate. For chlorothalonil a detection limit of 3.5 ng/l was obtained in salted tap water, whereas in Milli-Q water it could not be detected.

Recoveries of the organophosphorus compounds

noted here are generally similar to those reported by the group of Di Corcia using 250–300 mg of GCB [16,31], except for coumaphos, for which lower recoveries have been attained. Likely, this was due to the large-size extraction cartridge (500 mg) used here which required high eluate volumes to desorb quantitatively this compound in the forward-flushing compared to back-flushing elution mode [17].

Recoveries of atrazine and metabolites (DEA and DIA) from 1 l environmental water samples [17,27] generally compared favorably with those reported here. However, recoveries of DDA higher than 80% have been achieved using GCB cartridges with no significant breakthrough for sample volumes of 3 l [28]. These data contrast with results here, where the extraction efficiency (39%) for the 1 l Milli-Q water sample was markedly less than that (66%) for a 100 ml. As was described in section 3.1, using the eluting solvent described by these authors [28], a maximum recovery of 50% was achieved. These differences are most likely related to variations in the selected protocols, in particular the flow-rate and different batches of the sorbent.

3.4. LiChrolut EN versus Envi-Carb cartridges

Figs. 1 and 2 show the GC–NPD chromatograms obtained for the pesticide-spiked Milli-Q sample and blanks extracted using LiChrolut EN and Envi-Carb cartridges, respectively. Figs. 3 and 4 illustrate the corresponding GC–FPD chromatogram for the organophosphorus compounds and blanks extracted by the LiChrolut EN and Envi-Carb cartridges.

The comparison reveals that both sorbents recover a broad polarity range of compounds varying from polar organophosphorus pesticides (e.g., monocrotophos and dimethoate) through medium polar organophosphorus pesticides to non-polar pesticides (e.g., chlorpyriphos). They also allow the analysis of the thiocarbamate, molinate, and the atrazine metabolites (DIA, DEA), but fail to recover quantitatively the most polar one, didealkylatrazine (DDA: log $K_{ow}=0.11$). For this compound, only the Envi-Carb sorbent was successfully giving a detection limit of 14 ng/l.

According to the results here, LiChrolut EN does not suffer from strong adsorption as observed for some compounds (e.g., chlorothalonil) onto the Envi-Carb sorbent, although higher losses of some organophosphorus compounds and chlorothalonil were observed during the extraction of the tap water samples. These losses, however, were minimized for some compounds with the presence of NaCl in the water sample, in particular for dichlorvos and chlorothalonil. On the other hand, the recovery yields on the Envi-Carb cartridge were dependent only on the ionic strength of the water sample for the strongly retained chlorothalonil and coumaphos.

The detection limits for organophosphorus, molinate and triazine compounds were similar in both sorbents with the exception of DDA. They range between 0.5 and 10 ng/l. The detection limit for chlorothalonil on LiChrolut EN sorbent was 9 ng/l and 14 ng/l for DDA on Envi-Carb cartridges. All detection limits clearly comply with the detection level of 100 ng/l required by the European Union (EU) directive on drinking water (EEC 80/778) [44].

Owing to the low stability of the organophosphorus compounds and comparing Tables 2 and 3, it is postulated that these compounds are more prone to catalyzed hydrolysis by chelate-forming metals on the LiChrolut sorbent. In this sense, more research is needed to asses the losses of pesticides on the sorbents, and in particular upon storage. Some studies on pesticide stability during storage in a GCB cartridge have shown that best results were obtained by first minimizing the residual water remaining on the adsorbent using a suitable methanol washing before freezing the cartridges at −20°C [45]. In this study, it was concluded that three mechanisms of degradation upon storage on GCB occur: non-catalyzed hydrolysis by residual water; hydrolysis catalyzed by the GCB surface as a whole or by its surface chemical heterogeneity; and chemisorption caused by the same surface-active sites.

Blanks have been another aspect which was addressed in the analysis of pesticides by SPE [46]. The NPD and FPD chromatograms (Figs. 1D, 2D, 3D, 4D) illustrate that both cartridges contain very few extra peaks. They are subject to similar interferences, in particular to the industrial trialkylphosphates (TBP and TiBP), which are components of the plastic cartridges. These interferences are, however, slightly higher for the Envi-Carb cartridges, but

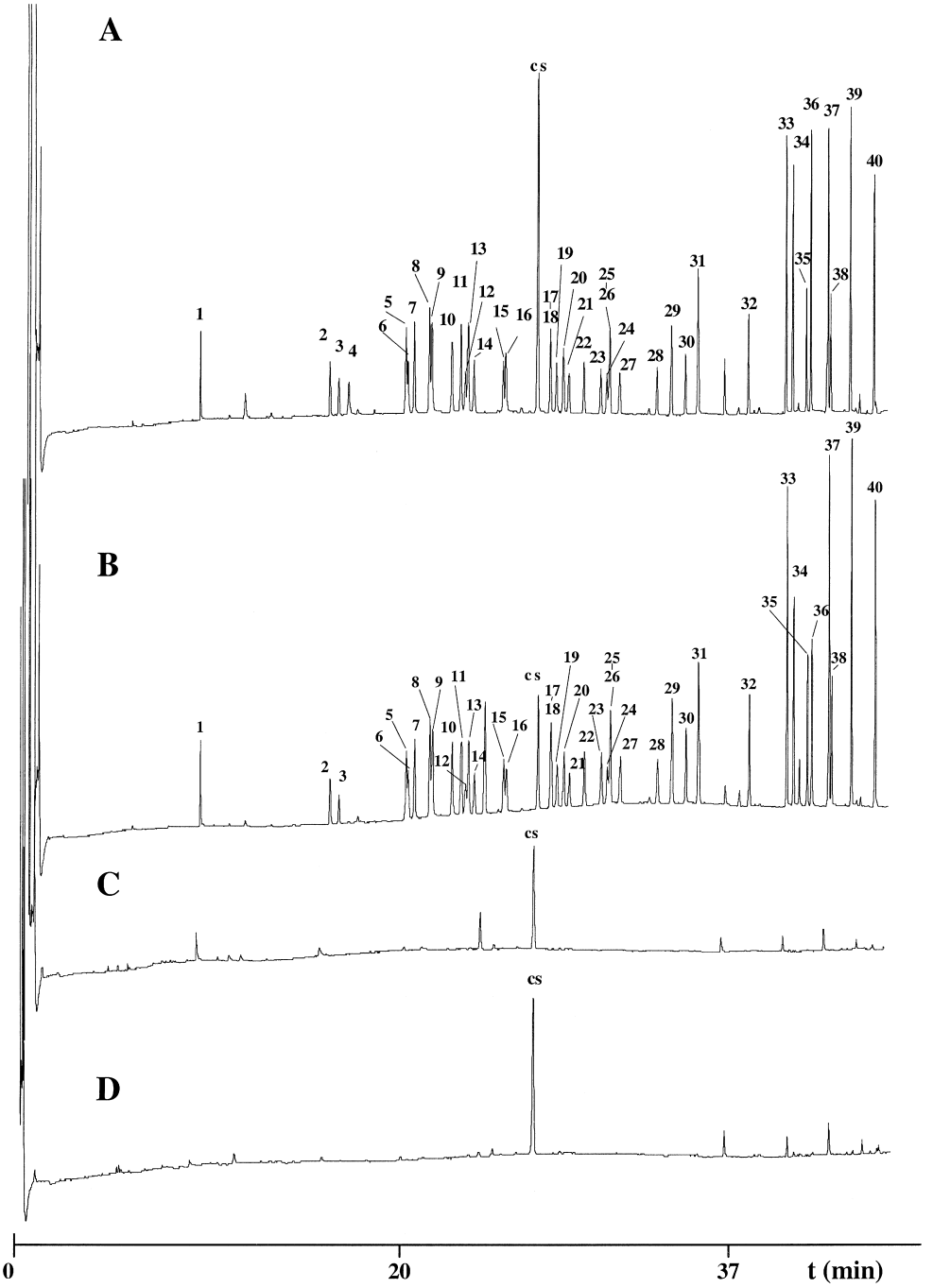

Fig. 1. GC–NPD chromatogram obtained for: (A) standards; (B) 1 l Milli-Q water spiked with the standards and extracted using the LiChrolut EN cartridge; (C) 1 l Milli-Q water (blank) extracted using the LiChrolut EN cartridge; (D) blank of LiChrolut EN cartridge. Chromatographic conditions as explained in the text. For peaks numbers see Table 1. c.s=Desmetryn (co-injected standard).

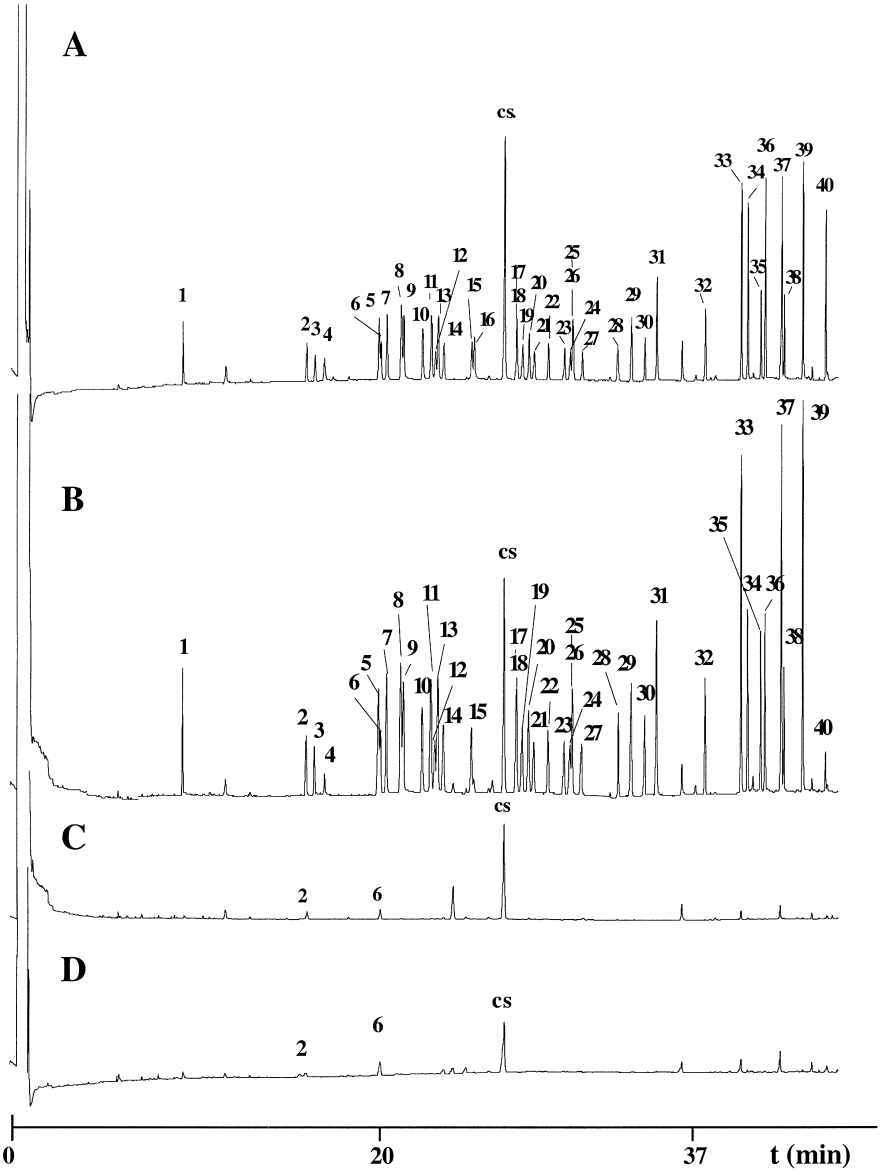

Fig. 2. GC–NPD chromatogram obtained for: (A) standards; (B) 1 l Milli-Q water spiked with the standards and extracted using the Envi-Carb cartridge; (C) 1 l Milli-Q water (blank) extracted using the Envi-Carb cartridge; (D) blank of Envi-Carb cartridge. Chromatographic conditions as explained in the text. For peaks numbers see Table 1. c.s.=Desmetryn (co-injected standard).

they do not interfere in the analysis of the pesticides studied here.

An important advantage offered by the LiChrolut EN cartridge is that the solvent volume necessary to elute all target compounds is less than that required using Envi-Carb. Other studies of SPE on GCB have also addressed the importance of the correct choice of the eluent and the required care on handling this material [29]. Indeed, they could not explain the low recoveries obtained for some compounds because the sorption mechanism is not known. The GCB has a very homogeneous carbonaceous structure made of large bands of delocalized electrons and also offers anion-exchange adsorption sites on its surface. With

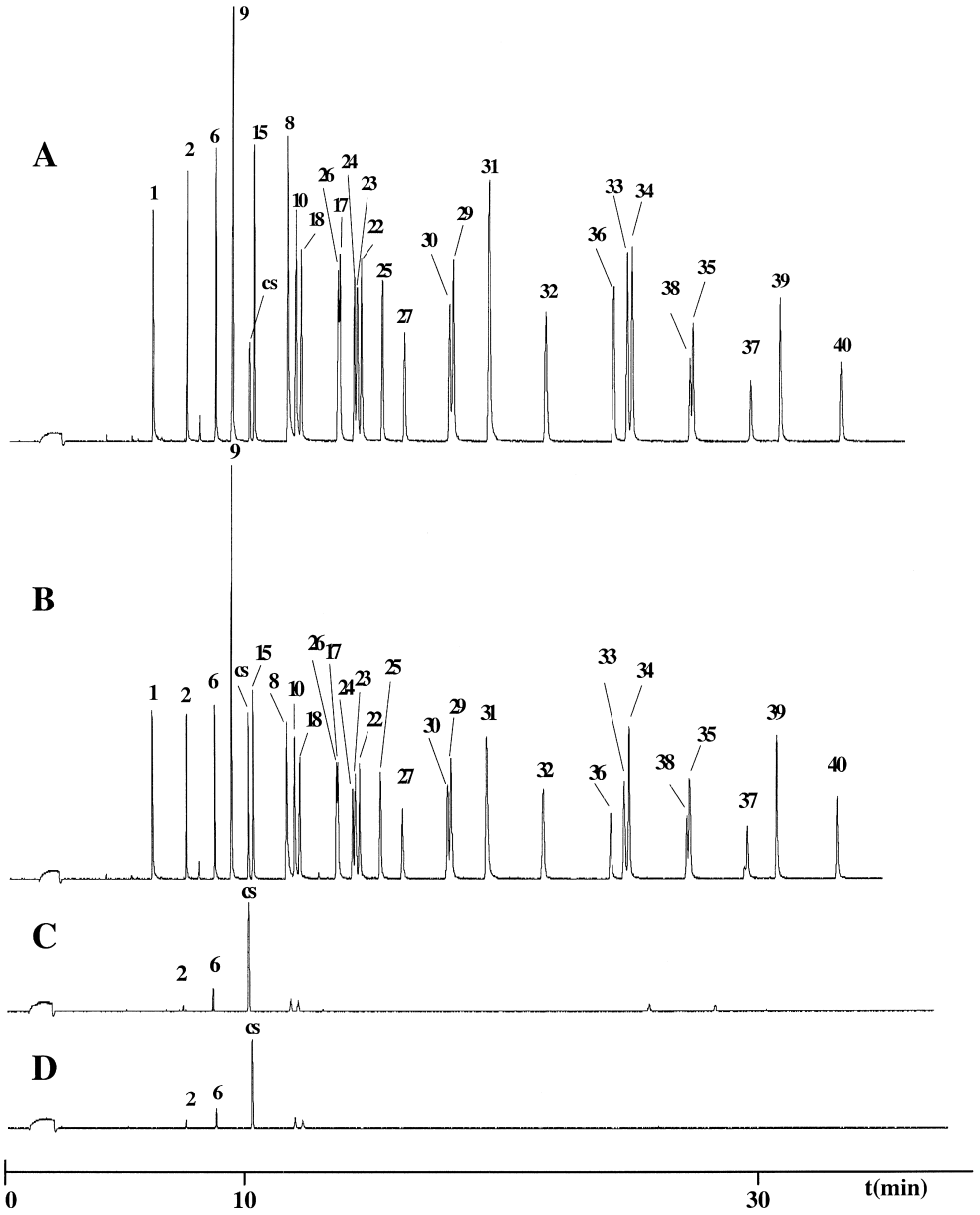

Fig. 3. GC–FPD chromatogram obtained for: (A) standards; (B) 1 l Milli-Q water spiked with the standards and extracted using the LiChrolut EN cartridge; (C) 1 l Milli-Q water (blank) extracted using the the LiChrolut EN cartridge; (D) blank of LiChrolut EN cartridge. Chromatographic conditions as explained in the text. For peaks numbers see Table 1. c.s.=Dibenzothiophene (co-injected standard).

these features, it can behave as a reversed-phase and anion exchanger, but the resulting surface properties from the manufacturing procedure also plays an important role.

On LiChrolut EN, although some anionic adsorption sites enable cation-exchange properties [47], the retention mechanism of analytes is mainly based on the $\pi-\pi$ interactions between the aromatic structure of the sorbent and π-electrons of the analyte. Therefore, as adsorption and desorption of the analytes in

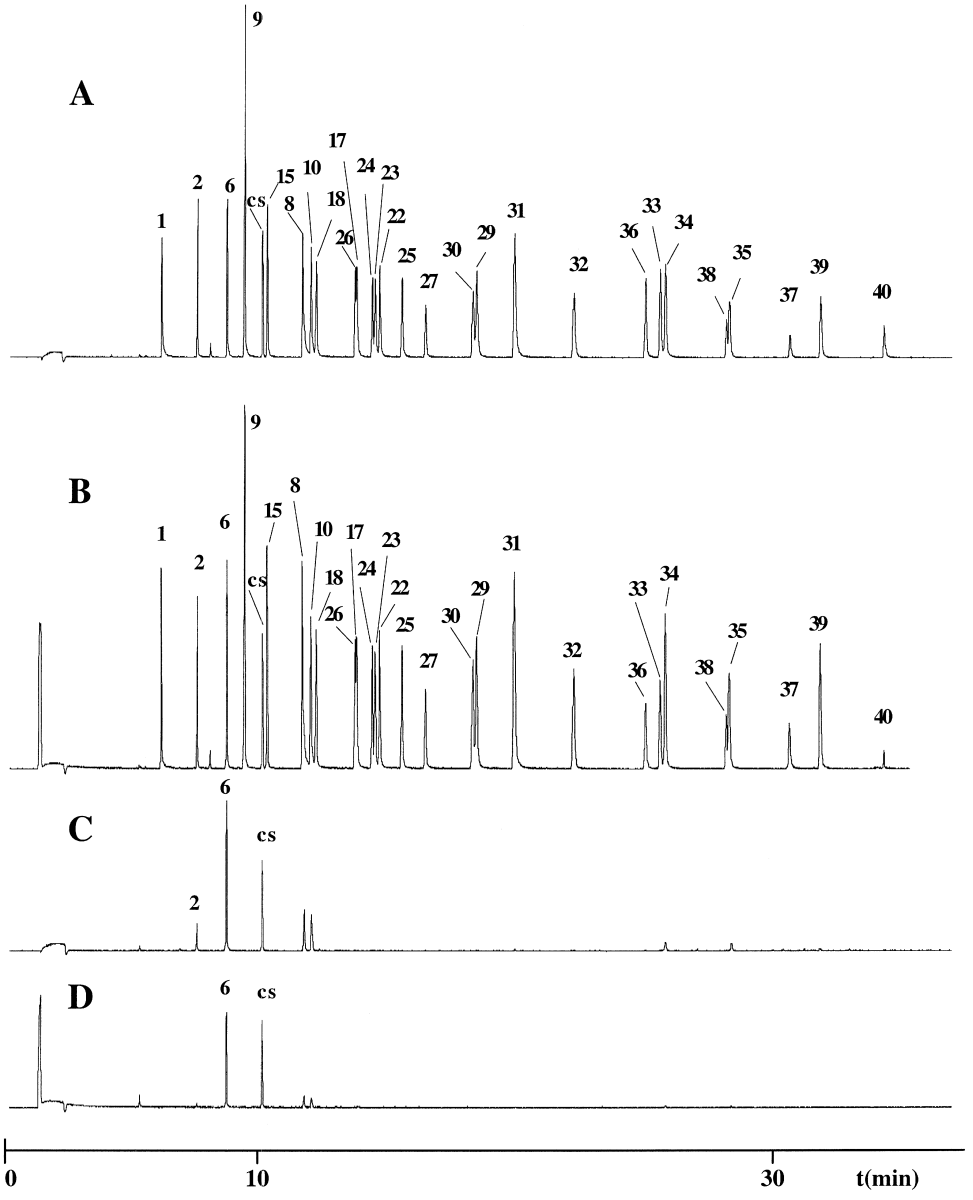

Fig. 4. GC–FPD chromatogram obtained for: (A) standards; (B) 1 l Milli-Q water spiked with the standards and extracted using the Envi-Carb cartridge; (C) 1 l Milli-Q water (blank) extracted using the Envi-Carb cartridge; (D) blank of Envi-Carb cartridge. Chromatographic conditions as explained in the text. For peaks numbers see Table 1. c.s.=Dibenzothiophene (co-injected standard).

LiChrolut EN occurs quickly, the required eluent volumes are quite small and therefore results in the consumption of less solvent compared to using the Envi-Carb phase.

4. Conclusions

The solid-phase process using LiChrolut EN cartridges enables a sample volume of 1 l to be

preconcentrated with acceptable recoveries for all compounds studied except the very polar DDA. By comparing recovery data of the compounds extracted from tap water under Envi-Carb, losses of some organophosphorus compounds are slightly higher on the LiChrolut EN sorbent. In this vein, stability studies of pesticides on these adsorbents will be conducted in the future to study its applications for the storage of pesticides preconcentrated from water samples.

Envi-Carb cartridges appeared to be superior to LiChrolut EN cartridges when extracting polar metabolites of atrazine, but it is clear that the use of this sorbent for the determination of chlorothalonil is not completely satisfactory due to its strong adsorption. In further studies, backflush mode in the elution step of Envi-Carb sorbent should be addressed after the introduction in the market of GCB reversible cartridges.

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