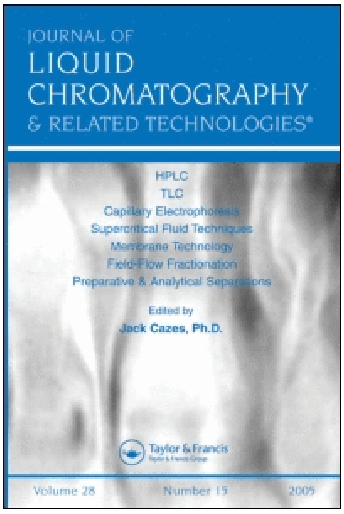

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DETERMINATION OF MECOPROP AND DICHLORPROP IN AQUEOUS SOIL SOLUTIONS BY HPLC WITH DAD

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ABSTRACT

A reverse phase high performance liquid chromatographic method was developed for the direct determination of mecoprop (MCPP) and dichlorprop (DCPP) in the presence of soil and peat constituents. Spiked aqueous soil or soil/peat samples were directly injected after centrifugation and filtration. The analytical sensitivity, 0.35 and 0.24 ng μL^{-1}, detection limit, 1.02 and 0.70 ng μL^{-1}, and precision, 1.28 and 0.80%, for MCPP and DCPP respectively, are very appropriate. The concentration ranges studied 0.0-94.2 ng μL^{-1} for MCPP and 0.0-103.1 ng μL^{-1} for DCPP are suitable for adsorption/desorption and mobility studies of these herbicides in soil. The two tests used to demonstrate the purity or otherwise of every chromatographic peak give valuable information.

INTRODUCTION

Mecoprop (MCPP) and dichlorprop (DCPP) are among the most frequently used pesticides in Europe.[1] They are important as selective pre and post emergency herbicides and can pollute surface and ground water[2] by leaching.

Besides, detrimental effects on following crops may result from their inadequate dosage. So, it is important to conduct studies on the adsorption/desorption and mobility of these herbicides in soil.

In principle, as only physico-chemical characteristics must be related to these processes, it is likely that their R and S enantiomeric forms show the same behaviour.

Various methods have been developed for the determination of MCPP and DCPP at very low concentrations[3-11] but, in most of them, either extractions, or derivatizations, or preconcentration steps, or other time consuming processes are necessary. Furthermore, the use of low polarity organic solvents must be avoided, since they make the interpretation of the adsorption/desorption and mobility processes of these herbicides in soil difficult.

A quick and simple method, with a wide range of applications, that avoids all the above mentioned inconveniences, is presented in this paper.

EXPERIMENTAL

Apparatus

A 1090 Hewlett-Packard liquid chromatograph, equipped with a 4.5 μm spectrometer cell, a diode array detector and a DPU multichannel integrator, as described in a previous paper[12] was used. A 125 x 4 mm stainless steel analytical column and a 4 x 4 mm precolumn were used, both packed with LiChrospher 100 RP-18, 5μm, as stationary phase. The Millex filters (Millipore) used were type HV_4, pore size 0.45 μm.

Soils

Three soils from "La Vega de Granada" (South-East of Spain) classified as silty loam, sandy loam, and clay loam, respectively and characterized as

Table 1

Physicochemical Characteristics and Textural Composition of the Three Soils

Textural Class	O.M. (%)	pH	C.E.C. (meq/100g)	Sand (%)	Silt (%)	Clay (%)
Silty loam	2.10	8.2	10.44	30.7	61.4	7.9
Sandy loam	1.50	7.5	6.38	67.6	32.9	---
Clay loam	1.42	8.1	22.41	22.0	45.3	32.7

indicated in Table 1, added or not with 10% of peat from Padul (Granada, Spain) which contains 78% of organic matter and a cation exchange capacity of 158 meq/100g, were used to obtain the aqueous solutions for the development of the analytical method.

Reagents

Acetonitrile HPLC grade and o-phosphoric acid were obtained from Panreac (Madrid, Spain). MCPP and DCPP of known purity (99.9%) were a gift from BASF (Limburgerhof, Germany) and water was purified with a Milli-Q water purification system (Millipore).

Sample Solutions

Samples were obtained, from adsorption/desorption studies, by centrifugation, at 17212g for 20 min, of the solutions derived from shaking 5 g of soil, added or not with 10% of peat, with 20 mL of an aqueous solution of the herbicides.

Samples were obtained, from mobility studies, by collecting the aqueous eluates produced by passing water throughout a 200 mm high x 93 mm i.d. soil column, added or not with 10% of peat, which had previously been prepared by addition of a determined quantity of herbicide. In both cases, after centrifugation under the above mentioned conditions, the aqueous soil solutions were diluted with acetonitrile v/v, filtered through Millex HV_4 filters and injected into the liquid chromatograph. The dilution with acetonitrile of the aqueous soil solutions was carried out to avoid precipitations inside the liquid chromatograph of water-soluble soil substances which are not soluble in acetonitrile.

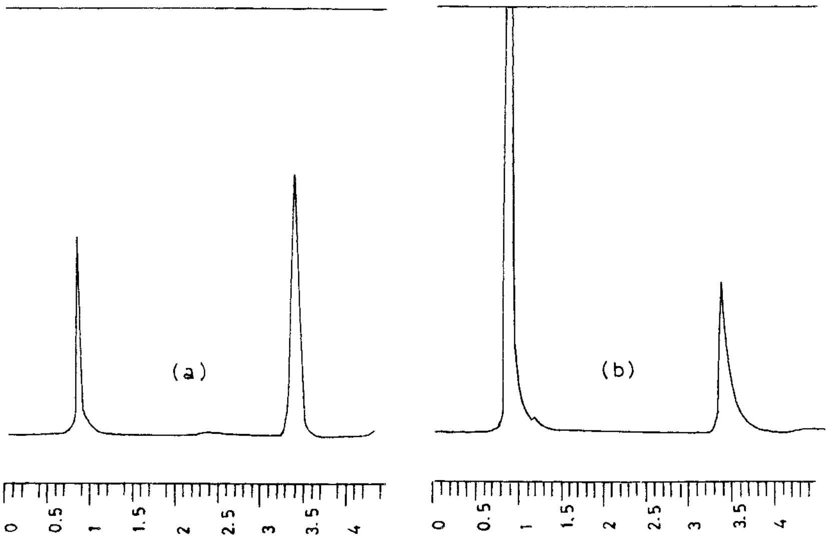

Figure 1. Chromatogram of (a) a clay loam soil - MCPP sample and of (b) a 10% peat added clay loam soil - MCPP sample.

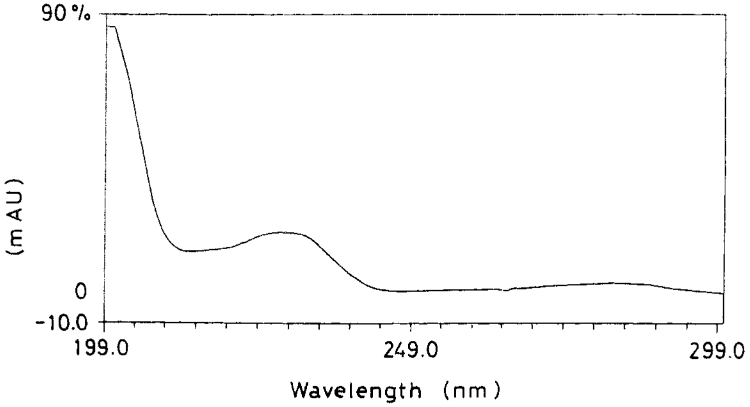

Figure 2. Spectra plots of the MCPP peak in a clay loam soil - MCPP chromatogram.

Calibration Solutions

Aqueous solutions of mecoprop at concentrations of 5.89, 11.77, 23.54, 47.08, and 94.15 ng μL^{-1}, and of dichlorprop at 6.45, 12.89, 25.77, 51.53, and 103.05 ng μL^{-1}, were prepared. This wide range of concentrations was sufficient for all the necessary adsorption/desorption and mobility studies.

Chromatography

The chromatographic conditions were as follows: mobile phase, acetonitrile/o-phosphoric acid aqueous solution 0.05 M at pH = 2.5 v/v, flow rate, 1 mL min^{-1}, column temperature, 40°C, detection wavelengths, 229,4-450,100, and 234,4-450,100 nm, range, automatic, injection volume, 10 μL, chart speed, 2cm min^{-1} and spectra setting in apex, base and slope from 200 to 300 nm.

RESULTS AND DISCUSSION

The calibration graphs obtained, from triplicate injections of each of the five respective calibration solutions, by plotting absorbances *vs* MCPP and DCPP concentrations were linear over the ranges 0.0-94.2 and 0.0-103.1 ng μL^{-1} respectively, for 10 μL injections and passed very close to the origin. The straight lines obtained correspond to the equations $y = 15.60\ x + 1.27$ for MCPP and $y = 13.26\ x + 3.15$ for DCPP, with determination coefficients of 0.9999 in both cases.

Figure 1 shows the chromatograms of (a) a clay loam soil - MCPP sample and of (b) a 10% peat added clay loam soil - MCPP sample. Very similar chromatograms are obtained with DCPP samples when treated in the same way. The MCPP peak area is about 300 mAU. Typical retention times for both herbicides are 3.3 min for MCPP and 3.6 min for DCPP. In all cases the separation of the herbicides from impurities seems to be adequate and no peak was observed when no spiked aqueous soil samples were chromatographed under the same conditions.

Figure 2 shows the spectra plots of the MCPP peak in a clay loam soil - MCPP aqueous solution chromatogram. The THREE spectra are overlaid, indicating that the peak corresponds to a pure substance.

The MCPP and DCPP spectra show a maximum of absorbance at 229 nm and a still high absorption at 234 nm and were the two wavelengths chosen for simultaneous integration. Figure 3 shows the ratio of the signals obtained at

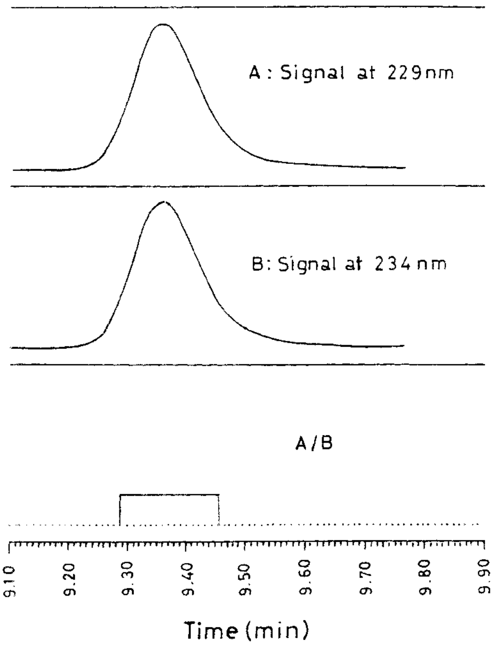

Figure 3. Ratio of signals of the MCPP peak in a clay loam soil - MCPP chromatogram.

these two wavelengths vs time for the MCPP peak shown previously. The linear relationship is a second demonstration of the peak purity. The same tests used for DCPP samples indicated the purity of the chromatographic peak for this herbicide.

Other analytical parameters calculated in accordance with Cuadros et al.[13] are, analytical sensitivity 0.35 and 0.24 ng μL^{-1}, detection limit 1.02 and 0.70 ng μL^{-1}, determination limit 3.39 and 2.32 ng μL^{-1}, and precision 1.28 and 0.80% at 23.5 and 25.8 ng μL^{-1}, for MCPP and DCPP respectively.

The method described is quick, specific, precise, and presents detection limits and working ranges which make it very suitable for adsorption/desorption and mobility studies of MCPP and DCPP in soils. Another advantage of this method, due to the use of a diode-array detector and a multichannel integrator, is that it provides valuable information on the purity, or otherwise, of every chromatographic peak.

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