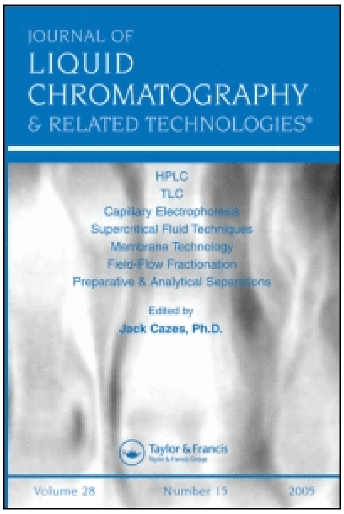

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Determination of Nematicide Aldicarb and Its Metabolites Aldicarb Sulfoxide and Aldicarb Sulfone in Soils and Potatoes by Liquid Chromatography With Photodiode Array Detection

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DETERMINATION OF NEMATICIDE ALDICARB AND ITS METABOLITES ALDICARB SULFOXIDE AND ALDICARB SULFONE IN SOILS AND POTATOES BY LIQUID CHROMATOGRAPHY WITH PHOTODIODE ARRAY DETECTION

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ABSTRACT

Solid phase extraction has been combined with High Perfomance Liquid Chromatography using a Photodiode Array Detector to isolate, determine, quantify and recover trace concentrations of aldicarb and its toxic metabolites, aldicarb sulfoxide and aldicarb sulfone, in soils and potatoes. A method is proposed which eliminates matrix interferences. The procedure involved extracting with acetonitrile or dichloromethane, initial separation and clean-up with a Sep-Pack Florisil or Silica cartridges. The extract can be successfully analyzed by HPLC-DAD and recoveries for pesticides were not influence by the use of this extraction method. The results have been applied to the systematic study of these compounds in growns of patatoes. The lowest detectable concentration for each pesticide is 40 µg kg-1 in soil and 15 µg kg-1 in potatoes.

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INTRODUCTION

Aldicarb, [2-methyl-2-(metylthio)propionaldehyde-O-(methylcarbamoyl)oxime;Temik®] is a systemic insecticide widely used for the protection of the potatoes cultures. The aldicarb (A) is degraded by oxidation to aldicarb sulfoxide (AX) and sulfone (AN) , although these two metabolites can undergo subsequent hydrolysis to their respective non toxic oximes (1). However, aldicarb, its sulfoxide and its sulfone are know to be the most toxic of these compounds. aldicarb sulfoxide is the most important compound, accounting for the high systemic activity and the long-term persistence of the insecticidal activity in soil (2, 3).

Previous methods for determining residues of aldicarb, aldicarb sulfoxide and aldicarb sulfone involved gas chromatography (4, 5). However, the increasing availability of liquid chromatographic methods is mainly due to the result of their sensibility for thermally labile and polar pesticides, which require derivatization prior to gas chromatographic analysis (6).

UV absorbance has been the most commonly used detection method in HPLC determination of N-methylcarbamate pesticides (7-9). UV detection is subject to interferences of other co-extractives taken from the sample and also to the lack of sensitivity for some compounds. The most serious drawbacks of UV detectors arise from matrix interferences and from working below 205 nm (10).

The development of diode-array detectors has been the most important advance in HPLC for the quantitative identification of compounds (11, 12). It provides an opportunity to explore all wavelengths in the UV and choose the monitoring wavelength which maximizes instrumental sensitivity. With the multi-signal capability of a diode-array detector, all the compounds can be analyzed at, or close to, their maximum wavelengths.

Most environmental sample extracts will require a preliminary clean-up procedure before determination by HPLC (13-15). The extent of clean-up required depends upon the type of sample being analyzed, the detection limit required and the detection technique used. Combining solid phase extraction with HPLC-DAD, the above-mentioned limitation can be overcome.

This paper describes a method for the high pressure liquid chromatographic using a Photodiode Array Detector in order to determine the quantity of aldicarb, aldicarb sulfoxide and aldicarb sulfone. A valid alternative method must also provide for elimination of possible interferences in soil and potatoes without increasing the analysis time.

MATERIALS

Instrumentation

A Hewlett-Packard (Palo Alto, CA., USA) model 1050 HPLC equipped with a HP 1040 M Diode Array detector has been utilized. A Hewlett-Packard data station has been used for data storage, comparison and mathematical manipulation of the acquired spectra.

The column was a cyanopropyl of 25 cm length and 4 mm ID., with a paking type Spherisorb of 5 µm (Tracer, Barcelona, Spain).

A centrifuge (Selecta, Barcelona, Spain) Model Centronic and a Selecta Model Vibromatic-384 have been used in the extraction procedure.

A Vac-Elut sample preconcentration system (Varian, Harbor City, CA., USA) for solid-phase extraction has been used in the purification procedure.

In the solid phase extraction two types of cartridges (Waters Associates, Milford, MA., USA) have been used. The Sep-Pack Florisil containing 500 mg of sorbent to stage of extraction in soil and the Sep-Pack 50 mg of Silica for extraction in potatoes.

Chemicals and Solvents

The pesticide standards were supplide by the Laboratory of Dr. Ehrenstorfer GmbH (Angsburg, Germany) with a purity of 99.9%.

Standard stock solutions were obtained by the dissolution of 10 mg of aldicarb, its sulfoxide and sulfone in 100 ml of acetonitrile. These solutions were diluted to final working solution in acetonitrile-water (30:70).

HPLC-grade solvents were used. The acetonitrile (LiChrosolv, Merck, Darmstadt, Germany) used in the mobile phase has a transmitance of 50% at 195 nm and 80% at 200 nm. Mobile phase was desgassed with helium prior to use. Distilled water was obtained from a Millipore (Milford, MA., USA) Milli-Q water purification system.

All solvent and samples were filtered through 0.22 μm Millipore membrane filters before injection.

METHODS

Chromatographic Conditions

In preliminary studies we tested the chromatographic behaviour of aldicarb and its metabolites using as mobile phase solvents which generally are used in liquid chromatography with UV detection: water, methanol, acetonitrile or mixture of them. The best result for those three compounds is obtained when it is used a mixture acetonitrile-water. Figure 1 shows the influence of acetonitrile content in the mobile phase on the capacity ratio k´. With increasing acetonitrile content, the

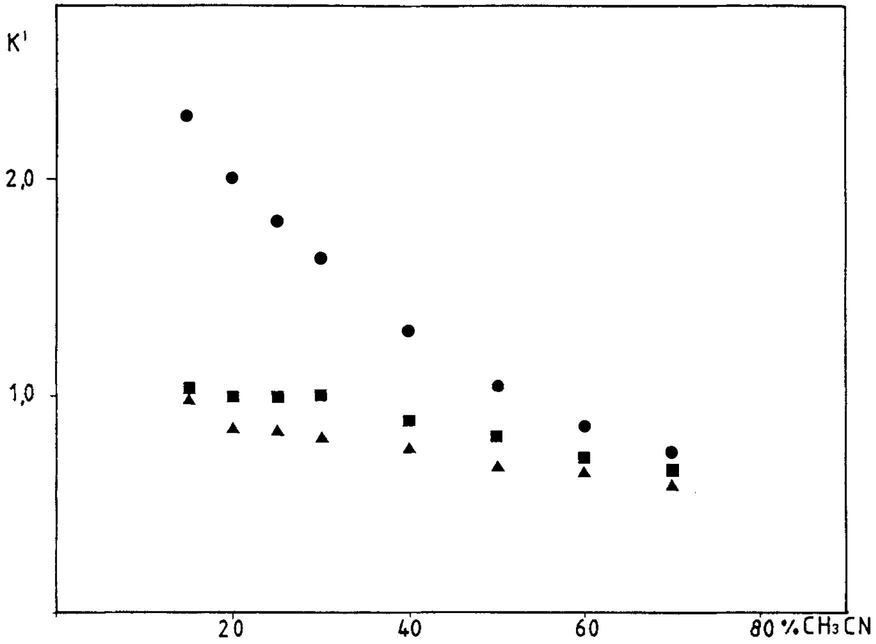

FIGURE 1. Influence of acetonitrile content in the mobile phase on the capacity ratios (k') of aldicarb (●), aldicarb sulfoxide (▲) and aldicarb sulfone (■). Flow rate: 1.2 ml min^{-1}, injection volumen: 50 µl, λ analytic: 202 nm

capacity ratio k'of aldicarb decreased, whereas those of aldicarb sulfoxide and aldicarb sulfone were influenced only slightly. As a result, the acetonitrile content was fixed at 30% V/V for experiments, and good separations were obtained in 4 minutes.

The separation of pesticides was carried out using isocratic elution at a flow rate of 1.2 ml/min with injection volume of 50 µl.

The UV absorbance of the elution profile of analytes was recorded at 202 nm for all measurements.

Extraction and Clean-up Procedures

The extraction and clean-up procedures are simple and can be adapted to plants and soils.

Extraction and Clean-up in Soil: A 25 g sample of homogeneized soil sieved to 2 mm was extracted with 25 ml of acetonitrile and shaken in a capped centrifuge tube for 30 min, centrifuged for 5 min at 3000 rpm (1000 g) and filtered by suction.

A Florisil cartridge was washed with 10 ml of acetonitrile for activation of the sorbent. The sample extract was passed through the cartridge by negative pressure of 7 in of Hg by station Vac-Elut.

3 ml was taken from the liquid which passes through the cartridge and contains aldicarb, aldicarb sulfoxide and aldicarb sulfone. The volume was made up to 10 ml with water and was injected into the HPLC system.

Extraction and Clean-up in Potatoes: A total of 20 g of the homogeneous sample of potatoes was extracted in a capped centrifuge tube with 10 g anhydrous sodium sulfate and 20 ml of dichloromethane shaken for 30 min. This mixture was centrifuged at 3000 rpm (1000 g) for 5 min and the supernatant collected over anhydrous sodium sulfate.

Silica cartridge was washed with 5 ml of anhydrous dichloromethane for activation of the sorbent. The extract was passed through the cartridge by negative presure of 7 in of Hg. The remaining solvent in the cartridge was evapored under a nitrogen purge at 5 psi for a period of 10 min.

The concentrated sample was eluted with 2 ml of acetonitrile. The extract was diluted with water at ratio 1:2 acetonitrile-water and injected into the HPLC.

RESULT AND DISCUSSION

The use of DAD detection has allowed the selection of the wavelength which determinate each pesticide in the analytical procedure in order to get improvement in sensitivity and selectivity. aldicarb and its metabolites exhibit strong UV absorbance characteristics at the shorter wavelength of 202 nm, in addition to secondary maximum at 248 nm for aldicarb and 236 nm aldicarb sulfoxide. In FIGURE 2 spectrum in optimal conditions is shown.

The linear dynamic range of the detector response was checked for the pesticides at a wavelength of 202 nm between 0.25 and 500 ng. A typical chromatogram of pesticide mixture under the best conditions is shown in Figure 3.

Linearity of response using area peak at 202 nm vs. quantity injected, was studied by sucessive injections of 50 µl of working solutions. The linear calibration corresponds to the equations:

$A_p = 1.747+1.838\ [A]$ $\qquad r = 0.9998$

$A_p = 0.504+1.641\ [AX]$ $\qquad r = 0.9999$

$A_p = 1.773+1.859\ [AN]$ $\qquad r = 0.9998$

where A_p is in mUA per second and concentration in ng.

The limits of detection are 0.06 ng of aldicarb, 0.05 ng of aldicarb sulfoxide and 0.1 ng of aldicarb sulfone for a relation signal/noise ratio S/N = 3.

Ten replicate injections of the standard solution containing 5 ng each to aldicarb, aldicarb sulfoxide and aldicarb sulfone were carried out to determine the precision of the method. The coefficients of variation were 1.72%, 2.45% and 2.92% for aldicarb, aldicarb sulfoxide and aldicarb sulfone respectively.

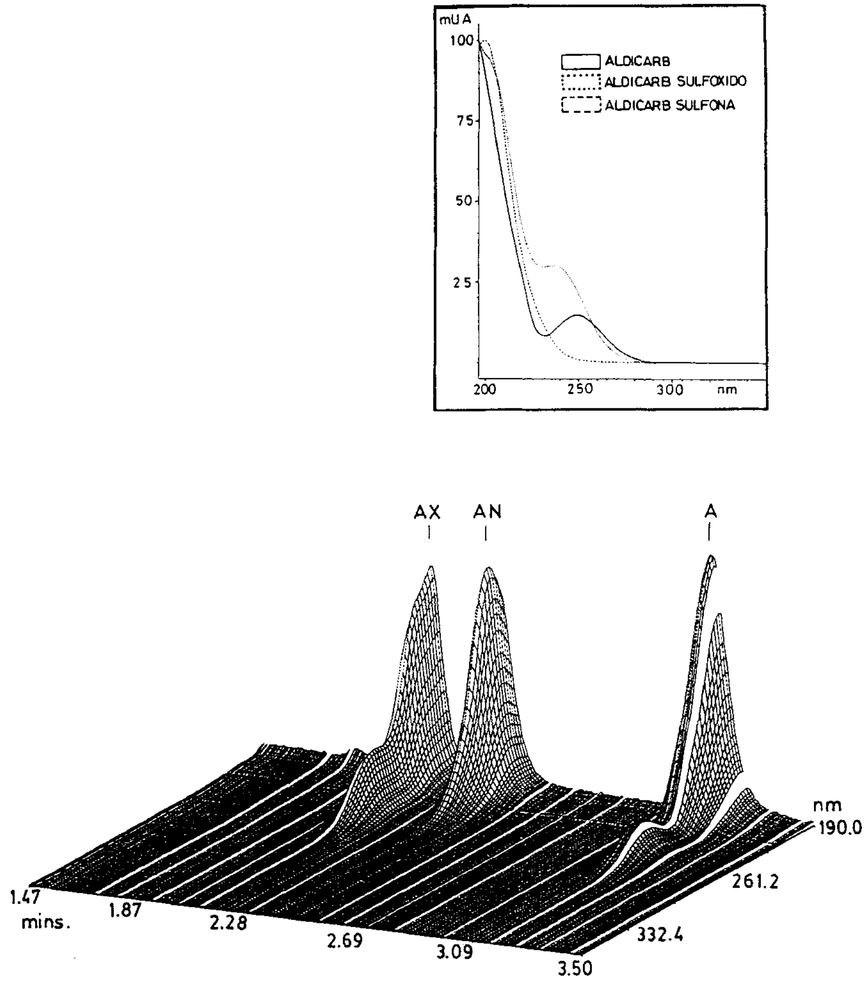

FIGURE 2. Evolution of the absorption spectra for the mixture of pesticides. Range λ: 190 - 350, Step: 2 nm, Threshold: 0.1 mUA, Total Spectra number: 1043, [A] = [AX] = [AN] = 500 ng injected
Other parameters in Figure1.

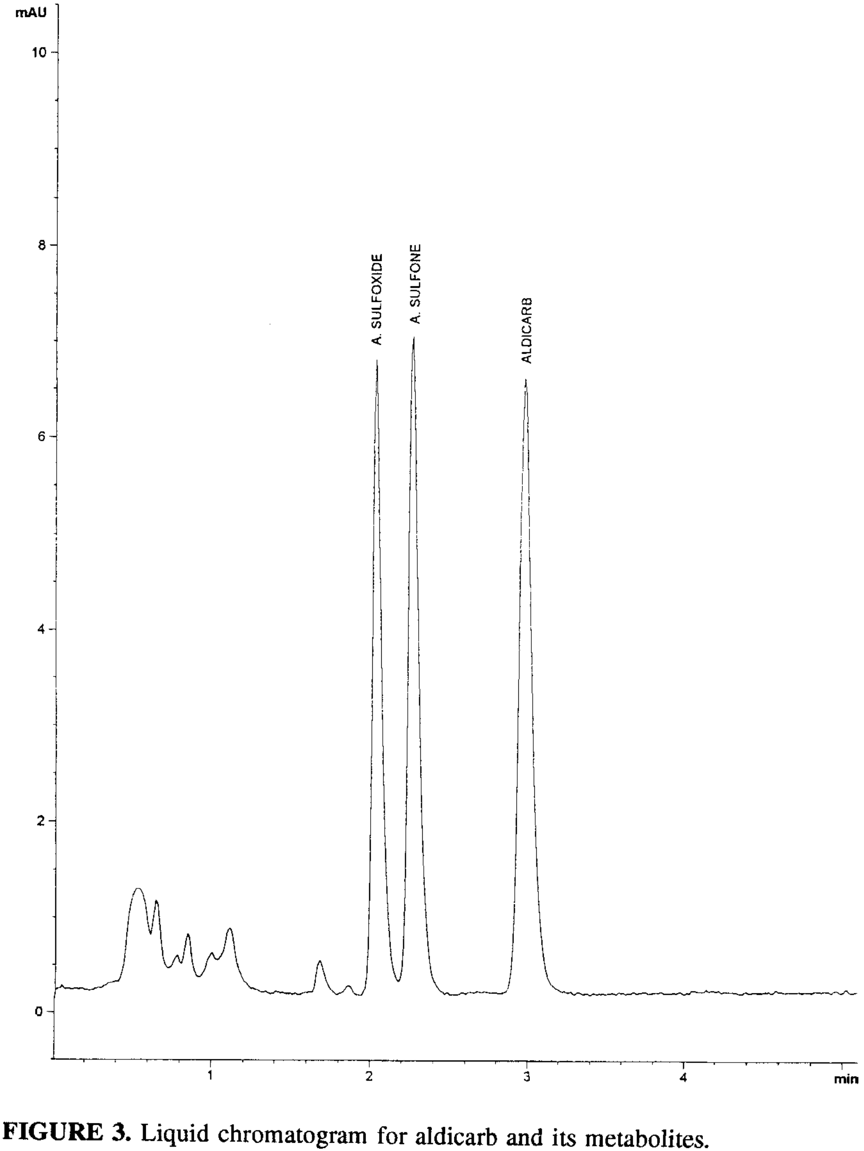

FIGURE 3. Liquid chromatogram for aldicarb and its metabolites.
Flow rate: 1.2 ml min^{-1}, injection volumen: 50 µl, λ analytic: 202 nm, [A] = [AX] = [AN] = 35 ng injected

The validity of the proposed method was proven by spiking with aldicarb and its metabolites in potato and soil samples over the range of 5 to 1000 μg kg^{-1} and subjecting the samples to the described analytical procedure. Average recoveries from fortified samples were 80-100% for aldicarb, aldicarb sulfoxide and aldicarb sulfone in soil and 60-100% for aldicarb and 80-100% for aldicarb sulfoxide and aldicarb sulfone in potatoes.

The proposed analytical method allows to reach the detection limits of 40 μg kg^{-1} in each pesticide in soil and 15 μg kg^{-1} in potatoes.

The proposed method is so quick and efficient that permits the systematic use to determine these compounds in soils and plants. It has been used to study the degradation of aldicarb in soils from Alava plain in the Basque Country (North of Spain).

The field treatments have taken place in grounds destined to be used for farming of sow and consume potatoes. The selection of grounds for this study was carried out taking account edaphologic criteria and that the area is representative as for surface, production and agricultural yields in the culture of potatoes.

In order to prove the possible change of behaviour that the metabolism can have for the plaguicide aldicarb depending on nature of the soils, were selected two grounds of diferent texture: clayey and sandy. The characteristics of soils selected for study can be observed in Table 1.

In these grounds, the Temik®, granule at 10% aldicarb, at rates of 20 kg/Ha was applied on April 1994. The samples of soil were collected in the course of the culture cycle of in periods of: 7, 15, 60 and 120 days from different depths: surface, 15 cm and 30 cm.

The samples of potatoes were taken randomly at the time of the harvest (October 1994).

TABLE 1

Characteristics of Soils Selected for Study

SOIL 1			
	SURFACE	**15 CM DEPTH**	**30 CM DEPTH**
TEXTURE	LOAM	LOAM-SAND	LOAM-SAND
HUMIDITY (%)	2.80	3.07	3.57
CONDUCTIVITY (µS/cm)	60.0	65.8	76.0
ORGANIC MATTER TOTAL (%)	1.27	1.40	1.30
pH (H_2O)	7.10	7.05	7.07
pH (KCl)	6.39	6.36	6.40

SOIL 2			
	SURFACE	**15 CM DEPTH**	**30 CM DEPTH**
TEXTURE	LOAM-CLAY	LOAM-CLAY	LOAM-CLAY
HUMIDITY (%)	3.72	3.90	4.01
CONDUCTIVITY (µS/cm)	100.6	108.8	94.7
ORGANIC MATTER TOTAL (%)	1.84	1.84	1.80
pH (H_2O)	7.91	7.82	7.85
pH (KCl)	7.35	7.27	7.36

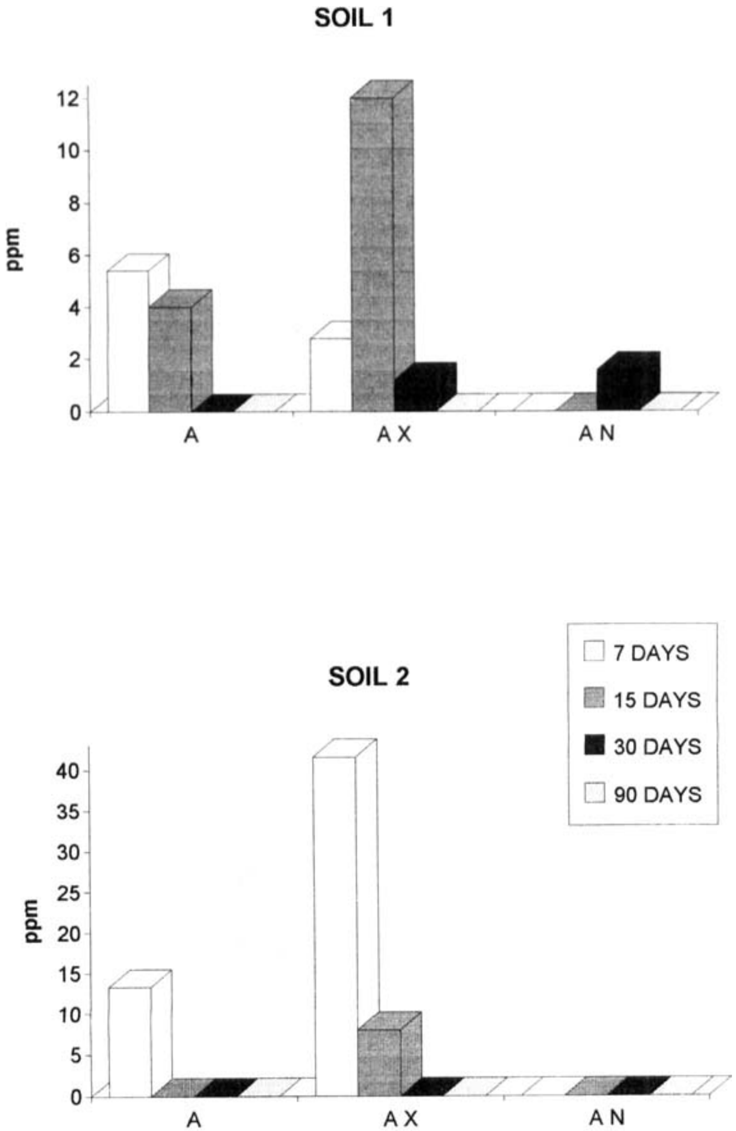

FIGURE 4. Persistence of nematicide aldicarb (A) and its metabolites aldicarb sulfoxide (AX) and aldicarb sulfone (AN) in the whole culture cycle in both selectionated soils.

With regard to the studies carried out with samples of soil one might consider that the maximum quantity of aldicarb has been observed during the first week after the treatment and at 15 cm depth.

The first product which is observed in the degradation process of the aldicarb in soils is the aldicarb sulfoxide, increasing its concentration progressively up to 15 days after the application; at this time, aldicarb sulfoxide and its respective aldicarb sulfone appear together.

120 days after the application were observed neither aldicarb nor its metabolites.

The Figure 4 shows the result obtained. It can be seen that the degradation of the aldicarb is favoured in those soils with clay-like texture (soil 2) compared to those of sandy texture or loamy (soil 1). This is so because the oxidation reaction is catalized by the components of clay.

The result obtained from potatoes samples allows us to conclude that none of the plaguicides are present in this vegetable at consumption moment for concentrations up to the detection limits.

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