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Determination of aryloxyphenoxypropionic acid herbicides in water using different solid-phase extraction procedures and liquid chromatography–diode array detection

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Abstract

For isolation and trace enrichment of aryloxyphenoxypropionic acid (ArPP) herbicides from drinking, spring, and ground water a sensitive, robust method is presented. A 1–2 l volume of aqueous samples was passed through a disposable solid-phase extraction cartridge, packed with 500 mg of Carbograph-1 at a flow-rate of 100 ml/min. After washing, ArPPs are selectively eluted with 8 ml of dichloromethane–methanol (80:20, v/v) with 50 mmol/l formic acid and evaporated to dryness. The mixture was reconstituted with 250 μl of water–acetonitrile (75:25, v/v) acidified with 0.1% trifluoroacetic acid and 100 μl was injected into the high-performance liquid chromatography system. The ArPPs were separated via a binary gradient of water and a mixture of methanol–acetonitrile. Detection and confirmation were performed by diode array detection. Recovery of the six acid herbicides ranged between 90% and 98%. The limits of detection of ArPPs were 7–20 ng/l for drinking water and 16–36 ng/l for spring water. In terms of recovery and selectivity the effectiveness of Carbograph-1 cartridges was compared with that of LiChrolut-EN cartridges and polystyrene–divinylbenzene Empore disks. Relevant parameters such as pH and flow-rate for solid-phase extraction with divinylbenzene resins were optimized.

Keywords: Water analysis; Environmental analysis; Pesticides; Aryloxyphenoxypropionic acids

1. Introduction

Aryloxyphenoxypropionic acids (ArPPs; Fig. 1) are a new class of herbicides used for the selective removal of most grass species from any non-grass crop. These compounds are more active in post-emergence (foliar) crops than when applied to soil [1]. Although commercially available as ester derivatives, in soil and in plants they undergo fast hydrolysis to the free acids [2]. Currently, no analytical method for determining these compounds in water has been described.

A recent European Union (EU) directive states that the pesticide level must not exceed 100 ng/l for individual compounds (500 ng/l for all compounds) in water intended for human consumption [3]. In order to judge with sufficient confidence whether a water matrix complies with this directive, analytical methods able to detect pesticides at levels which are below the EU tolerance limit of 100 ng/l by a factor of 3–5 are needed. Although capillary column gas chromatography (GC) remains the major technique for determining organic compounds present in water

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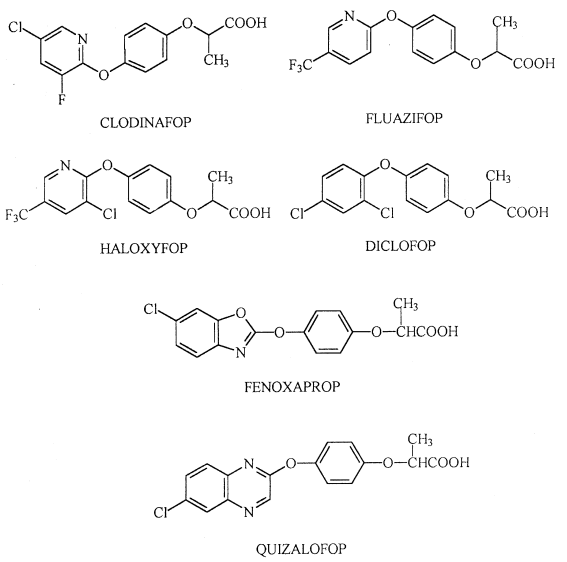

Fig. 1. Structures of the ArPP herbicides.

[4–6], the number of publications describing reversed-phase gradient elution high-performance liquid chromatography (HPLC) has steadily increased over the last ten years [7–10]. The properties of this new class of pesticides make them more amenable to HPLC than to GC. Extracting organic compounds from aqueous samples by means of suitable sorbents, i.e., solid-phase extraction (SPE), has aroused growing interest as it eliminates well-known problems associated with the use of liquid–liquid extraction. Several sorbents have been described for the analysis of acidic pesticides in water. Puig and Barcelò used both off-line and on-line SPE with Empore disks to extract acidic phenolic compounds from water [11]. Pichon et al. studied the efficiency of cartridges filled with a new type of polymeric sorbent [styrene–divinylbenzene, (SDB-1)] for the enrichment of water samples, with or without prior acidification, spiked with neutral and acidic pesticides, to investigate the potential of multiresidue analysis [12]. Off-line studies were made by Crescenzi et al. [13], who used graphitized carbon black (GCB) cartridges with very good recoveries for acidic pesticides. Of the above-mentioned sorbents, GCB presents the greatest advantages in terms of efficiency and selectivity in extracting organic acidic compounds [14–16]. The presence of some active centers bearing a positive charge enables GCB to behave as both a non-specific and an anion-exchange sorbent [17]. Anionic organic compounds are specifically adsorbed on to the GCB surface via electrostatic forces and can be desorbed only by adding a displacing agent to an organic solution. When extracting acidic analytes from water, a large amount of non-acidic compounds present in the sample may be co-extracted, rendering subsequent HPLC analysis difficult because of interfering peaks present in the final chromatogram. Using GCB this drawback may be overcome simply by washing the cartridge with a suitable neutral solvent mixture.

The objective of this work was to develop a sensitive assay for monitoring ArPPs in environmental aqueous samples so as to obtain limits of detection (LODs) below 100 ng/l. This can be achieved by using a particular type of sorbent (Carbograph-1) which was found to be much more effective in retaining the ArPP and eliminating the potential interferents, natural and strong acid substances, than the other extracting systems used (LiChrolut-EN and Empore disks).

2. Experimental

2.1. Reagents and chemicals

Authentic ArPPs and esters were purchased from LabService (Bologna, Italy), as follows: haloxyfop [(*RS*) - 2 - [4-(3-chloro - 5 - trifluoromethyl-2-pyridyloxy)phenoxy] propionic acid]; diclofop [(*RS*)-[2-(4-(2,4-dichlorophenoxy)phenoxy]propionic acid]; fluazifop [2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid); fenoxaprop-ethyl [(*RS*)-2-[4-[(6 - chlorobenzoxazol - 2 - yloxy)phenoxy]propionic ethyl ester]; clodinafop-propargyl [prop-2-ynyl (*R*)-2-[4-(5-chloro - 3 - fluoropyridin - 2 - yloxy)phenoxy]-propionic ester]; quizalofop-ethyl [(*RS*)-2-[4-(6-chloro - quinoxalin - 2 - yloxy)phenoxy]propionic ethyl ester]. For HPLC, distilled water was further purified by passing it through the Milli-Q RG apparatus (Millipore, Bedford, MA, USA). Methanol ‘‘plus’’ and acetonitrile ‘‘plus’’ of LC-gradient grade were from Carlo Erba (Milan, Italy). Trifluoroacetic acid (TFA) and tetrabutylammonium fluoride (TBAF) were purchased from Merck (Darmstadt, Germany) and from Aldrich (Milwaukee, WI, USA)

respectively. All other solvents were of reagent-grade (Carlo Erba) and were used as received.

2.2. Hydrolysis and standard preparation

Each ArPP was dissolved in acetonitrile to produce a concentration of 10–20 μg/ml (10 μg/ml for diclofop and 20 μg/ml for the others). Then 1 ml of each solution was mixed and diluted with acetonitrile to 10 ml to give a working standard solution. These solutions were used to spike water samples and prepare the calibration solution. The latter was prepared by adding an appropriate volume of the ArPP working standard solution to the same solution as used for elution of the pesticides from the system of extraction. This solution was, then, processed in the same way as for sample clean-up.

To obtain the acidic compounds from the corresponding esters (clodinafop-propargyl, fenoxaprop-ethyl and quizalofop-ethyl), an attempt was made to establish the most suitable hydrolysis conditions ensuring the best yield without any loss of analyte or its transformation into unwanted products. We noted that ArPPs were unstable in an acidic media at the conditions needed for their hydrolysis. We therefore focused our attention on studying the reaction in basic media. We added, in a different glass vial, 40 μg of each ester to 6 ml of deionized water basified with 50 mmol/l sodium hydrogencarbonate. Complete hydrolysis was obtained within 5 h at 50°C in a water bath. We obtained confirmation of complete conversion of esters to acids by injecting a small volume of the alkaline solution into the LC column until the complete disappearance of the peak having the same retention time as for the ester and the simultaneous appearance of a peak having the same retention time as the corresponding acid compound.

2.3. Sorbents

Carbograph-1 was purchased from Alltech (Deerfield, IL, USA). The particle size range was 37–150 μm. No particular precautions were taken when storing GCB. LiChrolut-EN (Merck), a ethylvinylbenzene–divinylbenzene (DVB) resin having a surface area of about 1200 m^2/g and a particle size range between 40 and 120 μm was purchased from Merck. Empore disks were purchased from Varian (Walnut Creek, CA, USA). The disks used in these experiments were 47 mm in diameter and 0.5 mm thick. Each disk contained about 500 mg of polystyrene–divinylbenzene (PS–DVB) resin.

2.4. Cartridge preparation

The Carbograph-1 extraction cartridges were prepared by filling a large diameter (1.3 cm I.D.) syringe-like polypropylene tube (Supelco, Bellefonte, PA, USA) with 0.5 g of Carbograph-1 extraction cartridges adsorbing material. Polyethylene frits were placed above and below the sorbent bed. Before using, the Carbograph-1 cartridges were conditioned by passing through them, 7 ml of a dichloromethane–methanol (80:20, v/v) solution acidified with 50 mmol/l formic acid, 5 ml of methanol followed by 20 ml of LC-grade water acidified with 10 mmol/l hydrochloric acid. Conversely, LiChrolut-EN cartridges were prepared by filling small diameter (0.9 cm I.D.) tubes with 200 mg of the resin and conditioned with 5 ml of a methanol–acetonitrile (50:50, v/v) mixture followed by 5 ml of LC-grade water.

2.5. Collection and sample preparation

Water was collected in bottles and stored at 4°C until used. Ground water and spring water were collected from various sources near Rome. Rome municipal drinking water samples were taken after the water had been allowed to run for 30 min. Water samples were spiked with a suitable volume of the composite working standard solution. After stirring for ca. 2 min, samples were subjected to the extraction procedure. When extracting ArPPs with LiChrolut-EN cartridges or Empore disks, the samples were acidified to pH 2, as these materials cannot retain deprotonated acidic species. No pH adjustment was necessary when using Carbograph-1.

2.6. Extraction and clean-up procedure

Cartridges were fitted into a side-arm filtering flask while PS–DVB membranes were mounted on the fritted glass support disk of a standard vacuum apparatus. Liquids were forced through the extraction device under vacuum from a water pump. When

passing samples through the cartridges or disks, the vacuum was reduced to a minimum. After the passage of the samples and washing with 30 ml (7 ml for Carbograph-1) of LC-grade water, different re-extraction and solvent removal procedures were followed, depending upon the type of adsorbing material used.

2.6.1. Carbograph-1 cartridges

Most of the water remaining in the cartridge was expelled under vacuum for ca. 5 min. The residual water content was further decreased by slowly passing 1 ml of methanol through the cartridge and drying it with air for 30 s. Thereafter, a suitably drilled cylindrical PTFE piston with one conical indented base and a Luer tip was forced into the cartridge until it reached the upper frit. The trap was turned upside down and neutral compounds co-extracted with ArPPs were washed out by passing through the cartridge 1 ml of methanol followed by 12 ml of a dichloromethane–methanol (80:20, v/v) solution at a flow-rate of ca. 8 ml/min obtained by suitably regulating the vacuum. A 1.4 cm I.D. glass vial with a conical bottom was, then, placed below the trap, and analytes were eluted by passing through the trap 8 ml of a dichloromethane–methanol (80:20, v/v) solution acidified with 50 mmol/l formic acid. The flow-rate at which the eluent phase was allowed to percolate through the cartridge was ca. 6 ml/min. The last few drops of this mixture were collected by further decreasing the pressure inside the flask. To the eluates was added 100 μl of methanol containing 0.4 mol/l TBAF and the mixture dried in a water bath at 40°C under a gentle nitrogen stream. The precaution was taken not to allow the residue-containing vial to stay in the water bath for more than a few minutes after the solvent appeared to have been completely removed. The residue was reconstituted with 250 μl of a water (0.1% TFA)–acetonitrile solution (75:25, v/v). Then 100 μl of the final extract was injected into the LC column.

2.6.2. LiChrolut-EN cartridges

After the passage of the water sample, the last part of the previously reported procedure involving the use of a LiChrolut-EN cartridge was slightly modified in order to obtain total recovery of the compounds of interest and to shorten the analysis time [18]. After partial water removal using an air-stream trough the cartridge for ca. 5 min, analytes were eluted by 2×3 ml of a methanol–acetonitrile (50:50, v/v) mixture. To the eluates was added 100 μl of methanol containing 0.4 mol/l TBAF and the mixture evaporated to dryness in a water bath at 40°C. After this, the procedures of reconstitution and the analysis of the extract were the same as for GCB cartridges.

2.6.3. PS–DVB Empore disks

The membrane was placed in the Millipore filtration apparatus attached to a water pump aspirator apparatus. First, the disk was washed with ca. 20 ml of the final elution solvent. Thereafter ca. 20 ml of deionized water was added to the reservoir and drawn slowly through the disk by applying a slight vacuum. The surface of the disk was prevented from becoming dry from the time the washing phase was added until the sample extraction was completed. Water samples were forced through the disk at a flow-rate of ca. 200 ml/min obtained by reducing the pressure in the vacuum apparatus to a minimum. Afterwards, the disk was washed with 30 ml of deionized water and the vacuum maintained for 5 min after its passage. The extraction funnel and frit assembly were transferred to a second vacuum filtration flask containing a 1.4 cm I.D. glass vial with a conical bottom. The analytes were recovered from the disk by passing through it 3×3 ml of a methanol–acetonitrile (50:50, v/v) mixture, taking care that after each fraction the disk was dried thoroughly in a vacuum for 2 min. The final extract was processed in the same way as for the LiChrolut-EN cartridges.

2.7. HPLC analysis

LC was carried out using a Model 400 chromatograph equipped with a Rheodyne Model 7125 provided with a 100 μl loop and a Waters 996 (Waters) diode array detector. A 25 cm×4.6 mm I.D. column filled with 5 μm (average particle size) LC-18 packing and a precolumn Supelguard 2 cm×4.6 I.D., both from Supelco, were used. For separating ArPPs, gradient elution was used. Solvent A was water acidified with 0.1% TFA; solvent B was methanol–acetonitrile (70:30, v/v) acidified with 0.025% TFA.

The initial mobile phase composition was 58% of solvent B linearly programmed to 63% in 10 min, then to 88% in adjunctive 10 min and hold for 5 min. The eluted compounds were monitored at 240 nm. The flow-rate of the mobile phase was 1.0 ml/min. The concentrations of the analytes in the final extract were calculated by measuring the peak area for each compound and comparing it with those obtained from a standard solution.

3. Results and discussion

3.1. Evaporation step

As well as the extraction of large water volumes, a high enrichment factor can be obtained by minimizing the final extract volume. However, even partial removal of the solvent is sometimes known to cause large analyte losses. These losses are strictly dependent on the conditions chosen for concentrating the extracts. In order to attain a high enrichment factor and to reduce evaporative loss of herbicides, the experimental conditions were varied in order to find the best conditions. To simulate the actual situation exactly, 100 ml fractions of LC-grade water were taken through the extraction and elution procedures. Eluates were spiked with known volumes of the working composite standard solutions, and then taken to dryness. These additions were made to simulate analysis of drinking water samples containing 50–100 ng/l of each analyte. Four sets of experiments were conducted in five-fold under the various solvent removal conditions. The results in Table 1 show that complete recovery of the six pesticides was obtained only by evaporating to dryness at 40°C from a neutral solution (dichloromethane–methanol, 80:20, v/v) or from an acid solution containing TBAF.

Table 1
Recoveries (n=5) of ArPPs at spike level of 50–100 ng/l after solvent removal

Compound	Recovery (%)±R.S.D. Solvent			
	1	2	3	4
Fluazifop	90±3	95±3	94±3	95±3
Clodinafop	88±3	94±4	93±2	92±3
Quizalofop	92±3	61±3	92±3	96±2
Fenoxaprop	91±3	15±2	80±2	91±3
Haloxyfop	93±3	94±2	93±3	96±2
Diclofop	90±3	93±3	91±3	90±3

1=CH_3OH–CH_2Cl_2 (20:80, v/v), dried at 40°C; 2=CH_3OH–CH_2Cl_2 (20:80, v/v) 50 mmol/l HCOOH, dried at 40°C; 3=CH_3OH–CH_2Cl_2 (20:80, v/v) 50 mmol/l HCOOH, dried at 20°C; 4=CH_3OH–CH_2Cl_2 (20:80, v/v) 50 mmol/l HCOOH with TBAF (0.4 mol/l), dried at 40°C.

When the experiment was performed using a solution acidified with formic acid, low recovery was obtained for fenoxaprop (15%) and quizalofop (61%). The loss of these pesticides is due to the fact that, in an acid environment, the acids are esterified (the respective methyl esters are formed, as confirmed by HPLC–MS) by the methanol in the solvent mixture. The addition of TBAF to the solvent mixture prevents methanolysis because TBAF forms ion pairs with the acid pesticides.

3.2. Evaluation of extraction efficiency of Carbograph-1 cartridges

Although the sorption capacity of this sorbent is far lower than that of conventional sorbents, the presence of active centers bearing a positive charge enables Carbograph-1 to behave as both non-specific and anion-exchange sorbent. Elution was performed in such a way as to obtain complete recovery with best selectivity. When extracting acidic compounds from environmental samples containing both basic–neutral and acidic compounds, the goal of avoiding the coelution of both was attained by 1 ml of methanol followed by 12 ml of dichloromethane–methanol (80:20, v/v) to elute the basic–neutral compounds and eluting ArPPs with a mixture containing formic acid as displacer. As shown elsewhere [13], an organic mixture containing a strong acid (TFA) is capable of eluting acid compounds with pK_a values of about 2, such as dicamba, 2,4,5-trichloroacetic acid (2,4,5-T) and 2,4-dichloroacetic acid (2,4-D). As ArPPs are less acid than the above compounds, we preferred to add an organic mixture containing formic acid to obtain complete recovery from the extraction cartridge.

It should be noted that many different acid substances are contained in surface water and, in particular, surfactants of the linear benzensulphonic acid type and humic acids are almost always present.

As a result, these substances can be extracted, together with the ArPPs, from the Carbograph-1 cartridge. The advantage of using formic acid in the eluent is that highly acid substances like linear alkylbenzensulphonates (LASs) and humic acids (pK_a less than 2) are not eluted by this phase because of strong interactions with positively charged sites on the Carbograph-1 surface, while formic acid is strong enough to obtain quantitative recoveries of the analytes investigated because of the lower acidity (pK_a around 3).

The effectiveness of this eluent was tested by carrying out a step-wise elution in the forward and back flushing modes. With forward-flushing elution low recoveries were obtained (quizalofop 37%, fenoxaprop 42%, haloxyfop 61% and diclofop 55%). Complete recovery (values between 93% for fluazifop and 97% for haloxyfop) was achieved by back-flushing elution.

The retention times were quite constant, with relative standard deviations of 0.3–1.1% ($n=10$).

3.3. Recovery experiments

The extraction efficiency of the Carbograph-1 cartridge was studied by spiking 2 l of municipal drinking water, 1 l of ground water and 1 l of spring water with 50–100 ng/l and 100–200 ng/l of each herbicide and then analyzing each aqueous matrix six times. No pH adjustment of the sample was made prior to extraction. Data are reported in Table 2.

A greater analyte enrichment factor was obtained in the case of drinking water, as no breakthrough of ArPPs occurred when 2 l of sample were allowed to percolate through Carbograph-1.

Analyte recoveries were invariably greater than 90% and were unaffected by the nature of the aqueous matrix in which the analytes were dissolved. The LODs calculated for drinking water were between 2 and 6 ng/l, and the limits of quantitation (LOQs) between 7 and 20 ng/l. The LODs for spring and ground water were between 5 and 11 ng/l, and the LOQs between 15 and 36 ng/l.

It follows that this method essentially satisfies the EU requirements of 100 ng/l referred to above.

3.4. Method comparison

In terms of recovery and selectivity the effectiveness of the Carbograph-1 cartridge extraction procedure was compared with that obtained using DVB resins, in particular, the LiChrolut-EN cartridge and PS–DVB Empore disk.

Aliquots of 1 l of drinking and ground water samples (without pH adjustment) were spiked with 100–200 ng/l of the six ArPPs and analyzed by extracting with Carbograph-1 and LiChrolut-EN cartridges and Empore disks.

Data concerning drinking water are reported in Table 3. Non-quantitative recoveries for both drinking water and ground water were obtained with DVB resins. This can possibly be accounted for by the fact that the acid herbicides considered may be present in water virtually as anions and that their retention in their ionic form is dependent on sample size, sug-

Table 2
Recoveries ($n=6$) and R.S.D.s of ArPPs after extraction on Carbograph-1 cartridge of 2 l of drinking water and 1 l of spring and ground water

Compound	Recovery (%)±R.S.D.		
	Drinking water[a]	Spring water[b]	Ground water[b]
Fluazifop	94±2	93±2	94±2
Clodinafop	93±2	96±3	95±3
Quizalofop	92±4	92±4	94±4
Fenoxaprop	91±4	90±4	90±4
Haloxyfop	98±3	97±2	98±2
Diclofop	93±3	96±3	97±3

[a] spike level at 50–100 ng/l.
[b] spike level at 100–200 ng/l.

Table 3
Recoveries ($n=6$) and R.S.D.s obtained on extracting, with three sorbents, ArPPs added to 1 l of drinking water samples (spike level 100–200 ng/l)

Compound	Recovery (%)±R.S.D.		
	Carbograph-1[a]	LiChrolut-EN[b]	Empore disk[c]
Fluazifop	95±2	69±6	70±4
Clodinafop	93±2	71±4	74±5
Quizalofop	93±3	56±9	42±5
Fenoxaprop	92±4	29±4	18±9
Haloxyfop	95±3	55±7	56±2
Diclofop	94±3	53±6	50±5

[a] flow-rate 80 ml/min.
[b] flow-rate 10 ml/min.
[c] flow-rate 200 ml/min.

gesting that breakthrough phenomena are responsible for analyte losses.

In order to investigate the feasibility of sampling 1 l of water, several samples adjusted to pH 2 with hydrochloric acid were analyzed. The results of these experiments show that quantitative recoveries were obtained only when the Empore disks were used, while significant losses (fenoxaprop 42% in drinking water and 50% in ground water) were incurred when LiChrolut-EN cartridges were used. Partial recoveries, particularly in the case of fenoxaprop, are not due to incomplete retention on the sorbing material but to the fact that the various pesticides, by being retained for about 90 min in a dilute mineral acid environment are broken down by hydrolysis, in the case of fenoxaprop to benzoxilane [19]. This was confirmed by measuring ArPP concentrations in an acid medium at regular intervals. In this environment, quizalofop and fenoxaprop begin to break down after about 45 min.

The subsequent optimization involved allowing the aqueous samples to percolate at higher flow-rates so as to reduce the retention time in the acid environment. Tests were run at flow-rates of 30 ml/min with LiChrolut-EN on 1 l water samples acidified to pH 2. Quantitative recoveries were obtained. It was also noted that recovery values were unaffected by extraction flow-rate, rising from 10 ml/min (flow-rate used in previous works [12,18,20]) to higher flow-rates. These results clearly show that, certainly when 1 l aqueous samples are taken, acidification is required for the extraction of acid pesticides using LiChrolut-EN cartridges.

The good performance of the Empore disk was achieved, as well as by acidifying the sample, by using our analytical protocol.

To minimize the analysis time and to reduce the losses of the analytes during the evaporation step, prior to processing the water sample the disk was washed and conditioned without allowing it to dry out at any stage. This procedure makes the disk more permeable to the water sample and increases the flow-rate through it. A flow-rate of 200 ml/min was then allowed. As an alternative to the normal way of eluting the analytes from PS–DVB disks involving the use of large amounts of solvent [11] (ca. 30 ml), we tried a modified procedure for minimizing the eluting phase volume. The analytes were eluted with 3×3 ml of acetonitrile–methanol (50:50, v/v), drying the disk after each fraction by creating the maximum vacuum in the extraction apparatus for ca. 2 min. The recoveries ranged between 99% for diclofop and 90% for haloxyfop ($n=6$).

As regards selectivity, Fig. 2 shows typical chromatograms obtained using the three extraction procedures. In the case of the two DVB systems, two unknown substances represented potential interferents with quizalofop and diclofop, these potentially interfering compounds were completely eliminated when using Carbograph-1, presumably partly by washing them out and partly by retaining them in the cartridge. As far as the compound that partially coelutes with diclofop is concerned, the interference is due to the presence of LAS in the sample (confirmed by injecting an aliquot of a commercial mixture of LASs). LASs are anionic surfactants commonly used in detergent formulations. Because of their widespread use, they have been found in many different environmental compartments. In view of their acidity (pK_a~0.2) these interferents are not desorbed from the Carbograph-1 surface by a weak acid such as formic acid. No information is available about the nature of the interferent coeluting with quizalofop.

The analytical method used in this paper allowed UV detection at levels as low as 20–30 ng/l. A good spectral resolution, which is essential for characterization, was obtained by the combined setting of the optical slit of the diode and the number of spectra acquired per second. In our case, the optical slit of the diode was set at 24 nm, and the system was operated at a speed of one spectrum per second.

The spectra of the individual compounds are shown in Fig. 3.

4. Conclusions

Use of the Carbograph-1 cartridge enhances the efficiency of ArPP extraction from water. Acid pesticides in the low ng/l range can be efficiently concentrated from large water samples without pH adjustment by SPE on Carbograph 1. Recoveries from water were in the range of 90% to 98%. Whether the present procedure can be extended to

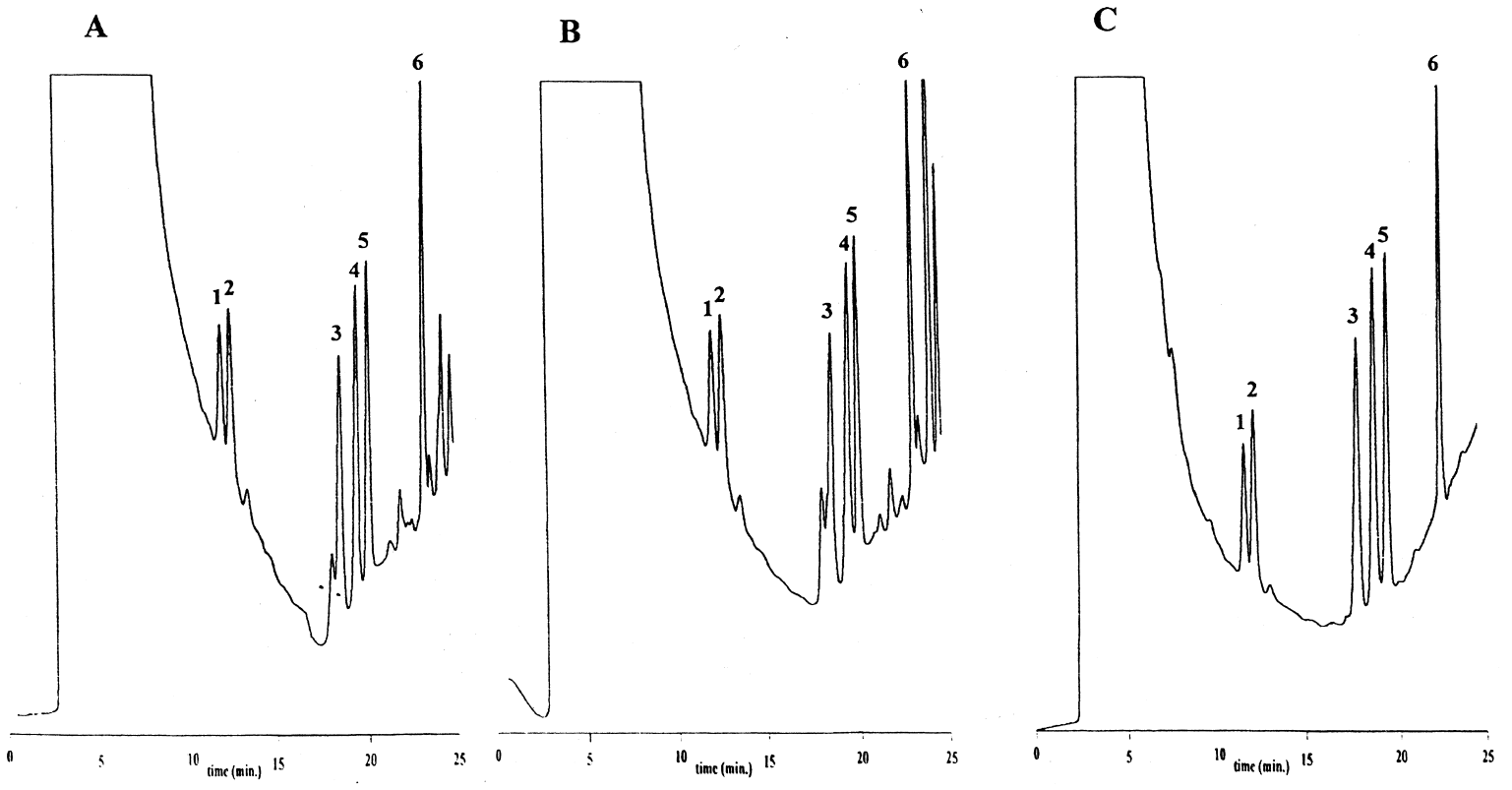

Fig. 2. Chromatograms obtained on analyzing 1 l of a ground water sample spiked with ArPPs at the individual level of 100–200 ng/l by three procedures involving the use of (A) the Lichrolut-EN extraction cartridge, (B) a PS–DVB Empore disk and (C) the Carbograph-1 cartridge. For the chromatographic conditions see Section 2. 1=fluazifop; 2=clodinafop; 3=quizalofop; 4=fenoxaprop; 5=haloxyfop; 6=diclofop.

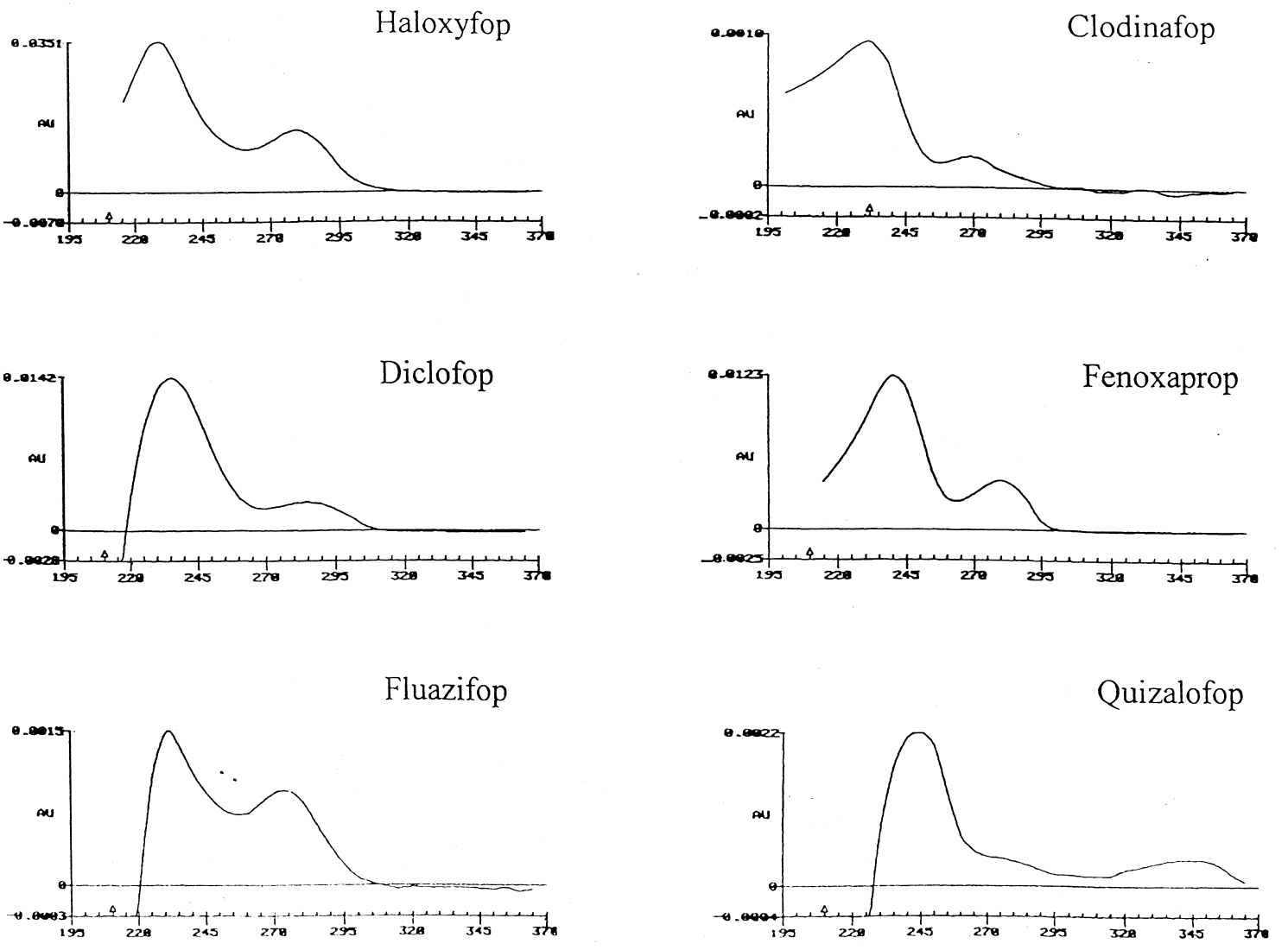

Fig. 3. UV diode array detection spectra of the six ArPPs investigated.

more environmental water (surface, river and lake water) will be investigated in the near future.

A good extraction efficiency for the six herbicides from acidified water was obtained with both the LiChrolut-EN cartridge and PS–DVB Empore disk, but these sorbents were less useful in field studies since the herbicides being tested passed through them practically unretained when the preliminary acidification step of the water sample was omitted. The PS–DVB Empore disk was found to be the only SPE material that allowed a sampling flow-rate as high as 200 ml/min.

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