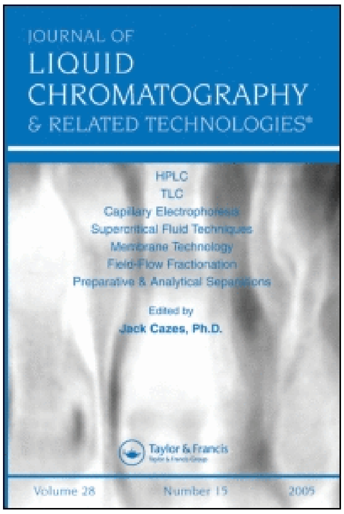

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Hernández-Mateos, M. A. , Pérez-Arribas, L. V. , Navarro-Villoslada, F. , León-González, M. E. and Polo-Díez, L. M.(1999) 'PRECONCENTRATION OF PHENOXY ACID HERBICIDE RESIDUES BY USING AN ION EXCHANGER BASED ON MFE-POLYMER', Journal of Liquid Chromatography & Related Technologies, 22: 5, 695 — 704

To link to this Article: DOI: 10.1081/JLC-100101691
URL: http://dx.doi.org/10.1081/JLC-100101691

J. LIQ. CHROM. & REL. TECHNOL., 22(5), 695–704 (1999)

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ABSTRACT

An anion exchanger based on MFE-Polymer (hydroxyethylmethacrylate, HEMA) containing quaternary ammonium functional groups has been used to pack a 150 x 4.6 mm id steel column, and the efficiency of this ion exchanger to preconcentrate phenoxy acid herbicides residues has been studied. The phenoxy acid herbicides studied were 2,4-dichlorophenoxy acetic acid (2,4-D), 4-(2,4-dichlorophenoxy)-butanoic acid (2,4-DB), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), 2-(2,4,5-trichlorophenoxy)-propanoic acid (2,4,5-TP), and 4-chloro-2-methylphenoxy acetic acid (MCPA). Dicamba (3,6-dichloro-2-methoxybenzoic acid), a benzoic acid herbicide usually used in technical products in mixtures with some of the related phenoxy acids, has also been included in the study. Retention of these herbicides on the referred ion exchanger is possible in aqueous acidic medium, probably because of the high polarizing power of the quaternary ammonium groups over the studied herbicides.

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Subsequent elution from the column was made with methanol containing nitric acid 60 mM and not more than 10 mL are required. The influence of the flow rate in the retention of the herbicides was evaluated in the 1.0 - 9.0 mL/min range, achieving recoveries around 100% for all of the herbicides studied. Regarding the capacity of the anion exchanger, the column prepared can retain up to 1000 μg of each herbicide. The good ability for retention and elution allows the LC determination of these herbicides in tomato samples at levels of 0.05 mg/kg with a minimum clean-up.

INTRODUCTION

Phenoxy acids are an important group of translocated herbicides extensively used to control broad-leaved weeds. All members of this group have a chlorine atom attached to C-4 of the benzene ring and either a chlorine atom or a methyl group on C-2. Sometimes an additional chlorine atom is present on C-5. Due to their low cost and good selectivity, these herbicides are widely used, so there is a need for multi-residue analytical approaches for the trace level determination in several matrices. Thus, several procedures have been proposed to determine these residues in samples like water,[1,2] soil, and cereals[3,4] and other vegetable products,[5] using in all cases chromatographic techniques (GC or LC). However, due their low levels of occurrence and the complexity of the matrices it is necessary to extract and preconcentrate the sample before analysis and this is usually carried out by liquid extraction using organic solvents like acetonitrile, acetone, diethyl ether, or dichloromethane.[1,3,6] All these method are laborious and, in general, require large volumes of expensive and sometimes toxic and flammable organic solvents.

Consequently, in the last years significant efforts have been done to find alternative preconcentration and clean-up methods, the solid-phase extraction (SPE) being the technique of choice. Several materials have been proposed for this purpose, the most commonly employed being the C_{18} and C_8 bonded silica[2,4,7-9] and macroporous polystyrene-divinylbenzene copolymer[10-12] cartridges or pre-columns.

The use of ion exchange resins has been proposed to extract ionic and ionizable pesticides, resulting in major selectivity and, consequently, the sample requires less or no purification before chromatographic determination.[13] Unfortunately, although ion exchange resins were found to absorb pesticides well, they showed poor desorption characteristics. This problem has been overcome by using ion strong exchangers polystyrene-divinylbenzene copolymer type, functionalized with quaternary ammonium groups, and by pre-concentrating the sample in aqueous acidic media. In this case, the analyte retention is due to the high polarizing power of the ion exchangers over the analytes. Under these conditions, phenols and triazines were quantitatively retained from water and easily desorbed when pure methanol or acetonitrile were used as eluent.[14,15]

The aim of this work is to explore the ability of an anion exchanger based on MFE®-Polymer (hydroxyethylmethacrylate, HEMA) containing quaternary ammonium functional groups to preconcentrate phenoxy acid herbicides residues. The phenoxy acid herbicides studied were 2,4-dichlorophenoxy acetic acid (2,4-D), 4-(2,4-dichlorophenoxy)-butanoic acid (2,4-DB), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), 2-(2,4,5-trichlorophenoxy)-propanoic acid (2,4,5-TP), and 4-chloro-2-methylphenoxy acetic acid (MCPA). All of them are translocated herbicides and growth regulators and they are frequently used mixed with each other or with 3,6-dichloro-2-metoxybenzoic acid (Dicamba), which is another important translocated herbicide; for this reason, this compound has also been included in our study. Finally, the proposed preconcentration method has been applied to determine these herbicides in spiked tomato samples by liquid chromatography without a previous clean-up of the colored and other co-extracted compounds.

EXPERIMENTAL

Equipment

For preconcentration, a Series II Digital Pump, supplied by Konik-Tech, equipped with one pump head capable to dispense up to 10 mL/min was used. As extractant solid phase, a preparative chromatographic column 150 x 4.6 mm id packed with about 3 g of MFE-Polymer SAX (50 μm particle size), supplied by Análisis Vínicos, was employed. Evaluation of the recoveries of the phenoxy acids and Dicamba was made with a Hewlett-Packard HP 8452-A diode array spectrophotometer interfaced to a HP Vectra AT computer and a HP Think Jet printer.

The chromatographic determination of the preconcentrated herbicides was carried out in a HPLC system with a gradient Beckman 125S Solvent Module SYSTEM GOLD and a Beckman UV programmable variable wavelength 166 Detector SYSTEM GOLD, both of them interfaced to a DELL Computer equipped with a MMX Pentium Processor and containing a Gold Nouveau Chromatography Workstation Software for Windows. A 250 x 4 mm id HP Analytical Column packed with 5 μm Spherisorb ODS(2) was used in the chromatographic separation of the herbicides studied.

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%) and MCPA (95-97% pure) from Sigma, and Dicamba (99%) from Chem Service. All Chemicals for sample preparation were analytical grade and methanol HPLC grade was used for chromatographic mobile phase and standard solution preparation. Purified water was obtained from a Milli-Q apparatus.

Stock solution of the phenoxy acids and Dicamba (200 mg/L) were prepared in methanol containing 1% (v/v) of HNO_3 6M and stored in the dark at not more than 4ºC. Working standard solutions were prepared by suitable dilution of the stock solutions with methanol.

Herbicide Pre-concentration

The column containing the MFE-Polymer SAX anion exchanger was cleaned and regenerated with 30 mL of 60 mM nitric acid in 99% methanol solution at 0.5 mL/min and conditioned with 15 mL of pure water passed at 2 mL/min. The evaluation of the MFE-Polymer SAX to retain the phenoxy acid herbicides and Dicamba was made by passing 100 mL of acidic aqueous solution containing 50 μg of each analyte through the packed column. After preconcentration step, the elution of these herbicides was made with 10 mL of the methanol-nitric acid solution at a flow rate of 2 mL/min.

Tomato Sample Preparation and LC Determination

Hydrolysis of the tomato samples was made by following a previous method proposed by Gökmen and Acar.[16] Tomato samples were spiked with each herbicide in the concentration range between 0.04 and 0.42 mg/Kg for Dicamba; 2,4,5-T, 2,4,5-DB, and 2,4,5-TP, and between 0.09 and 0.40 mg/Kg for 2,4-D and MCPA. Amounts of 25 g of the spiked samples were thoroughly blended with 15 mL of 1M NaOH and 50 mL of water and the mixture was hydrolyzed in a water bath at 95ºC for 2 h.

After cooling, the mixture was acidified adding 2 mL of 1:1 H_2SO_4 solution, the suspension was then filtered through a paper filter and the residue was carefully washed with three volumes of c.a. 20 mL of pure water. The resulting solution was passed through the column at 8 mL/min and the retained herbicides were eluted with 10 mL of the methanol-60 mM nitric acid solution. Once pre-concentration was carried out, 20 μl of the eluate were injected into the chromatographic system. As the mobile phase, a mixture of 65% methanol-

34.6% H_2O-0.4% H_3PO_4 was used and the flow rate set at 1.0 mL/min in the LC determination, which is an adaptation of the procedures proposed in the literature.[9,16] Detection of the chromatographic peaks was at 232 nm.

RESULTS AND DISCUSSION

Selection of the Working Conditions

Previous assays showed that the studied herbicides were retained by the MFE-Polymer SAX anion exchanger packed into the column when acidic water solutions contained less than 40% methanol, while, on the other hand, herbicides were not retained when water contained more than 80% methanol. This behavior suggests the possibility of retaining these herbicides on the MFE-Polymer SAX anion exchanger with mixtures containing high ratios of water, and subsequently eluting them with mixtures containing high ratios of methanol.

Hydrodynamic variables affecting the preconcentration process were studied by UV spectrophotometry at the maximum wavelength of each herbicide. Recoveries of the studied phenoxy acids and Dicamba were determined by comparing the spectra of the recovered herbicides with standard solutions.

The influence of the flow rate on the retention of the herbicides was evaluated in the 1.0 to 9.0 mL/min range and, in all cases, the recovery found was between 85 and 103%. The flow rate of 8.0 mL/min was chosen as a compromise between sample throughput and suitable performance of the pump. Elution was carried out at 2.0 mL/min and, with 10 mL of nitric acid 60 mM methanolic solution, good recoveries were achieved.

Analytical Characteristics of Standards

The capacity of the MFE-Polymer SAX anion exchanger packed into the column was studied. Different amounts (between 100 and 1000 µg in 100 mL of water) of each phenoxy acid and Dicamba were passed through the column and, as can be seen in Table 1, recoveries were in all cases around 100%.

This means that the capacity of the anion exchanger to retain these herbicides is very good, at least under the ideal conditions used in this experiment. Finally, the reproducibility of the preconcentration process has been evaluated for the studied phenoxy acids and Dicamba.

Table 1

Retention Capacity of the Packed Column

	Recoveries, %*			
	100 µg	**400 µg**	**600 µg**	**1000 µg**
2, 4-D	96	87	95	102
2,4-DB	94	98	88	101
2,4,5-T	86	92	93	98
2,4,5-TP	102	93	94	101
MCPA	97	96	99	103
Dicamba	85	97	90	89

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* Mean of three determinations.

Table 2

Reproducibility of the Preconcentration Process

	Recoveries, %	**SD, %***
2,4-D	99	2.1
2,4-DB	100	1.5
2,4,5-T	92	1.1
2,4,5-TP	99	6.6
MCPA	99	6.5
Dicamba	90	3.4

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* n = 5.

In all cases, five replicates containing 50 µg of each herbicide in 100 mL of acidic water solution (nitric acid 60 mM) were passed through the column and then eluted with 10 mL of acidic methanol solution, as in the previous experiments. Table 2 shows the percent recoveries and the standard deviations found, in all cases being equal to or lower than 6.6%.

Phenoxy Acid Herbicides and Dicamba in Tomato Samples

Tomato samples were spiked with different amounts of the studied phenoxy acids and Dicamba and hydrolyzed according to the procedure referred

Table 3

Recovery of Phenoxy Acid and Dicamba Added to Tomato Samples

Herbicide	Added (mg/kg)	Found (mean ± S.D., %)*
Dicamba	0.40	88±6
	0.20	73±15
	0.05	140±23
2,4-D	0.40	76±9
	0.17	67±9
	0.09	86±10
MCPA	0.40	94±16
	0.18	102±22
	0.09	89±21
2,4,5-T	0.38	62±8
	0.19	70±3
	0.05	120±23
2,4-DB	0.42	86±9
	0.18	92±16
	0.05	90±14
2,4,5-TP	0.36	78±12
	0.16	108±15
	0.04	133±19

* n = 3.

above. After hydrolysis, the sample was preconcentrated in acidic media using the column packed with the MFE-Polymer SAX anion exchanger without a previous clean-up of the colored and other co-extracted compounds, which usually are previously removed by acid-base partition when the extraction is carried out in other sorbents such as C_{18} or styrene-divinylbenzene copolymer.[16] Once the preconcentration process was carried out, the herbicides were eluted from the column as described previously and were determined by LC with no volume reduction. The spiked samples were prepared with an amount of each herbicide so as to give the maximum permitted concentration established by the Food and Agricultural Organization/World Health Organization (FAO/WHO) in

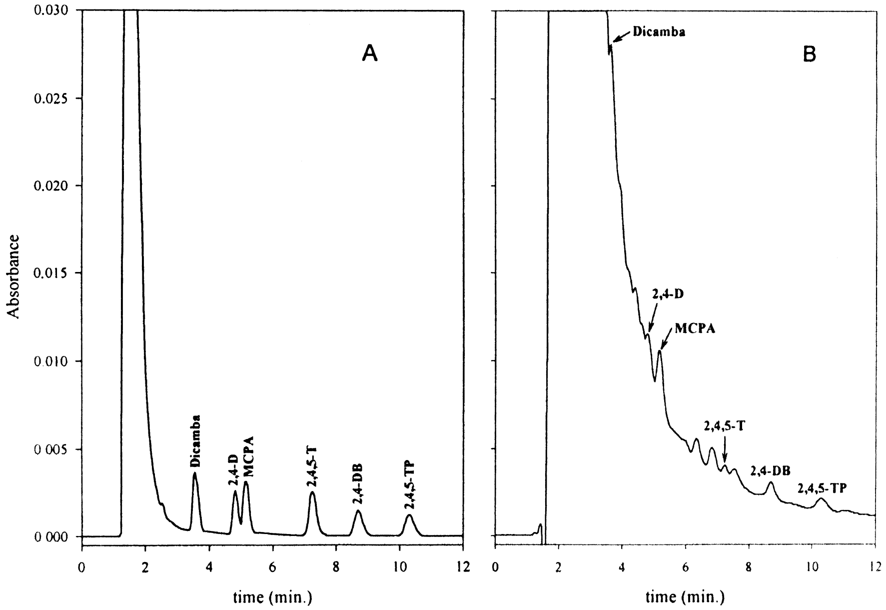

Figure 1. Liquid chromatogram of Dicamba and the phenoxy acids: **A** under optimum conditions (20 ng each); **B** extract of a tomato sample spiked with 0.20 mg/kg.

different kinds of food in the range of 0.05-0.5 mg/kg,[17] or by the Spanish and European regulations which establish 0.10 mg/kg as the maximum level for 2,4-D and MCPA and 0.05 mg/kg for Dicamba, 2,4,5-T, 2,4-DB, and 2,4,5-T in tomato samples.[18] Because the amounts that can be found in food are quite different, three levels of spiking were studied; one near the maximum allowed by FAO/WHO, one intermediate, and the last one near the minimum level established by FAO/WHO and the maximum allowed by the Spanish and European regulations.

Three samples for each spiked level were analyzed and the results are shown in Table 3. As can be seen, in general, good recoveries are achieved, especially for the high and medium level of spiking, where the recoveries are, in these cases, between 67 and 102%. For the low spiking level, matrix effect has been observed for Dicamba, 2,4,5-T, and 2,4,5-TP, leading to recoveries largely higher than 100%. Figure 1 illustrates the chromatogram obtained for Dicamba, 2,4-D, MCPA, 2,4,5-T, 2,4-DB, and 2,4,5-TP under ideal conditions and the one for a tomato sample spiked with intermediate concentrations of the herbicides.

CONCLUSIONS

The proposed preconcentration method based on solid phase extraction with an anion exchanger of MFE-Polymer SAX is suitable for the LC determination of herbicide residues of Dicamba, 2,4-D, MCPA, 2,4,5-T, 2,4-DB, and 2,4,5-TP in tomato samples spiked at levels around the maximum allowed by the FAO/WHO and European regulations with a minimum clean-up.

ACKNOWLEDGMENT

The authors wish to thank the Spanish DGICYT for financial support (project PB96-0642).

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Received April 20, 1998
Accepted June 18, 1998
Manuscript 4774

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