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Short Communication

Liquid chromatographic determination of carbendazim in the presence of some normal soil constituents with photodiode-array detection

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ABSTRACT

A reversed-phase high-performance liquid chromatographic method was developed for the determination of carbendazim in the presence of some normal soil constituents (kaolinite, montmorillonite and peat). Spiked aqueous soil samples were injected after centrifugation and filtration. Quantitative recoveries were observed and good precision was obtained. The concentration range studied, 1.6716–8.3580 mg/l, is the most suitable for adsorption–desorption studies of carbendazim on soil and soil constituents.

INTRODUCTION

Carbendazim (methyl benzimidazol-2-ylcarbamate) is a systemic fungicide which controls a wide range of pathogens of cereals, vegetables, fruits grapes and ornamental plants. Its solubility in water at pH 6–6.5 is about 10 ppm.

In some solvents [1] and in contact with water or under moist conditions in soil [2], dissociation of benomyl occurs to form carbendazim. The EPA [3] has pointed to the possible mutagenicity, teratogenicity and reduction in spermatogenic activity of benomyl under certain conditions, which increases the toxicological interest in carbendazim.

Because of the possible toxicity of carbendazim for man, through contaminated plants and waters, we decided to study the adsorption–desorption mechanisms of this fungicide on kaolinite, montmorillonite and peat, in order to be able to predict its behaviour in different soils and in the environment.

Gorbach [4] published a review of analytical methods for carbendazim, benomyl and related fungicides, and many other papers (*e.g.*, [5–8]) have subsequently appeared on the same topic.

A reversed-phase high-performance liquid chromatographic (HPLC) method with methanol–water as the eluent has been developed for the direct determination of

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carbendazim in supernatants of aqueous solutions of carbendazim and soil constituents. This was done in order to avoid either preconcentration steps [9] or derivatization processes necessary in gas–liquid chromatography [5], to eliminate organic solvents [10] of low polarity which would make difficult the interpretation of the adsorption–desorption process of carbendazim on soil and to minimize small changes in pH [8] which could influence both retention times and peak areas if acidic or basic substances were present in the mobile phase.

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 1090 liquid chromatograph, equipped with a 4.5-μl spectrometer cell, a diode-array detector and DPU multi-channel integrator, as described in a previous paper [11], was used. A Hewlett-Packard 799160D-552 stainless-steel column (100 mm × 2.1 mm I.D.) packed with ODS-Hypersil (5 μm) was used.

The Millex filters (Millipore, Bedford, MA, U.S.A.) used were Type HV_4, 4 mm, pore size 0.45 μm.

Soil constituents

Kaolinite from Lage, montmorillonite from Almería and peat from Padul (all in Spain) were used.

Reagents

Methanol of HPLC grade was obtained from Panreac (Madrid, Spain). Water was purified with a Milli-Q water purification system (Millipore). Carbendazim samples, as analytical standards of known purity, were gifts from BASF (Limburgerhof, F.R.G.) DuPont (Wilmington, DE, U.S.A.) and Hoechst (Frankfurt am Main, F.R.G.).

Calibration solutions

A solution of carbendazim standard in water was prepared at 8.3580 mg/l and four other solutions were prepared by dilution with water at 6.6864, 5.0148, 3.3432 and 1.6716 mg/l. Taking into account the very low solubility of carbendazim in water (10 ppm), a wider range of concentrations is not feasible.

Sample solutions

Approximately 0.2 g of peat, or 1.0 g of the other soil constituents, was weighed (to the nearest 0.1 mg). A 20-ml volume of carbendazim solution at a concentration within the range 1.6716–8.3580 mg/l was added and shaken mechanically for a certain period (the time necessary for the study of adsorption–desorption behaviour). The solution was then centrifuged at 12 062 *g* for 20 min and an aliquot of the supernatant was filtered through a Millex HV_4 filter into a small vial fitted with a cap.

Chromatography

The chromatographic conditions were as follows: mobile phase, methanol–water (65-35); flow-rate, 0.3 ml/min; column temperature, 40°C; detection wave-

lengths, 285 and 243 nm (bandwidth 4 nm); reference wavelength, 550 nm (bandwidth 100 nm); range, automatic; and injection volume, 10 μl.

RESULTS AND DISCUSSION

The calibration graph, obtained by plotting absorbance *versus* carbendazim concentration, was linear over the range 1.6716–8.3580 mg/l for 10-μl injections and passed through the origin. The straight line obtained corresponds to the equation $y = 86.5166x + 4.0979$, with a correlation coefficient of 0.9999.

The chromatography of various samples is shown in Fig. 1. The carbendazim peak area is about 250 milliabsorbance units. The separation of carbendazim from impurities seems to be adequate in each instance and no peak was observed at the retention time of carbendazim when blank samples of montmorillonite, kaolinite and peat were chromatographed under the same conditions.

UV spectra measured for each chromatographic peak prior to, at and after the carbendazim maximum were very similar, demonstrating the purity of the carbendazim peak. This purity was also demonstrated by the linear relationship between the signals obtained at 285 and 243 nm.

The standard addition technique was used to test the ability of the HPLC system to determine accurately carbendazim added to a peat carbendazim supernatant. To five 2-ml aliquots of peat carbendazim supernatant, at a concentration of 0.5841 mg/l, were added 0, 1, 2, 3 and 4 ml of a 14.700 mg/l carbendazim solution in methanol and correspondingly 4, 3, 2, 1 and 0 ml of methanol. The detector response to carbendazim,

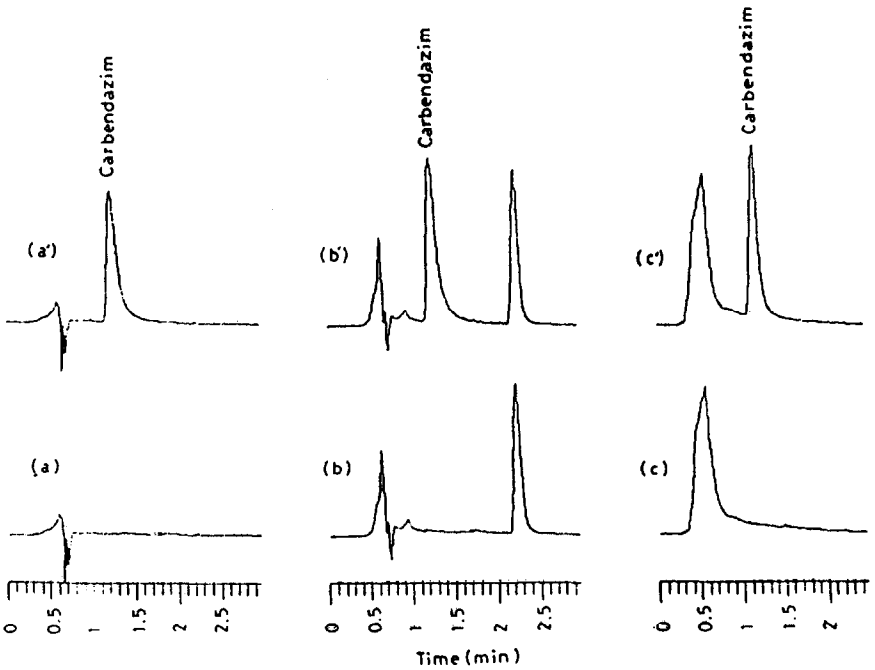

Fig. 1. Chromatography of (a), (b) and (c) montmorillonite, kaolinite and peat samples (blanks), and of (a'), (b') and (c') montmorillonite–carbendazim, kaolinite–carbendazim and peat–carbendazim samples.

in the presence of coextracted constituents of the peat soil, ranged from 97.9% to 102.9 of theoretical. A peat carbendazim sample was chosen for this experiment because the components of peat extracts are chromatographically separated from carbendazim with more difficulty than those of either montmorillonite or kaolinite, as can be seen in Fig. 1.

The relative standard deviations for eleven repeated injections of two carbendazim samples at 0.5760 and 8.7709 mg/l were 1.05 and 0.54%, respectively.

The detection limit, for a standard sample, defined as the amount which produces a signal equal to three times the background noise level, was 0.06 ng of carbendazim, equivalent to 10 μl of solution of concentration 6 μg/l.

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