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Short communication

Liquid chromatographic determination of methabenzthiazuron in soil aqueous solutions with photodiode-array detection

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Abstract

A reversed-phase high-performance liquid chromatographic method has been developed for the determination of methabenzthiazuron in aqueous solutions in the presence of soil constituents. Spiked aqueous soil samples were injected after centrifugation and filtration. Quantitative recoveries were observed and high precision was obtained. The concentration range studied, 2.93–46.92 mg/l, is very suitable for adsorption–desorption studies of methabenzthiazuron in soil.

Keywords: Soil; Environmental analysis; Methabenzthiazuron; Pesticides.

1. Introduction

Methabenzthiazuron (MBT) [1-(1,3-benzothiazol-2-yl)-1,3-dimethylurea] is a selective herbicide which controls a broad spectrum of weeds in cereals, legumes, vineyards and orchards. Its solubility in water, at 20°C, is 59 mg/l. It is unstable in strong acids and alkalis. Its photodegradation rate is very slow and increases in the presence of humic substances.

There is a great deal of concern about the biological degradation and transport of MBT in soil [1–6], not only because its residues may decrease the number of microorganisms and the quantity of calcium and magnesium in soil [7] but also due to the possible contamination of surface and groundwater by this chemical. For these reasons it was decided that the adsorption–desorption of MBT in Spanish soils, and the influence on these processes of the different soil components, specially montmorillonite, kaolinite and peat, should be studied.

Some methods have been proposed for the extraction and/or determination of MBT in soil [8,9] and many others for the determination of urea herbicides, e.g., gas chromatography–nitrogen phosphorus detection (GC–NPD) [10], GC–electron-capture detection (ECD) [11], GC–mass spectrometry (MS) [12], high-performance liquid chromatography–electrochemical detection (HPLC–ED) [13], supercritical-fluid extraction [14], supercritical-fluid chromatography [15] and bioassays [16].

In this paper a reversed-phase HPLC method, with acetonitrile–water as the eluent, is presented for the direct determination of MBT in supernatants of aqueous solutions of MBT and either soils or soil constituents. This method has

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been developed in order to avoid the time consuming analytical methods mentioned above, derivatization processes and preconcentration steps [17], as well as to eliminate organic solvents of low polarity which would make the interpretation of the adsorption–desorption process of MBT on soil difficult. A further advantage of this method is that a chromatographic run takes only 3.5 min.

2. Experimental

2.1. Apparatus

A Hewlett-Packard Model 1090 liquid chromatograph, equipped with a 4.5-ml spectrometer cell, a diode-array detector and a DPU multi-channel integrator, as described in a previous paper [18] was used. A Hewlett-Packard 799160D-552 stainless-steel column (100 × 2.1 mm I.D.) packed with ODS-Hypersil (5 μm) and a Hewlett-Packard 79916KT-110 guard cartridge (20 × 2.1 mm I.D.) packed with the same ODS-Hypersil (5 μm) were used.

The Millex filters (Millipore, Bedford, MA, USA) used were type HV_4, 4 mm, pore size 0.45 μm.

2.2. Adsorbents

Montmorillonite from Almeria, kaolinite from Lage, peat from Padul (all in Spain) and a silt clay loam soil from the south-west of Spain, having the following properties: organic matter 1.2%, pH 8.1, phyllosilicates 46% and smectites 30%, were used.

2.3. Reagents

Acetonitrile of HPLC grade was obtained from Panreac (Madrid, Spain). Water was purified with a Milli-Q water purification system (Millipore). MBT, as an analytical standard of known purity (99.9%), was obtained from Dr. Ehrenstorfer (Augsburg, Germany).

2.4. Calibration solutions

A solution of MBT standard in acetonitrile–water (1:1) was prepared at a concentration of 46.92 mg/l and four other solutions were prepared, by dilution with the same solvent, at concentrations of 23.46, 11.73, 5.87 and 2.93 mg/l, respectively. A wider range of concentrations was considered unnecessary for the purposes of our study.

2.5. Sample solutions

Aqueous solutions of MBT, at concentrations within the range of 5–50 mg/l, were added to the adsorbents, left to stand the time necessary for the study to be undertaken, and the resulting solutions being centrifuged at 12 000 *g* for 20 min. Aliquots of the supernatants were treated with equal volumes of acetonitrile, shaken, filtered through a Millex HV_4 filter into a 2-ml vial and capped. The dilutions with acetonitrile of the adsorbent aqueous solutions were carried out in order to avoid precipitations inside the liquid chromatograph of water-soluble soil substances which are not soluble in acetonitrile.

2.6. Chromatography

The chromatographic conditions were as follows: mobile phase, acetonitrile–water (1:1); flow-rate, 0.3 ml/min; column temperature, 40°C; detection wavelengths, 225 and 267 nm (bandwidth, 4 nm); reference wavelength, 550 nm (bandwidth, 50 nm); range 500; injection volume, 5 μl; stop time, 3.5 min.

3. Results and discussion

The calibration graph, obtained by plotting absorbance versus MBT concentration, was linear over the range 2.93–46.92 mg/l for 5-μl injections and passed very close to the origin. The straight line obtained corresponds to the equation $y = 69.7095x + 0.1760$, with a correlation coefficient of 1.0000.

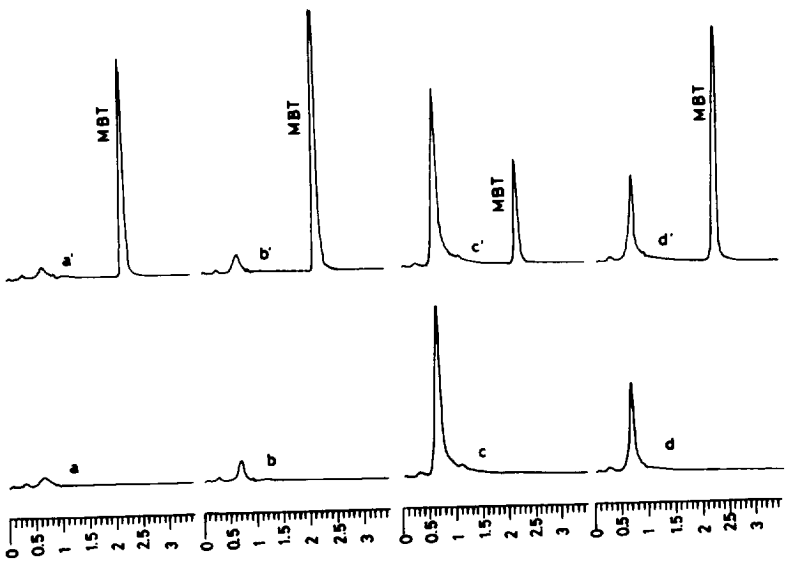

Fig. 1. Chromatography at 225 nm of: a, montmorillonite, b, kaolinite, c, peat and d, soil samples, and of: a', montmorillonite–MBT, b', kaolinite–MBT, c', peat–MBT and d', soil–MBT samples.

Chromatograms of various samples are shown in Fig 1. The separation of MBT from impurities seems to be adequate, hence no peak was observed at the MBT retention time when blank samples of montmorillonite, kaolinite, peat and soil were chromatographed under the same conditions.

UV spectra measured for each chromatographic peak prior to, at and after the MBT maximum were very similar, demonstrating the purity of the MBT peak. This purity was also demonstrated by the linear relationship between the signals obtained at 225 and 267 nm.

The standard addition technique was used to test the ability of the HPLC system to accurately determine MBT added to a soil–MBT supernatant. For this purpose, three repetitions were performed of the following solutions: 0, 5, 10, 15 and 20 ml of an MBT solution in acetonitrile–water (1:1), at a concentration of 47.14 mg/l, and subsequent addition of 20, 15, 10, 5 and 0 ml of acetonitrile–water (1:1) to five 5-ml aliquots of a soil–MBT supernatant at a concentration of 1.72 mg/l. The detector response to MBT in the presence of coextracted constituents of soil ranged from 97.3% (R.S.D. = 4.75) to 102.7% (R.S.D. = 0.29) of the theoretical value for the three replicates. A soil–MBT sample was chosen for this experiment because the soil and peat extracts show a greater quantity of components than those of either montmorillonite or kaolinite, as can be seen in Fig. 1.

The R.S.D. for eleven repeated injections of two MBT samples at 5.02 and 36.82 mg/l were 0.60% and 0.19%, 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 2 ng of MBT, which is equivalent to 5 μl of a solution at a concentration of 0.4 mg/l.

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