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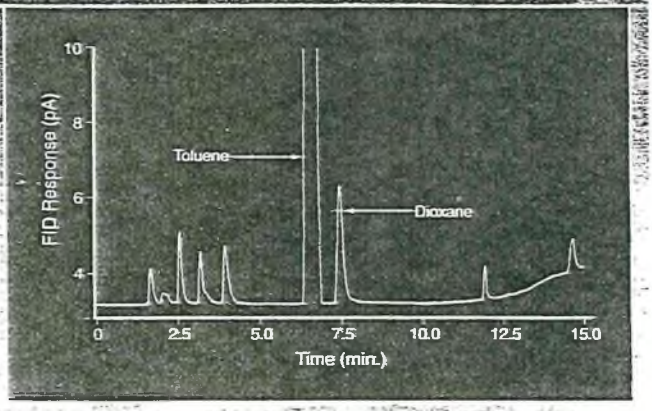

GC Determination of Dioxane in Toluene – Less Straightforward than Expected

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High Performance Liquid Chromatographic Screening and Gas Chromatography-Mass Spectrometry Confirmation of Tebuthiuron Residues in Drinking Water

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1 Introduction

Tebuthiuron (*N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N,N'*-dimethylurea) is a phenylurea herbicide used in sugar cane culture for the pre- and post-emergence control of weeds [1, 2]. Analysis of tebuthiuron (**Figure 1**) and of other phenylurea herbicides in environmental samples can be performed by HPLC [3–10], or by gas chromatography using selective detectors such as nitrogen-phosphorus detector (NPD), electron-capture detector (ECD), or a mass spectrometer (MS) [11–16]. Although Loh *et al* [17] reported that the use of temperatures above 280 °C permits quantitative tebuthiuron breakdown, thus permitting the analysis of the products of decomposition formed, methods based on gas chromatography usually involve a derivatization step to permit analysis of this thermal unstable herbicide in its unchanged form [11, 12, 18]. These methods have been applied to the determination of tebuthiuron residues in soil, foods, and plant material but none of them has been reported for the evaluation of this compound in water.

In the present study we describe two methods for tebuthiuron analysis in water samples. The samples were first analyzed by HPLC and the results were confirmed by GC-MS after acetic anhydride derivatization. The methods were applied to the analysis of this herbicide in surface and ground water samples collected from the Espraiado Stream watershed (Ribeirão Preto region, state of São Paulo, Brazil). This watershed represents one of the reloading points of the Botucatu ground water table, the largest and most important one in the center-south region of Brazil, including eight Brazilian states and parts of Argentina, Uruguay, and Paraguay, and covering an area of approximately 1.200.000 km^2 [19].

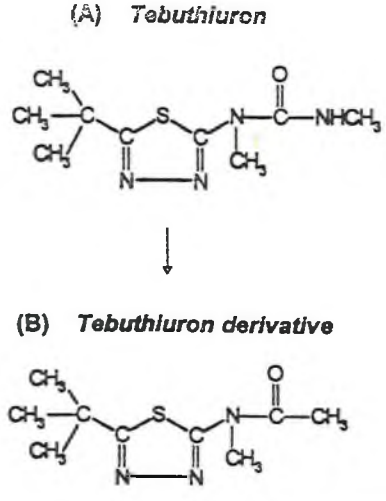

Figure 1. Structures of tebuthiuron (A) and its derivative formed in the reaction with acetic anhydride (B).

2 Material and Methods

2.1 Reagents and Standard Solutions

A stock solution of tebuthiuron (99.8% Chemical Service, USA) was prepared at a concentration of 1.0 mg/mL and working solutions at concentrations of 0.08, 0.2, and 0.4 µg/mL were prepared by dilution. The solutions used for HPLC analysis were prepared in methanol HPLC-grade (Merck, Darmstadt, Germany) and the solutions used for GC-MS analysis were prepared in acetone pesticide-grade (EM Science, Gibbstown, USA). The caffeine solution was prepared in methanol HPLC-grade at the concentration of 5 µg/mL. The solvents used in the extraction procedures were HPLC or pesticide-grade (EM Science, Merck).

2.2 Water Samples

Nine water sampling points were selected in the Espraiado Stream watershed, 8 of them corresponding to surface water and 1 to ground water. The collections were made from October 1995 to July 1996. Four collections were made at each site for a total of 250 samples. The water samples (1000 mL) were stored in amber flasks and kept at 4 °C prior to extraction.

2.3 Sample Preparation and Chromatographic Analysis

HPLC analysis of tebuthiuron was performed with a Shimadzu liquid chromatograph (Kyoto, Japan) consisting of a LC-10AD pump, a variable-wavelength UV detector (SPD-10AV) operating at 254 nm, an automatic injector (SIL 10A) with a 100 µL

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loop and a Chromatopac C-R6A integrator. The separation was obtained on a 125 × 4 mm Lichrospher® 100 RP-8 reversed-phase column (5 µm particle size, Merck) protected with a Lichrospher® 100 RP-8 precolumn (Merck). The mobile phase used was 0.05 mol/L phosphate buffer, pH 5.5-acetonitrile (73:27, *v/v*) at a flow rate of 1 mL/min.

Aliquots of 100 mL of water samples (filtered through 0.22 µm membranes) were alkalinized with 25 µL of 4 mol/L NaOH solution, and extracted for 1 h in a horizontal shaker (220±10 cycles/min) using 12 mL dichloromethane-isopropanol (9:1, *v/v*). The samples were left to stand for 10 min and the organic phases were centrifuged at 1800 *g* for 10 min to separate any portion of the aqueous phase. The organic phases (6 mL) were evaporated under a nitrogen stream at 35 °C. The residues were dissolved in 200 µL of the mobile phase and 100 µL aliquots were chromatographed.

The presence of tebuthiuron in the water samples was confirmed using a Shimadzu GC-MS system model QP5000 (Kyoto, Japan) consisting of a gas chromatography equipped with a split/splitless injector and a mass selective detector with ions monitored in the electron impact mode (70 eV). Internal standard solution (caffeine, 0.12 µg) was added to the water samples and extracted as previously described. To the residues obtained in the extraction procedure were added 1 mL toluene pesticide-grade and 100 µL p.a. grade acetic anhydride. The tubes were sealed and heated to 270 °C for 2 h in a sand bath [12]. The solutions were then transferred to conical tubes and toluene was evaporated off under a stream of air at room temperature (25 °C). The residues obtained were dissolved in 25 µL acetone pesticide-grade immediately before chromatographic analysis. Tebuthiuron was analyzed using a fused silica DB-5 capillary column (30 × 0.25 mm i.d., 0.25 µm film thickness (J & W Scientific, Folsom, USA) under the following conditions: from 60 °C (held for 1 min) to 150 °C at 20 °C/min and from 150 °C to 240 °C at 10 °C/min. The injector was maintained at 240 °C and 2 µL aliquots of the samples were chromatographed in the splitless mode. The MS detector was kept at 230 °C and operated in the SIM acquisition mode, monitoring the 171 and 156 ions for tebuthiuron derivative and the 194 and 109 ions for caffeine.

2.4 Calibration Curves and Quantitation Limits

The calibration curves for HPLC analysis were obtained by spiking 100 mL aliquots of water purified in a MILLI Q®-plus system (Millipore) with 25 µL of each standard tebuthiuron solution, resulting in concentrations of 0.02, 0.05, and 0.1 µg/L of water (n = 2). For GC-MS analysis, 100 mL aliquots of water were spiked with 25 µl of the internal standard solution (caffeine, 5 µg/mL), in addition to the tebuthiuron standard solutions.

The quantitation limits were considered as the lower concentration that could be analyzed with errors less than 10% (n = 5).

3 Results and Discussion

The extraction procedure adopted in the present study permitted complete recovery of the herbicide (100.1%, CV = 6.4%) and elimination of interfering substances both in the HPLC (**Figure 2**) and GC-MS procedures. Caffeine, which does not suffer the derivatization reaction, was used as the internal standard only to correct errors of injection into the gas chromatography.

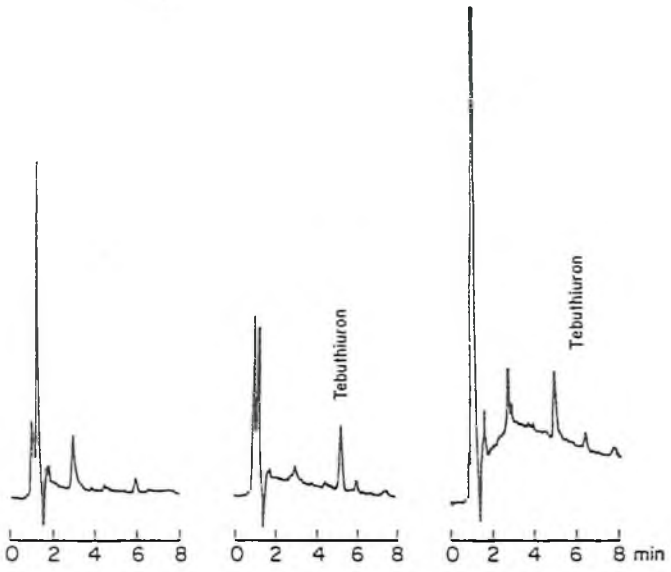

Figure 2. HPLC Chromatograms of tebuthiuron in water. A, water blank; B, water spiked with tebuthiuron (0.05 µg/L); C, water obtained from a region of intensive sugar cane culture. Column: Lichrospher® 100 RP-8, 5 µm particle size (125 × 4 mm); mobile phase: 0.05 mol/L phosphate buffer, pH 5.5-acetonitrile (73:27, *v/v*); UV detector: 254 nm.

The calibration curves obtained by the two methods showed a linear relationship between concentrations and peak areas in the 0.02 to 2.0 µg/L range for analysis by HPLC (r = 0.998) and in the 0.02 to 0.1 µg/L range for GC-MS analysis (r = 0.999). The quantitation limits of the methods (0.02 µg/L) indicate high sensitivity, permitting the analysis of concentrations below those established by international agencies of environmental control and similar to the quantification limits reported in the literature for other phenylurea in water [9, 14, 15]. It should be pointed out that the EPA has established a Lifetime Health Advisory (LHA) of 500 µg/L [20] for tebuthiuron in drinking water, a value much higher than the quantitation limit of 0.02 µg/L established in the present study.

The methods described were employed for the analysis of 250 samples obtained from the Espraiado Stream watershed, Ribeirão Preto region. The presence of tebuthiuron was confirmed only in surface water samples collected in May 1996. The concentration of 0.03 µg/L was lower than the admissible concentration of 0.1 µg/L given by the rigid criteria of the European Community [21] for any individual pesticide with a limit of up to 0.5 µg/L for the total content of pesticides. The presence of tebuthiuron was not confirmed in the ground water samples analyzed.

4 Conclusion

The HPLC and GC-MS methods reported here were suitable for the determination of residues of tebuthiuron in drinking water samples. The quantification limit of 0.02 µg/L for both methods indicates high sensitivity and make them suitable for the evaluation of environmental contamination.

Acknowledgements

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