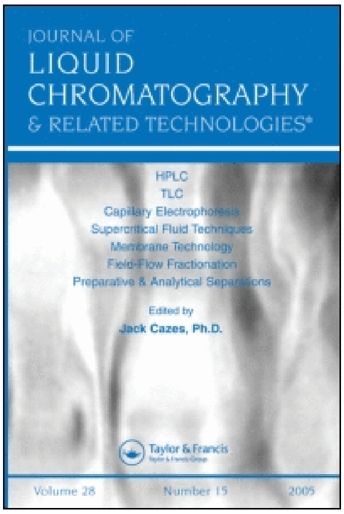

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SOLID-PHASE EXTRACTION OF CHLOROPHENOXY ACID HERBICIDES BY MEANS OF POLYMERIC RESINS FUNCTIONALIZED WITH QUATERNARY AMMONIUM GROUPS

S. Menor-Higueruelo[a]; L. V. Pérez-Arribas[a]; M. E. León-González[a]; L. M. Polo-Díez[a]
[a] Departamento de Química Analítica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid, Spain

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SOLID-PHASE EXTRACTION OF CHLOROPHENOXY ACID HERBICIDES BY MEANS OF POLYMERIC RESINS FUNCTIONALIZED WITH QUATERNARY AMMONIUM GROUPS

S. Menor-Higueruelo, L. V. Pérez-Arribas,*
M. E. León-González, and L. M. Polo-Díez

Departamento de Química Analítica, Facultad de Ciencias
Químicas, Universidad Complutense de Madrid,
E-28040 Madrid, Spain

ABSTRACT

Two different polymeric resins, one of them based on hydroxyethylmethacrylate (HEMA), and the other on polystyrene-divinylbenzene (PS-DVB), both containing quaternary ammonium groups, have been tested for solid phase extraction of chlorophenoxy acid herbicides. Retention and elution performance in off-line and on-line mode for 2,4-D, 2,4-DB, 2,4-DP, 2,4,5-T, 2,4,5-TP, and MCPA have been studied and compared. Higher and more reproducible recoveries were obtained with the two sorbents in on-line operation, those being for 100 mL of water samples higher than 92% for the based HEMA polymer and 85% for PS-DVB. Reproducibility, expressed as relative standard

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*Corresponding author. E-mail: leongon@quim.ucm.es

deviation, was between 1.3 and 6.7% ($n = 5$). Breakthrough volumes, pH effect, and retention capacity for these compounds has also been studied. The effect of complex polar matrices in the retention-elution process was studied by spiking the phenoxy acid herbicides in pear samples. The extracted chlorophenoxy acids were determined in all cases by liquid chromatography with UV detection.

INTRODUCTION

In the last few years, solid-phase extraction (SPE) has become an important technique for sample preparation, being regarded as a cost-effective and recognized alternative to liquid-liquid extraction (LLE), because it overcomes many of the drawbacks of the latter (1). Several types of sorbents have been developed, those based on silica with functional bonded groups, such as C_{18}, C_8 and CN being the most widely used. Nevertheless, the main drawback of such sorbents is their narrow pH stability range. Consequently, when SPE has to be carried out in extremely acidic or basic media, reversed-phase polymeric sorbents are used. The most frequently used polymeric sorbents are the styrene-divinylbenzene copolymers (PS-DVB). In addition to their broader pH stability range, they have a greater surface area per gram and show higher analyte retention than bonded silicas, mainly for very polar compounds that are not retained by reversed-phase sorbents, such as C_{18}.

Another feature of these aromatic sorbents is their selective interactions with the aromatic ring of analytes by specific π-π interactions. Included in this group of sorbents are the commercially available XAD-2 and XAD-4 resins, that show good capability to retain triazines, phenols, and other aromatic polar compounds (2,3), and PRP-1 and PRP-S, widely used for the extraction of organic pollutants (4,5). The introduction of hydrophilic groups increases water movement into the sorbent and improves mass transfer, which generally makes the sorbent more effective. Nevertheless, polymeric sorbents have some drawbacks, such as their lack of selectivity and low breakthrough volumes for highly polar compounds, which lead to incomplete analyte extraction from predominantly aqueous samples. These drawbacks can be overcome by using modified resins containing polar groups, mainly acyl-derivatives with one or more carboxylic acid groups (6). In recent years, the performance and suitability of modified resins containing several polar functional groups for SPE has been studied and compared with other SPE materials for preconcentration of pesticides and phenolic compounds, yielding higher breakthrough volumes and higher recoveries for the more polar compounds (7–11).

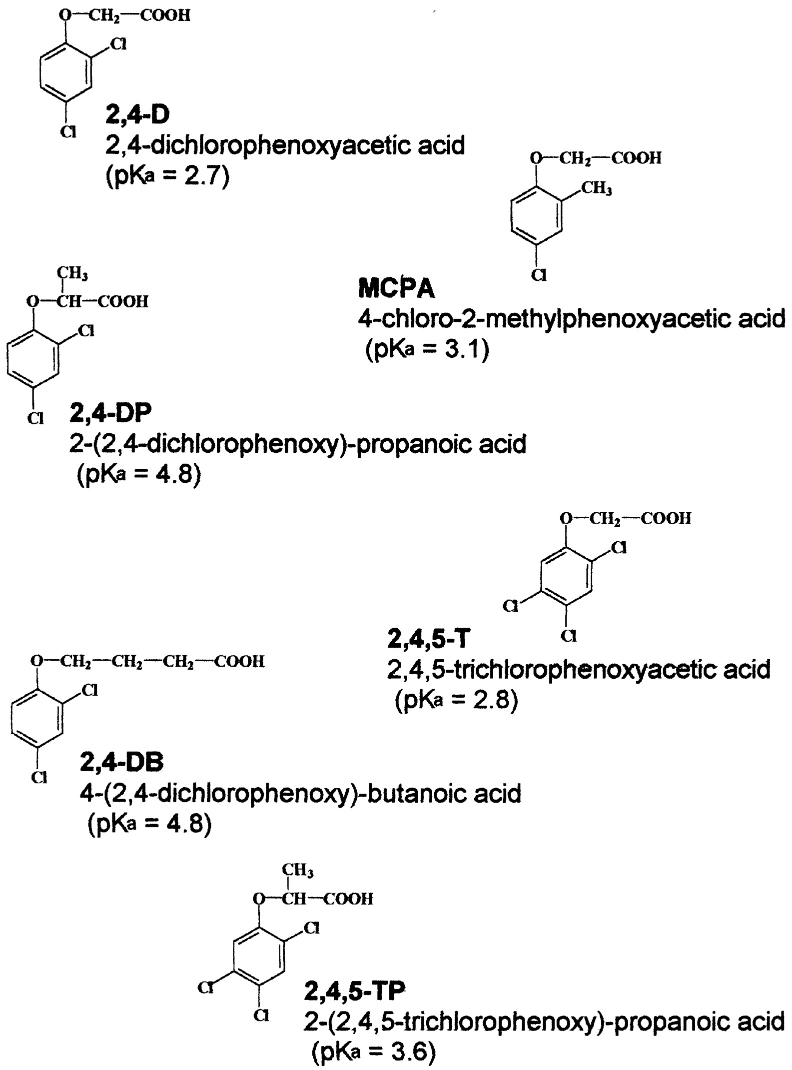
Trying to achieve higher retention capacities and higher breakthrough volumes for very polar analytes, other modified resins with partially substituted quaternary ammonium or slightly sulfonated groups have been studied (7,8). These sorbents have an excellent hydrophilicity and, since they are also ion exchangers, they can be used by taking advantage of two mechanisms of retention, based on π-π and ion exchange interactions, depending on whether the analyte contains an ion exchange site, or the molecule is neutral with aromatic rings or unsaturated bonds for π-π interactions. To date, there are few applications based on ion-exchange interactions to concentrate organic compounds from aqueous samples. One of the recent applications is the isolation of glyphosate and its main metabolite, aminophosphoric acid (12), and negatively-charged pesticide-degradation products (13,14). Regarding the extraction mechanism based on π-π interactions, it has been used to preconcentrate triazines or phenols in acidic media (15,16) by means of a column packed with an anion exchanger based on PS-DVB containing quaternary ammonium groups. Analytes were quantitatively retained from acidified water and easily desorbed when pure methanol or acetonitrile were used as eluents, with recoveries around 95% when 1000 mL of water was preconcentrated.

In this paper, two different polymers, one based on hydroxyethylmethacrylate (HEMA) and the other based on polystyrene-divinylbenzene (PS-DVB), both containing quaternary ammonium groups, have been tested for solid phase extraction of phenoxy acid herbicides, a group of translocated herbicides extensively used to control broad-leaved weeds. These compounds are polar chlorinated herbicides with a carboxylic group (acetic, propanoic or butanoic acid) attached to the benzene ring by means of an oxygen atom. Retention and elution performance in off-line and on-line modes for 2,4-D, 2,4-DB, 2,4-DP, 2,4,5-T, 2,4,5-TP, and MCPA have been studied and compared. The extracted chlorophenoxy acids were determined by liquid chromatography with UV detection in spiked water and pear samples. Names, structural formulae, and pKa's of these herbicides are shown in Figure 1.

EXPERIMENTAL

Chemicals

2,4-D (99% pure), 2,4,5-T (98% pure), and 2,4,5-TP (97% pure) were obtained from Aldrich; 2,4-DB (97%), MCPA (95-97% pure), and 2,4-DP (95% minimum) were from Sigma. All chemicals for sample preparation were analytical grade and methanol HPLC grade was used for chromatographic mobile phase and standard solutions preparation. Purified water was obtained from a Milli-Q apparatus.



2,4-D
2,4-dichlorophenoxyacetic acid
(pKa = 2.7)

MCPA
4-chloro-2-methylphenoxyacetic acid
(pKa = 3.1)

2,4-DP
2-(2,4-dichlorophenoxy)-propanoic acid
(pKa = 4.8)

2,4,5-T
2,4,5-trichlorophenoxyacetic acid
(pKa = 2.8)

2,4-DB
4-(2,4-dichlorophenoxy)-butanoic acid
(pKa = 4.8)

2,4,5-TP
2-(2,4,5-trichlorophenoxy)-propanoic acid
(pKa = 3.6)

Figure 1. Names, structural formulae, and pKa's of chlorophenoxy acid herbicides.

Stock solutions of the chlorophenoxy acids (200 mg · L^{-1}) were prepared in methanol and stored in the dark at not more than 4°C for 2 months maximum. Working standard solutions were prepared by suitable dilution of the above stock solutions with methanol.

SPE Materials

Two commercial polymeric sorbents functionalized with quaternary ammonium groups were tested. One was MFE®-Polymer SAX (hydroxyethylmethacrylate, HEMA) (50 µm particle size, 0.4–0.8 meq/g, 35 nm pore size), supplied by Análisis Vínicos (Ciudad Real, Spain), packed in a steel column (150 × 4.6 mm id). The other one was disposable Lida Sep-IC-OH Cartridges containing 0.5 mL of PS-DVB SAX (0.6 meq exchange capacity), supplied by Teknochroma (Barcelona, Spain).

Equipment

For off-line preconcentration in preconcentration columns, a Series II Digital Pump, supplied by Konik-Tech, equipped with one pump head capable to dispense up to 10 mL/min was used. For preconcentration in cartridges, a 20 place vacuum manifold supplied by Varian was used, coupled to a Selecta membrane vacuum pump. In on-line preconcentration mode, the Series II Digital Pump was used for sample preconcentration (pump 2), coupled to a programmable Varian ProStar 210 Solvent Delivery Module (pump 1) and switched to a Rheodyne LabPRO 6-Valves, capable of operating by remote control from the Varian pump. The connection scheme of the devices and the switching to preconcentration and analytical columns are shown in Figure 2.

Chromatographic analyses of the preconcentrated herbicides was performed with a Perkin-Elmer isocratic LC pump coupled with a Perkin-Elmer model LC 290 UV-Vis detector. Chromatographic separation of the chlorophenoxy acids was performed with a reverse-phase column HP Analytical column 5 ODS(2) (250 × 4 mm id). The analyte quantitation was carried out by the Nelson v.5.1 software package. When preconcentration and analysis was carried out on-line, the Varian ProStar 210 Solvent Delivery Module was also used as a chromatographic pump.

Procedures

Herbicide Preconcentration

Different procedures have been carried out depending on the sorbent used for SPE. When preconcentration was carried out on the MFE polymer, the column containing the anion exchanger was cleaned by passing 30 mL of 60 mM nitric acid in 99% methanol solution at 0.5 mL/min, and conditioned with 15 mL of aqueous solution, at the same pH as that of the experiment to be carried out at

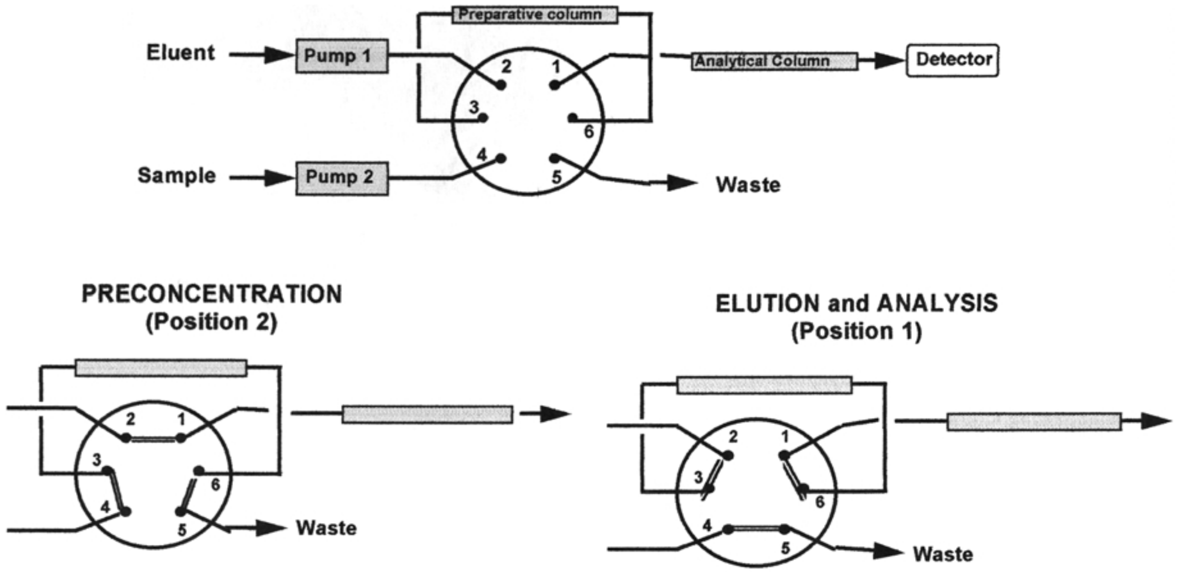


Figure 2. Scheme of the experimental setup for the on-line extraction and liquid chromatography analysis of the chlorophenoxy acid herbicides.

Table 1. Time Table for On-Line SPE Preconcentration Process

Step	Position of Switching Valve	Flow Rate, mL/min	Time, min	Event
1	2	2	8	Conditioning sorbent
2	2	5	20	Sample preconcentration
3	2	5	1	Washing
4	1	1	3	Analyte desorption
5	2	0.5	30	Cleaning sorbent

2 mL/min. For preconcentration on the Lida Sep-IC-OH cartridges, the first step was to swell the resin by passing 250 mL of pure water at around 10 mL/min. Then, the cartridge was cleaned with 10 mL of methanol containing 60 mM hydrochloric acid, passed at 5 mL/min, and afterwards, was conditioned with 25 mL of aqueous solution at the same pH as that of the experiment to be carried out. Once the conditioning step has ended, the evaluation of the SPE sorbents to retain the phenoxy acid herbicides was made by passing 100 mL of aqueous solution containing a mixture of 20 μg of each analyte through the packed column or cartridges. After the preconcentration step, the elution of these herbicides was made with 5 mL of the methanol-nitric acid solution at a flow rate of 2 mL/min.

In on-line preconcentration, the general procedure followed was quite similar to that of the off-line procedure. Cleaning, conditioning, preconcentration, and elution were performed by means of the device diagrammed in Figure 2. In this case, a step involving a wash of the packed column was included. The program with times, flow rates, and position of the switch valve are reported in Table 1. Since the operation of the switch valve in remote mode always starts at position 2 (according to the specifications of the manufacturer), the cycle of the overall process of preconcentration-elution-analysis ended with a cleaning of the sorbent (position 2). During this last step, the chromatographic analysis of the chlorophenoxy acid herbicides was carried out.

Chromatographic Determination of the Chlorophenoxy Acids

The LC separation of the five herbicides was performed using the C_{18} analytical column at a flow-rate of 1 mL/min of a mobile phase containing 65% methanol–34.6% H_2O–0.4% H_3PO_4. Detection of the chromatographic peaks was at 232 nm. When the analysis was carried out in the off-line mode, 20 μL of extracted sample was injected into the liquid chromatograph.

Preparation of Pear Samples

Pear samples were spiked with each herbicide in the concentration range between 0.04 and 0.15 mg · kg^{-1} for 2,4,5-T, 2,4,5-DB, 2,4-DP, and 2,4,5-TP, and between 0.09 and 0.20 mg · kg^{-1} for 2,4-D and MCPA. Amounts of 100 g of the spiked samples were thoroughly blended with 15 mL of 0.1M NaOH and 35 mL of water, and the mixture was hydrolyzed in a water bath at 95°C for about 30 min. After cooling, the suspension was filtered through a paper filter and the residue was carefully washed with three volumes of ca. 10 mL of pure water; the resulting solution was adjusted to pH 10 and passed through the cartridges containing Lida Sep-IC-OH anion exchanger. The retained herbicides were eluted with 5 mL of methanol–60 mM nitric acid solution (2 mL/min), and 20 μL were injected in the LC system and determined under the conditions described previously.

RESULTS AND DISCUSSION

Evaluation of MFE Polymer and Lida Sep-IC Anion Exchangers for the Extraction of Chlorophenoxy Acids

The potential of the two polymeric sorbents containing quaternary ammonium groups, was first investigated by passing different amounts of several chlorophenoxy acids in acidic water and acidic water–methanol solutions through the sorbents. In general, herbicides solutions containing more than 80% methanol were not retained, but they were retained in both sorbents when aqueous solutions containing low levels of methanol were used. This behavior suggested the possibility of retaining these herbicides on the studied polymers by passing the chlorophenoxy acids in aqueous media and, once they have been retained, eluting them with mixtures containing high ratios of methanol. The evaluation of the MFE-Polymer SAX and Lida Sep-IC-OH sorbents was first carried out by measuring the recoveries using off-line extraction percolating solutions containing 20 μg of each herbicide in 100 mL of LC-grade water.

Since the two studied sorbents are anion exchangers and different mechanisms can be involved in the retention process (adsorption, π-π interaction and ion exchange), initially various experiments at different pH values were carried out. In general, the column with the MFE polymer showed a higher adsorption capacity at acidic pH and elution was more reproducible at pH around 1 than at higher pH. Moreover, Lida Sep cartridges present two ranges of high retention, as can be seen in Figure 3, showing a typical behavior of the recoveries obtained for the chlorophenoxy acids at different pH. In general, recoveries around 100% were obtained at pH close to 1 and to 10, with a minimum retention

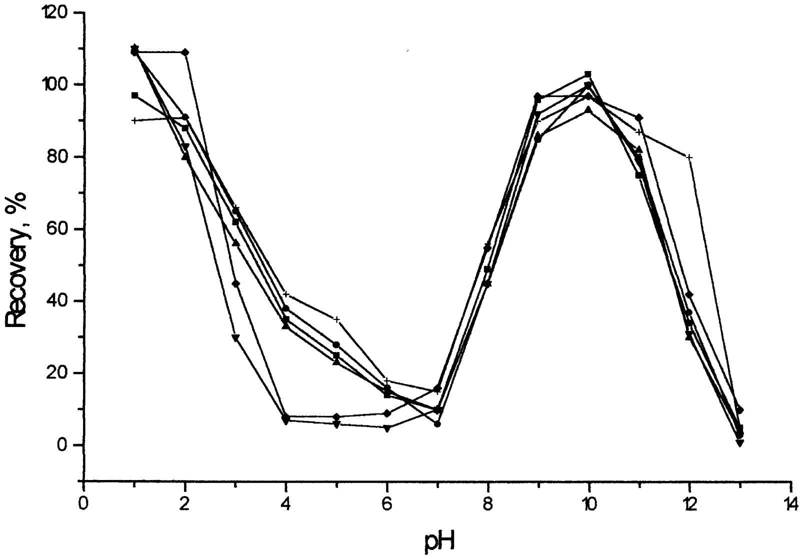


Figure 3. Influence of the pH on the extraction of the chlorophenoxy acids with the Lida Sep-IC. (■) 2,4-D; (●) 2,4-DP; (▲) 2,4,5-T; (▼) 2,4,5-TP, (◆) MCPA; (+) 2,4-DB.

at a pH 1-2 units over the pK's of the chlorophenoxy acids. This performance suggested that, in acidic media, the predominant retention mechanism was the π-π and van der Waals interactions, while at higher pH where the acid-base equilibrium is clearly displaced to the ionic form, the ion-exchange mechanism was predominant.

In very basic media, at pH around 12-13, recoveries decrease dramatically. It could be due to the competence of the OH^- for the anion-exchange sites of the resins. The elution of the retained herbicides into the MFE-Polymer SAX was more difficult and required higher volumes of methanol–nitric acidic eluent than when the extraction was carried out in the Sep-IC-OH cartridges. The reason could be that, although the exchange capacity per gram of the MFE-Polymer SAX is lower than that of the anion exchanger in the cartridges, the amount of packing material in the MFE column is about five times higher. Consequently, subsequent studies of preconcentration behavior will be in acidic media for this sorbent and in basic media for the Sep-IC-OH.

Regarding the breakthrough volume, this is a critical factor for the enrichment of an analyte in the sorbents used for SPE, and corresponds to the volume sample that can be percolated through the sorbent without appreciable loss of analyte. The breakthrough volume can be determined experimentally by using graphs that plot the recovery as a function of the volume containing a fixed

Table 2. Recoveries Obtained Off-Line with the MFE Polymer Using Different Volumes of Water Containing 20 µg of Each Herbicide at pH 1

	Recovery, %*					
Compound	25 mL	50 mL	100 mL	250 mL	500 mL	750 mL
2,4-D	96.2	100	95.6	75.1	50.0	40.2
2,4-DB	98.3	101	99.0	79.7	68.2	45.9
2,4,5-T	93.1	91.6	91.5	90.3	84.6	70.2
2,4,5-TP	98.4	101	102	98.0	93.8	70.5
MCPA	95.8	97.0	96.6	82.2	45.7	36.8
2,4-DP	94.6	93.9	91.9	80.3	63.7	48.5

*Mean of three determinations.

Table 3. Recoveries Obtained with the Lida Sep-Cartridge IC-OH Using Different Volumes of Water Containing 20 µg of Each Herbicide at pH 10

	Recovery, %*					
Compound	25 mL	50 mL	100 mL	250 mL	500 mL	750 mL
2,4-D	94.5	95.1	91.6	71.3	64.0	50.8
2,4-DB	88.1	91.5	89.0	65.7	60.4	55.3
2,4,5-T	89.9	88.6	91.0	81.8	74.2	65.6
2,4,5-TP	98.6	96.2	99.0	92.3	73.8	30.0
MCPA	85.8	87.1	86.5	66.5	53.1	46.4
2,4-DP	87.0	91.9	89.1	63.0	59.0	48.9

*Mean of three determinations.

amount of analyte. In order to calculate the recovery for each compound, different sample volumes, between 25 and 750 mL, of the chlorophenoxy acid mixtures were preconcentrated in the two sorbents. Recoveries of these herbicides are shown in Tables 2 and 3 and, as can be seen, good results, between 90 and 100%, were obtained for all compounds when 100 mL of standard solution containing 20 μg of each chlorophenoxy acid was analyzed. For chlorophenoxy acids containing three chlorine atoms (2,4,5-T and 2,4,5-TP) retention was better, being retained without appreciable loss of analyte until volumes of 300 mL or more have been percolated. Figure 4 shows the breakthrough obtained for 2,4,5-TP and 2,4,-D, the best and the worst analytes retained for both studied sorbents, and Table 4 presents the breakthrough determined for each chlorophenoxy acid. In general, breakthrough volumes are similar for each chlorophenoxy acid in either

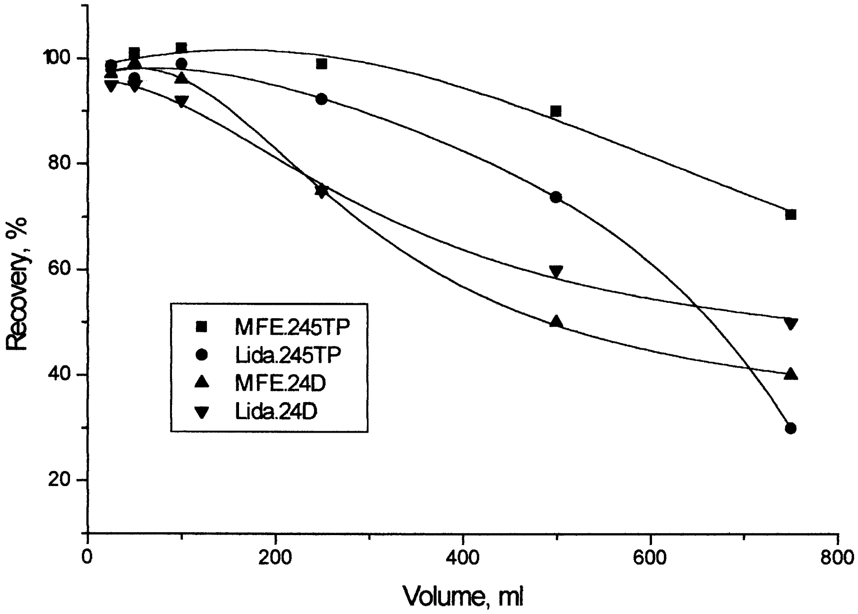


Figure 4. Breakthrough curves for 2,4-D and 2,4,5-TP obtained for the two sorbents.

Table 4. Breakthrough Volumes Calculated for the Six Phenoxy Acids (20 μg) and Each Sorbent Studied (Off-Line Mode)

	Breakthrough Volumes, mL	
Compound	MFE Polymer	Lida Sep-Cartridge IC
2,4-D	110	110
2,4-DB	120	200
2,4,5-T	360	310
2,4,5-TP	420	400
MCPA	150	150
2,4-DP	120	150

of the two sorbents, except for 2,4-DB, that was better retained on the Lida Sep-cartridge IC, and for the 2,4,5-T, which had higher breakthrough volume with the MFE Polymer.

With respect to the adsorption capacity, the maximum amount of each herbicide retained by the column or the cartridge was evaluated by using solutions

Table 5. Recoveries Obtained for Each Polymer Using 100 mL of Standard Solution Spiked with 15 μg of Each Phenoxy Acid (Off-Line Mode)

	Recovery, % (RSD)*	
Compound	MFE Polymer	Lida Sep-Cartridge IC
2,4-D	98.6 (2.5)	91.9 (3.0)
2,4-DB	99.7 (1.8)	85.0 (3.5)
2,4,5-T	92.4 (1.3)	89.0 (3.4)
2,4,5-TP	99.1 (6.7)	100 (4.1)
MCPA	95.1 (6.1)	96.3 (2.4)
2,4-DP	93.2 (3.4)	91.1 (3.5)

*Mean of four determinations.

with different amounts of chlorophenoxy acids in 100 mL of water. Lida Sep-IC cartridges retained amounts between 200 and 600 μg, whereas the amount of chlorophenoxy acids retained by the MFE Polymer column can go up to around 1000 μg.

The reproducibility of the preconcentration process of the six chlorophenoxy acid herbicides was determined by analyzing 100 mL of standard solutions containing 15 μg of each compound at pH 0-1 during evaluation of the MFE Polymer and at pH 10 when the Lida Sep cartridge was evaluated. Table 5 shows the mean recoveries of four determinations and the relative standard deviation obtained for each compound. Results were similar for the two sorbents, slightly better when the extraction was carried out with the MFE Polymer. Nevertheless, all recoveries found were higher than 85% and the relative standard deviations were equal to or lower than 6.7%.

On-Line Preconcentration Using the MFE Polymer Precolumn

Since the MFE Polymer SAX was purchased packed in a steel column capable to tolerate the typical pressure of a LC analysis, it can be used for on-line preconcentration. In on-line solid-phase extraction, there is little or no sample manipulation between preconcentration and analysis, so loss and contamination risk are avoided, and detection limits and reproducibility values can be better. One of the main problems in the on-line SPE procedures is the compatibility between the eluents used for the analyte desorption and the chromatographic analysis. In our approach, it is clear that it is not advisable to use methanol–nitric acid mixtures to desorb the retained compounds and introduce them in a silica gel C_{18} analytical column; so, other less aggressive eluents were tested, like methanol and

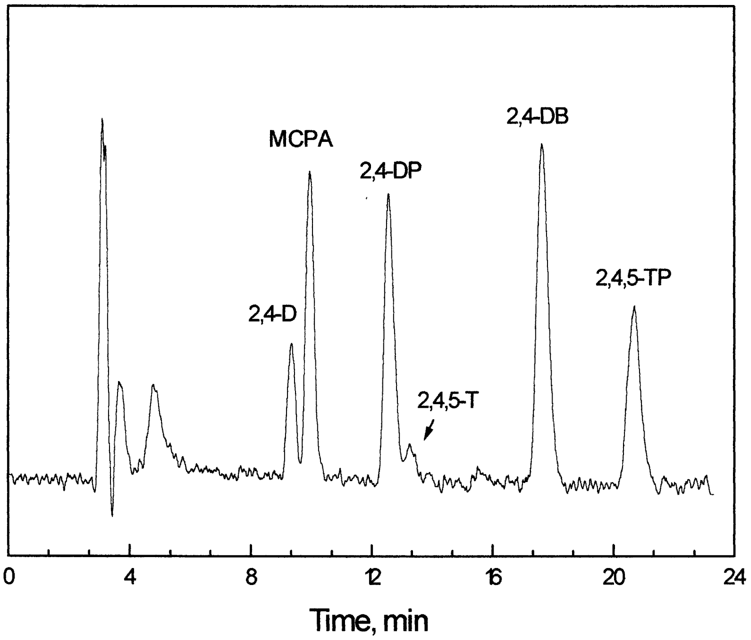


Figure 5. Liquid chromatogram obtained after on-line preconcentration of tap water spiked with 8 μg/L of each chlorophenoxy acid.

acetonitrile without nitric acid and mixtures of methanol–water. Desorption with pure acetonitrile or methanol produced LC chromatograms with poorly resolved peaks, while methanol–water mixtures in proportions around 70/30 avoided this problem. Therefore, the same mobile phase used in the chromatographic analysis (65% methanol–34.6% H_2O–0.4% H_3PO_4) was used to desorb the analytes from the SPE precolumn.

No significant peak broadening, which is another typical problem in on-line SPE procedures, was found with this eluent, but a poor desorption was achieved for the compounds better retained in this sorbent, 2,4,5-TP and 2,4,5-T, the last one hardly being desorbed. Figure 5 shows the chromatogram obtained by on-line trace enrichment of 100 mL of tap water spiked with 8 μg/L of each chlorophenoxy acid. The linearity of response for the total on-line analytical system was studied by analyzing standard solutions of 100 mL of pure water containing the six chlorophenoxy acids in different concentrations, ranging between 0.001 and 0.032 mg/L. Linearity ranges and detection limits calculated for 2,4-D, 2,4-DB, 2,4,5-TP, MCPA, and 2,4-DP are shown in Table 6. These detection limits are better than or similar to those for off-line preconcentration.

Table 6. Linearity Range and Detection Limits in On-Line Preconcentration and LC Determination of the Chlorophenoxy Acids by Using MFE Polymer

	On-Line		Off-Line
Compound	Linearity Range, mg/L	Detection Limit, μg/L	Detection Limit, μg/L
2,4-D	0.003–0.032	2	2
2,4-DB	0.003–0.032	1	3
2,4,5-T	–	–	3
2,4,5-TP	0.005–0.032	4	5
MCPA	0.003–0.032	2	2
2,4-DP	0.003–0.032	2	3

Off-Line Preconcentration Using the Lida Sep-IC Cartridges and Determination of the Chlorophenoxy Acids in Pear Samples

One of the main problems in SPE for preconcentration of trace analytes from complex samples like food, fruits, and vegetables is the loss of efficiency of the extraction. That is partly due to the fact that the general procedure for extraction of these residues in food involves a sample homogenization with the appropriate solvent, using a homogenizer, blender, or sonicator, yielding a suspension of food pulp in the extractant liquid, which is difficult to separate and flush. Another cause of analyte loss is the competence of the matrix components for the active sites of the sorbent that leads to a reduction in the recovery. The first cause cited can be reduced by careful sample handling and treatment, but the second one depends, to a great extent, on the characteristics of the sorbent chosen for SPE. In this part of our approach, we have studied the capability of the Lida Sep-IC cartridges to extract and preconcentrate the chlorophenoxy acid herbicides from pear samples. The samples were spiked with different amounts of the studied phenoxy acids and hydrolyzed according to the procedure referred above. After hydrolysis, the sample was preconcentrated at pH 10 using the Lida Sep IC Cartridges and eluted with 5 mL of methanol containing 60 mM of nitric acid prior to the LC analysis. The spiked samples were prepared with such an amount of each herbicide that a concentration around the maximum permitted by the European regulations was obtained; maximum levels established are 0.10 mg/kg for 2,4-D and MCPA and 0.05 mg/kg for all the other studied chlorophenoxy acids in fruit samples (17).

By following the proposed procedure, no chlorophenoxy acid herbicides were detected in these samples. Samples were spiked with between 0.04 and 0.15 $mg \cdot kg^{-1}$ for 2,4,5-T, 2,4,5-DB, 2,4-DP, and 2,4,5-TP, and between 0.09 and 0.20 $mg \cdot kg^{-1}$ for 2,4-D and MCPA. Figure 6 shows the chromatograms obtained for pear samples with and without spiked herbicides, and Table 7 shows recovery

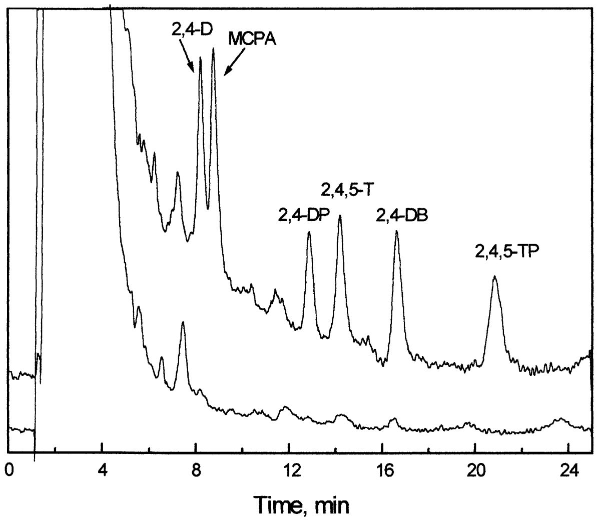


Figure 6. Liquid chromatograms of a pear extract with and without spiked chlorophenoxy acids. The amounts spiked were 0.15 mg/kg of 2,4-D and MCPA and 0.10 mg/kg of 2,4-DB, 2,4,5-T, 2,4,5-TP, and 2,4-DP.

Table 7. Recovery of Chlorophenoxy Acids Added to Pear Samples

Compound	Added, mg/kg	Recovery (S.D.)*, %
	0.09	52 (4)
2,4-D	0.15	50 (2)
	0.20	53 (3)
	0.04	50 (5)
2,4-DB	0.10	53 (2)
	0.15	58 (3)
	0.04	89 (4)
2,4,5-T	0.10	87 (3)
	0.15	85 (3)
	0.04	72 (5)
2,4,5-TP	0.10	66 (3)
	0.15	65 (3)
	0.09	54 (1)
MCPA	0.15	64 (2)
	0.20	59 (4)
	0.04	56 (3)
2,4-DP	0.10	58 (4)
	0.15	53 (3)

*Mean of four determinations.

results and standard deviation of different samples spiked with the chlorophenoxy acids at three concentration levels. As can be seen, recoveries decrease with respect to the experiments carried out in purified water, so it is reasonable to think that this decrease is mainly due to the effect that the high content of non-polar compounds present in these types of samples has on the breakthrough volume of the chlorophenoxy acids in the preconcentration step. This can be confirmed by the fact that 2,4,5-T and 2,4,5-TP, which show higher breakthrough volumes, now have higher recoveries. In general, these results are similar to or better than those reported for some of these herbicides using other extraction methods in food analysis (18,19).

CONCLUSIONS

The two studied sorbents, based on hydroxyethylmethacrylate (HEMA) and on polystyrene-divinylbenzene (PS-DVB), both containing quaternary ammonium groups, are suitable for SPE of chlorophenoxy acid herbicides from water. All of them are retained by the functionalized polymeric resins and can be eluted with methanol–nitric acid in off-line operation mode, and with the same mobile phase as that used for the subsequent liquid chromatography determination in on-line mode. Finally, the off-line preconcentration in Lida Sep-IC cartridges allows the LC determination of chlorophenoxy acid herbicides in pear samples at levels around the maximum permitted by the European regulations.

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