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Short communication

Liquid chromatographic determination of imazosulfuron in drinking water and in soil using ultraviolet detection

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Abstract

Reversed-phase liquid chromatography (LC) is used to determine a relatively new sulfonylureic herbicide, imazosulfuron, 1-(2-chloroimidazo-[1,2-a] pyridin-3-ylsulfonyl)-3-(4,6-dimethoxy-2-pyrimidinyl)-urea (TH-913), in drinking water and in soil. TH-913 is extracted from water using solid-phase extraction on C₁₈ bonded silica. Soil samples (20 g) are extracted with 300 ml of methanol–water (50:50) and the acidified extracts are transferred onto Sep-Pak C₁₈ and processed as described for water samples. Off-line desorption is done with 20 ml of methanol–water (50:50). The eluate is evaporated to dryness, the residue dissolved in acetonitrile and analysed by LC with UV detection at 238 nm. The recoveries of TH-913 from water were over 95% (at 0.05 µg/l level) and from soil over 90% (at 0.005 mg/kg level). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Soil; Water analysis; Pesticides; Imazosulfuron

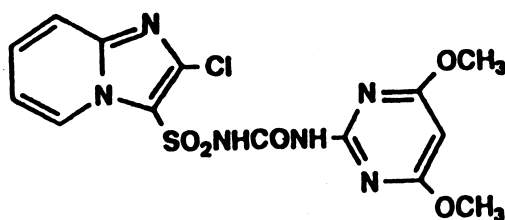
1. Introduction

The sulfonylureic herbicides are used to control common weeds and other cereal crops [1]. They are selective systemic herbicides absorbed by the foliage and roots with rapid translocation to the meristematic tissues. These herbicides act by inhibiting cell division and plant growth and have a relatively low acute toxicity for mammals. Because of their long persistence, they can migrate into surface, ground and

finally into drinking water and could be degraded by different mechanisms [2]. Therefore, there is an increasing need for rapid, reliable methods to measure trace levels of these compounds in crops, soil and in natural waters to minimize the risks associated with pesticide use. This paper describes a rapid, sensitive and reliable reversed-phase liquid chromatography (LC) method for determining a relatively new sulfonylureic herbicide, imazosulfuron, 1-(2-chloroimidazo-[1,2-a] pyridin-3-ylsulfonyl)-3-(4,6-dimethoxy-2-pyrimidinyl)-urea (TH-913) in soil and in drinking water following solid-phase extraction (SPE).

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2. Experimental

2.1. Apparatus

A HPLC instrument equipped with a pump (JASCO PU-980, Japan), a UV detector (JASCO UV-975, Japan) connected to a printer-plotter (EPSON Stylus Color 400-EPSON Italy s.p.a.) was used.

2.2. Chromatographic conditions

The column was a Intersil ODS 2, 5 μm , 4.6 mm (I.D.) \times 250 mm (GL Sciences, Tokyo, Japan). The mobile phase was acetonitrile–0.1% acetic acid (45:55) maintained at a flow-rate of 1.0 ml/min. The UV detector was operated at a wavelength of 238 nm. A 20- μl volume of sample was injected.

2.3. Reagents

All solvents were analytical reagent grade from Lab-scan (Del Chimica Scientific Glassware s.r.l., Napels, Italy). Imazosulfuron (TH-913) purity 100%, was obtained from Takeda Chemical Industries (Japan). ENVI™-18 SPE tubes were obtained from Supelco (Sigma–Aldrich s.r.l., Milan, Italy). Standard stock solution of TH-913 at a concentration of 1.0 mg/ml was prepared in acetonitrile.

3. Procedure

3.1. Water extraction

Water samples of 1.0 l (drinking water) each were spiked with the imazosulfuron standard solution (1.0

$\mu\text{g/ml}$) achieving final concentrations of 0.00, 0.05, 0.10, 0.25, 0.50 and 1.00 $\mu\text{g/l}$. Methanol (5 ml) was added to the water sample to allow a better extraction [3,4] and the pH was adjusted to 2 with 0.1 M HCl. The sample was then extracted by SPE using an ENVI™-18 SPE tube. The tube was preconditioned by elution with 3.0 ml of methanol followed by 3.0 ml of water. Air contact with the cartridge was avoided until the sample extraction had been completed. The acidified water sample was mixed well and then passed through the conditioned extraction cartridge at 5.0 ml/min under slight vacuum. After careful evaporation of the solvent under nitrogen flow, from bottom to top, the imazosulfuron, trapped on the sorbent, was desorbed by using 20 ml of methanol–water (50:50). The eluate was evaporated to dryness and the residue dissolved in 2.0 ml of acetonitrile and analysed by HPLC with UV detector at 238 nm. Four replicates at each fortification level were extracted and analysed as described above.

3.2. Soil extraction

A sandy-silty soil, with a composition of 10.25% clay, 24.35% silt, 64.40% sand and 0.80% organic carbon and a pH 7.56 obtained from SIPCAM (Salerno sul Lambro, LO, Italy) was used. Soil samples of 20 g each were placed in centrifuge tubes and spiked with the imazosulfuron standard solution (1.0 $\mu\text{g/ml}$) at final concentrations of 0.000, 0.005, 0.010, 0.050, 0.100 mg/kg. Four replicates at each fortification level were extracted with 100 ml of methanol and 40 μl of ammonia in water (25%). These suspensions were shaken for 30 min, then 100 ml of water were added to the samples and then they were shaken for 30 min again. After centrifugation (10 min, 3000 rpm Sorvall-RC2, Superspeed, Newton, Connecticut, US) the aqueous solutions were filtered and collected. The sediment was rinsed with 100 ml of methanol–water (50:50) and the rinsings were combined with the filtrates. The solutions obtained (approximately 300 ml) were concentrated to 100–120 ml by rotary evaporator and acidified using 0.1 M HCl to pH 2 and transferred onto ENVI™-18 SPE tubes. The tube conditioning, sample extraction and elution procedure were performed

as described for the water samples. The eluates were dried and analysed as described above.

3.3. Results and discussion

The solid-phase extraction (SPE) has been extensively applied to the extraction of pesticides present in water samples and to the clean-up of pesticides present in soil samples [5]. ENVI™-18 SPE cartridges that were able to withstand 1.0 l of water without breakthrough of the analyte occurring despite the small amount of sorbent were used. The recovery of imazosulfuron from water at different concentrations (four replicates) were satisfactory (between 91 and 97%). The values of RSD (0.5–2.5%) confirmed a good repeatability of the method. It was necessary to adjust the pH of the sample (pH 2) to ensure that the compound was in the form suitable for an efficient retention by the solid phase. Fig. 1 shows the chromatograms of samples, unspiked and spiked with 0.05 µg/l of imazosulfuron. Despite the limited purification procedure, the chromatograms were free of interfering peaks in the retention region of interest. The limit of quantitation of the imazosulfuron in water was 0.05 µg/l; this

quantitation limit is lower than the maximum residue limit tolerated for water in Europe (0.1 µg/l) [6]. The equation of calibration graph, obtained by plotting peak areas against concentrations of water samples spiked with imazosulfuron within the range 0.05–1 µg/l was: $y = 52875.125x + 425.5$. SD in the slope was $\pm 0.97\%$ and SD in the intercept was $\pm 26.8\%$. The mean correlation coefficient was 0.99993 (between 0.99991 and 0.99994). Fig. 2 shows the chromatograms of extracted soil samples, unspiked and spiked with 0.005 mg/kg of TH-913. The unspiked chromatogram (a) was interference-free at the retention time of the herbicide. The results of analyses of the imazosulfuron added to 20 g of soil at different concentrations gave a mean recovery of 93% (between 91 and 96%). The equation of analytical calibration graph, obtained by plotting peak areas against concentrations of soil samples spiked with imazosulfuron within the range 0.005–0.5 mg/kg was: $y = 1074893.8x + 193.2$. SD in the slope was $\pm 0.57\%$ and the SD in the intercept was $\pm 36.8\%$. The mean correlation coefficient was 0.99997 (between 0.99995 and 0.99998). The limit of quantitation was 0.005 mg/kg. The study presented here proposes a reproducible and accurate

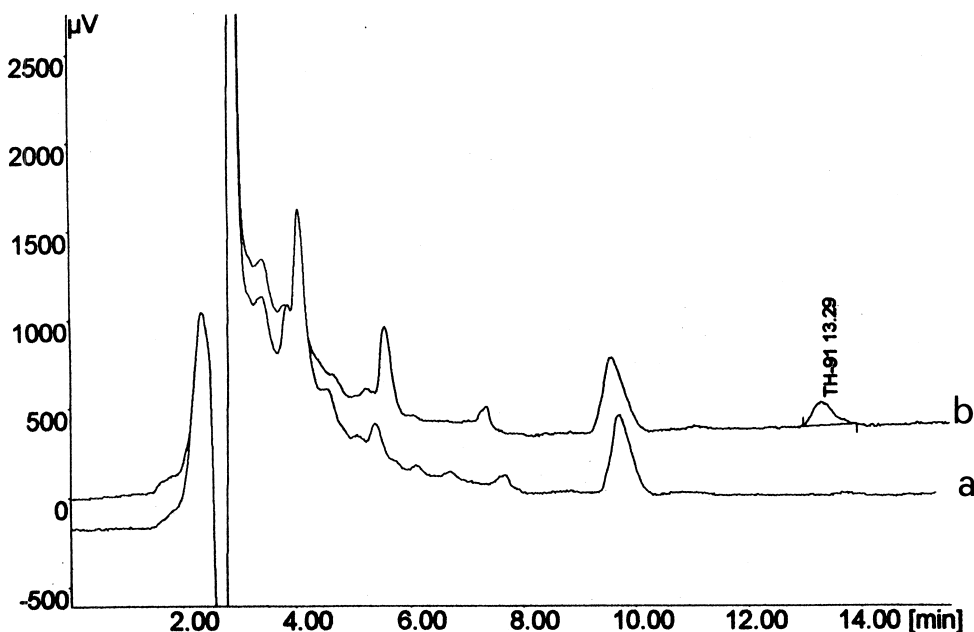


Fig. 1. HPLC chromatograms of water samples: (a) blank; (b) spiked with 0.05 µg/l of TH-913.

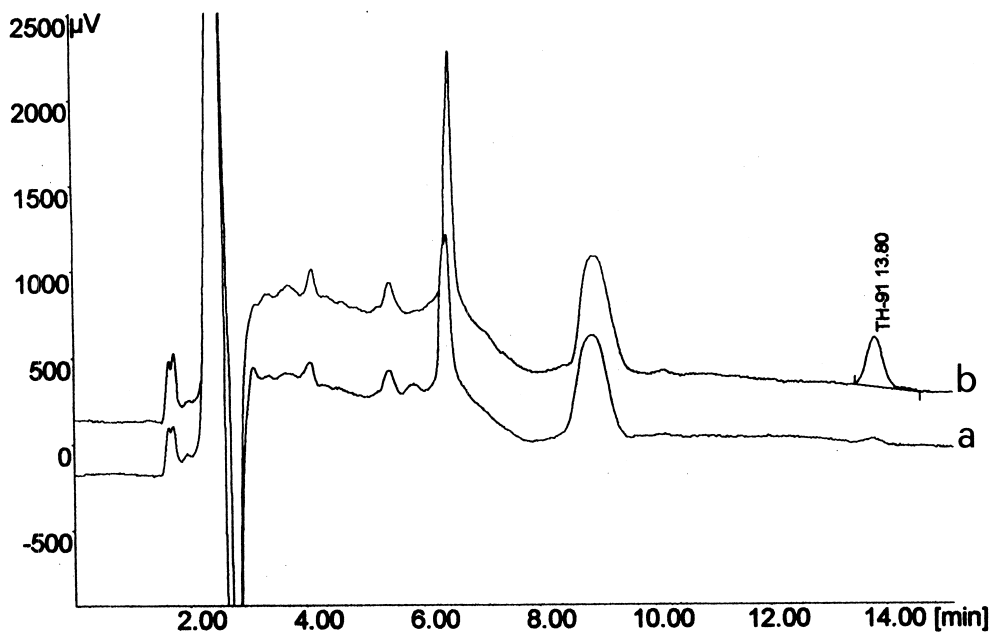


Fig. 2. HPLC chromatograms of soil samples: (a) blank; (b) spiked with 0.005 mg/kg of TH-913.

method for analysis of trace amounts of imazosulfuron in drinking water and soil samples.

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