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Analysis of primisulfuron and triasulfuron in water and soil samples by micellar electrokinetic capillary chromatography

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Abstract

A capillary electrophoresis (CE) method was developed to separate and determine residues of two sulfonylurea herbicides (primisulfuron and triasulfuron) in water and soil samples. Fortified water samples were extracted by solvent partitioning with methylene chloride and analysis by CE. Fortified soil samples were extracted by shaking in methanol–phosphate buffer (1:1) followed by partitioning of the residues into methylene chloride and analysis by CE. The method was simple, rapid and yielded excellent recoveries. Average recoveries were greater than 90% for both herbicides fortified at 10 μg/l in lakewater samples and at 50 μg/kg in soil samples. Our results demonstrate that capillary electrophoresis provides a powerful analytical tool for determination of the residues of primisulfuron and triasulfuron in water and soil samples.

Keywords: Soil; Water analysis; Environmental analysis; Primisulfuron; Triasulfuron; Pesticides; Sulfonylureas

1. Introduction

Primisulfuron (Beacon) and triasulfuron (Amber) (Fig. 1) are members of the sulfonylurea class of herbicides, manufactured by Ciba-Geigy. Primisulfuron and triasulfuron are used for control of weeds in corn and wheat, respectively. Because corn and wheat often are grown in adjacent areas, there is a potential for these two compounds to coexist in environmental samples. Sulfonylurea herbicides are popular for weed control because of their high herbicidal activity and low mammalian toxicity [1]. As with other sulfonylureas, primisulfuron and triasulfuron are applied at very low rates (20–40 and 15–30 g active ingredient/10 000 m^2, respectively). The lower application rate of sulfonylureas creates a

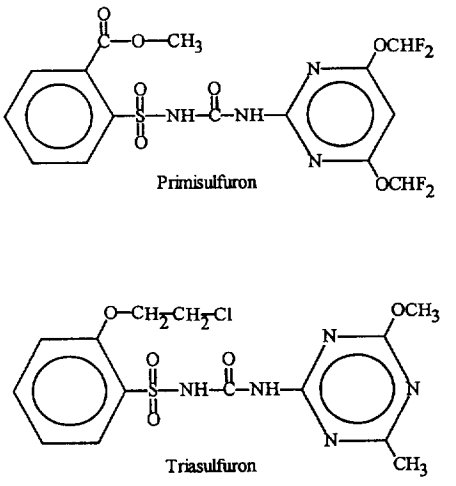

Fig. 1. Structures of primisulfuron (Beacon) and triasulfuron (Amber).

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challenge for residue analysis of these chemicals in the environment. In addition, the analytical determination of sulfonylureas is very challenging because of their polarity and thermal instability.

Available methods for sulfonylurea herbicide analysis include bioassay [2], enzyme-linked immunoassay [3], gas chromatography [4,5], high-performance liquid chromatography (HPLC) [6,7], HPLC with mass spectrometric detection (LC–MS) [8] and capillary electrophoresis (CE) [9–13]. To date there are no reports describing the use of CE for determination of primisulfuron and triasulfuron residues in environmental samples.

This paper describes the application of CE with ultraviolet (UV) detection for separation and detection of primisulfuron and triasulfuron. The CE–UV method was validated by analyzing water and soil samples fortified with known concentrations of the two herbicides.

2. Experimental

2.1. Materials

Primisulfuron and triasulfuron (each 95%) were a generous gift from Ciba-Geigy (Greensboro, NC, USA). All buffers were obtained from Sigma (St. Louis, MO, USA). All solvents (HPLC grade), and anhydrous sodium sulfate were obtained from J.T. Baker (Phillipsburg, NJ, USA). The fused-silica column used for CE was obtained from Polymicro Technologies (Phoenix, AZ, USA).

2.2. Apparatus

A Beckman P/ACE 2200 (Fullerton, CA, USA) unit equipped with UV detector was employed for CE analysis. The capillary used for separation was a 50 cm×75 μm I.D. housed in a cartridge configured for UV detection. Standard/sample injections were made using pressure injection (3.45 kPa) for 10 s, corresponding to an injection volume of 60 nl. The separations were performed at 25°C and the separation voltage was 18 kV with a resulting current of 63 μA. All operations of the P/ACE unit were controlled by an IBM personal computer with Beckman Gold Software. At the beginning of each day the capillary was rinsed with 0.1 *M* NaOH for 10 min, followed by 5 min with deionized water and 15 min with run buffer. Before each sample injection, the capillary was rinsed for 2 min with 0.1 *M* NaOH followed by 2 min with run buffer. At the end of each day, the capillary was rinsed with 0.1 *M* NaOH for 10 min followed by 5 min with deionized water. When the instrument was not in use, the electrodes were left immersed in deionized water.

2.3. Preparation of stock and calibration standards

A stock solution (1 mg/ml) was prepared by dissolving 10 mg of primisulfuron and triasulfuron in methanol in a 10 ml volumetric flask. Working standards were prepared by making appropriate dilutions of the stock solution in methanol to obtain a final concentration of 100 μg/ml, 10 μg/ml, and 1.0 μg/ml. Calibration standards were prepared by taking appropriate amounts from the working standards, evaporating the methanol to dryness using a gentle stream of nitrogen at room temperature and diluting with appropriate amounts of LC-grade water. The concentration of the calibration standards ranged from 0.1 to 10 μg/ml. The stock and working standards were stored in the dark at −20°C and the calibration standards were stored at 4°C.

2.4. Capillary electrophoresis method development

Water and soil samples were analyzed using a buffer consisting of 25 m*M* sodium phosphate (NaH_2PO_4) and 50 m*M* lithium dodecyl sulfate (LiDS), pH 6.5. Preliminary experiments were conducted with sodium dodecyl sulfate (SDS), but LiDS was chosen since the background current with SDS was high (95 μA). The compounds were detected at 214 nm. Peak area was used for the calibration curve and quantitation of primisulfuron and triasulfuron.

2.5. Water sample fortification and extraction

One liter deionized water samples ($n=3$) were buffered by adding mono- and dibasic potassium phosphate to a total of 0.1 *M*. The buffered water samples were fortified by adding a combined standard of primisulfuron and triasulfuron dissolved in

methanol to obtain a concentration of 10 μg/l of the two compounds and the pH of the fortified water was then adjusted to pH 6.0 with 1.0 *M* phosphoric acid. The samples were then transferred to 2 l separatory funnels and extracted three times with 60 ml of methylene chloride. The methylene chloride extracts were combined, dried over anhydrous sodium sulfate and evaporated to about 2 ml using a rotary evaporator at 40°C. The samples were then transferred to a 15 ml graduated test tube and the flask was rinsed twice with 5 ml of methylene chloride. The rinses were transferred to the test tube and the methylene chloride was evaporated to dryness using a gentle stream of nitrogen at room temperature. The dried samples were reconstituted with 1 ml of LC grade water, vortexed and allowed to stand overnight in a refrigerator at 4°C prior to CE–UV analysis.

Lake-water samples ($n=9$) were obtained from Lake Raleigh, Raleigh, NC, USA and filtered through a glass-fiber filter. The samples were buffered, fortified and extracted using the procedure described above. Unfortified deionized and lake-water samples served as the blank controls.

2.6. Soil sample fortification and extraction

Two types of soil samples were used for fortification of primisulfuron and triasulfuron. A sandy loam soil and clay loam soil were obtained from Central Crops Research Station, Clayton, NC and Upper Piedmont Research Station, Reidsville, NC, USA, respectively. The average soil composition for the sandy loam was 78.5% sand, 8.8% silt, 12.7% clay, 0.42% humic matter, 3.29 meq/100 g cation-exchange capacity and pH of 6.21. The average soil composition for the clay loam soil was 38.6% sand, 22.4% silt. 39.0% clay. 0.46% humic matter, 8.87 meq/100 g cation-exchange capacity and pH of 6.64.

A 20 g (dry basis) sample of soil was weighed into 250 ml PTDE bottles. The soil samples ($n=5$ for each soil type) were fortified by adding a combined standard of primisulfuron and triasulfuron dissolved in methanol to obtain a concentration of 50 μg/kg of the two compounds and the fortified samples were mixed well by hand shaking. To the fortified soil samples, 100 ml of methanol–0.1 *M* potassium phosphate buffer (1:1), pH 7.0 was added and the suspension was shaken for 1 h on a shaker table. The samples were centrifuged for 10 min at 3000 rpm ($1000\times g$) and the supernatant was filtered through a glass-fiber filter. The extraction was repeated and the liquid extracts were combined. The pH of the sample extract was adjusted to 6.0 using 1.0 *M* phosphoric acid and the samples were transferred to 500 ml separatory funnels. The samples were extracted three times with 30 ml of methylene chloride and the methylene chloride extracts were combined, dried over anhydrous sodium sulfate and evaporated to about 2 ml using a rotary evaporator at 40°C. The samples were then transferred to a 15 ml graduated test tube and the flask was rinsed twice with 5 ml of methylene chloride. The rinses were transferred to the test tube and the methylene chloride was evaporated to dryness using a gentle stream of nitrogen at room temperature. The dried samples were reconstituted with 0.5 ml of LC grade water, vortexed and allowed to stand overnight in a refrigerator at 4°C prior to CE–UV analysis.

3. Results and discussion

3.1. Capillary electrophoresis method development

Initially, a buffer consisting of 25 m*M* NaH_2PO_4+50 m*M* SDS, pH 7.2 was used for the separation of primisulfuron and triasulfuron. The separation was good, but the background current was high (95 μA). To reduce the background current we used 50 m*M* LiDS instead of SDS. Fig. 2 shows a typical electropherogram of a 10 μg/ml standard of primisulfuron and triasulfuron using a 25 m*M* NaH_2PO_4+50 m*M* LiDS buffer (pH 6.5). Baseline separation was achieved with this buffer and the analysis was complete in less than 8 min.

The detector response was linear from 0.1 to 10 μg/ml with a five-point calibration curve, with a correlation coefficient of 0.999 for primisulfuron and triasulfuron. Detection limits were calculated for a signal-to-noise ratio of 3 and were 0.2 μg/ml for primisulfuron and 0.1 μg/ml for triasulfuron. This corresponds to an injection on-column of about 12 pg of primisulfuron and 6 pg of triasulfuron. The reproducibility of migration times and peak area was tested by repeated injections of a 3.0 μg/ml combined standard of primisulfuron and triasulfuron on

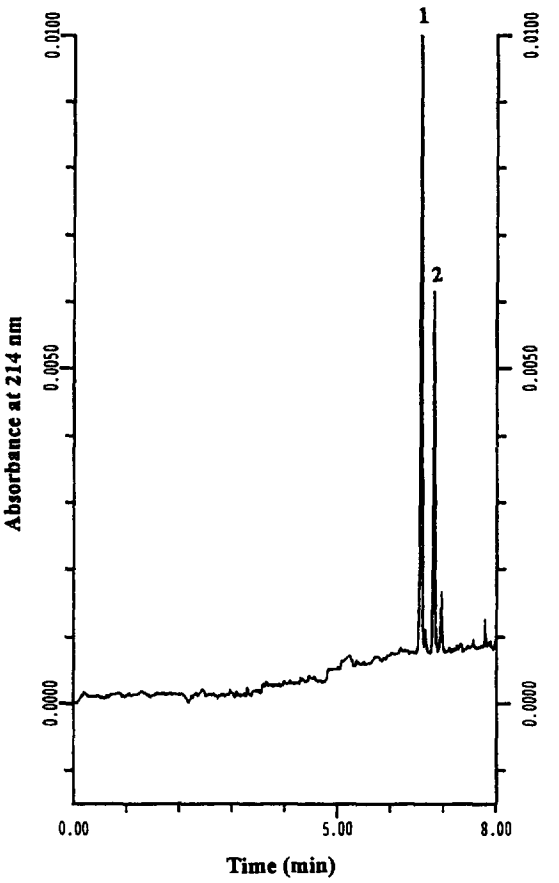

Fig. 2. Electropherogram of a 10 μg/ml standard mixture in LC-grade water: (1) triasulfuron, (2) primisulfuron. Analysis conditions: 50 cm×75 μm I.D. capillary column; pressure injection (10 s=60 nl); 25 m*M* NaH_2PO_4+50 m*M* LiDS buffer, pH 6.5; 18 kV (63 μA); 214 nm UV absorbance.

the same day (intra-day) and on different days (inter-day). The results indicate good reproducibility and quantitative accuracy of the method (Table 1). The reproducibility of migration times and peak areas are comparable to those obtained for other sulfonylureas using CE in our previous research projects [9] and by other investigators [12,13].

3.2. Sample extraction and quantitation

Primisulfuron and triasulfuron have pK_a values of 5.1 and 4.6, respectively [14]. They are soluble, on a percentage basis, in water-miscible organic solvents such as methanol or acetonitrile and are readily soluble in water at neutral or slightly alkaline pH (pH 7–9) [14]. The extraction recovery of sulfonylurea herbicides from water samples is dependent on sample pH [15]. Initial experiments with our laboratory deionized water (pH 5.1) yielded poor recoveries for primisulfuron and triasulfuron. The poor recoveries were probably due to poor partitioning of the residues of primisulfuron and triasulfuron into methylene chloride at this sample pH. Therefore, to improve recoveries it was necessary to buffer our laboratory deionized water to bring it to neutral pH prior to fortification and adjust the pH of the fortified sample before partitioning with methylene chloride. The pH of the lake-water at the time of collection was 7.0 and it was buffered prior to fortification to maintain identical experimental conditions with that of deionized water samples. The recoveries of the two herbicides were excellent at pH 6.0 and therefore the pH of the fortified water samples was adjusted to 6.0 prior to solvent partitioning of residues into methylene chloride. A similar approach of buffering and pH adjustment of water samples prior to extraction was taken by other investigators working with different sulfonylurea herbicides [7,15].

Figs. 3 and 4 show typical electropherograms of water and soil samples fortified with primisulfuron and triasulfuron. The electropherograms of fortified and control samples show no matrix interferences at

Table 1
Intra-day and inter-day migration time and peak area reproducibility (±S.D.)[a]

Compound	Migration time (min)		Peak area	
	Intra-day	Inter-day	Intra-day	Inter-day
Triasulfuron	6.35±0.01	6.42±0.09	0.12964±0.002	0.13512±0.007
Primisulfuron	6.58±0.01	6.65±0.09	0.06122±0.001	0.06403±0.003

[a] Average of eight injections of 3.0 μg/ml combined standard in the same day (intra-day) and on different days (inter-day).

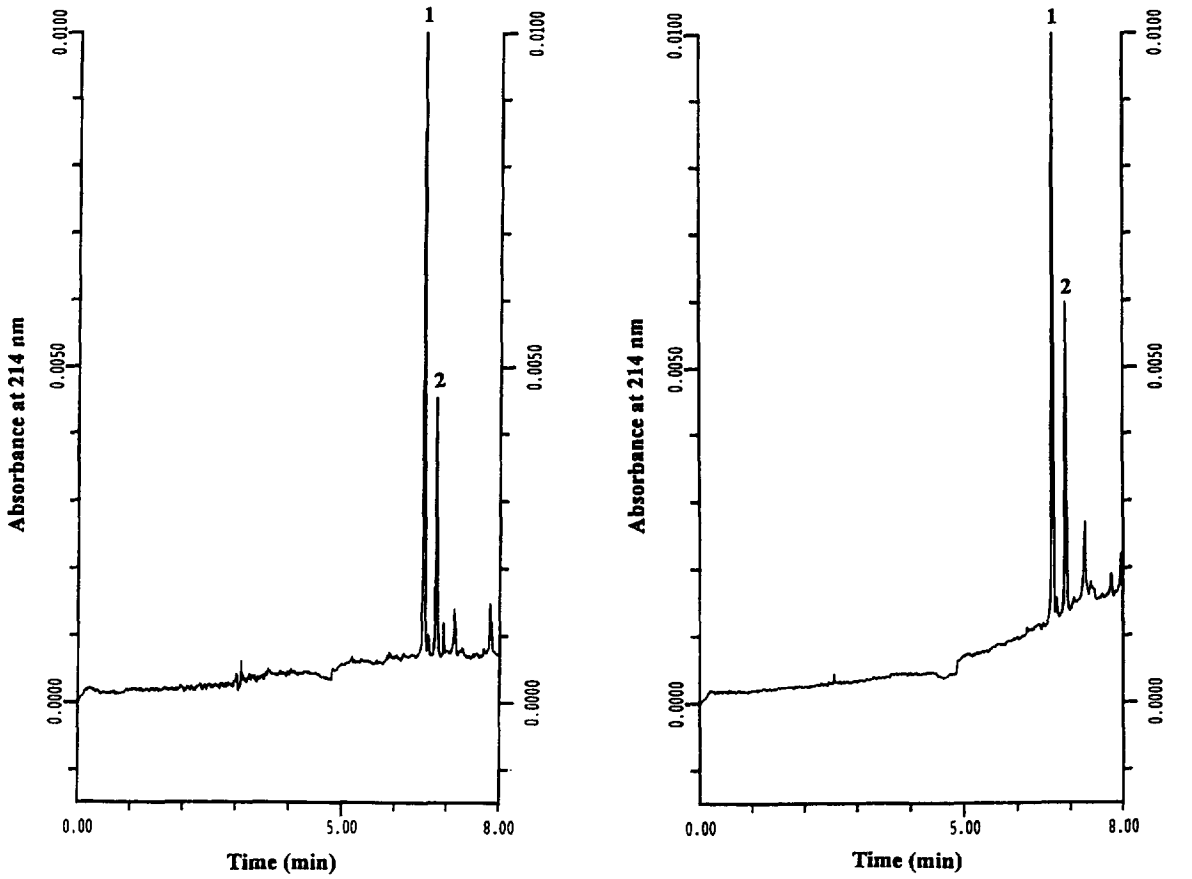

Fig. 3. Electropherograms of (left) deionized water sample and (right) lake-water sample fortified with 10 μg/l primisulfuron and triasulfuron followed by liquid–liquid extraction: (1) triasulfuron, (2) primisulfuron. Analysis conditions are the same as described in the legend to Fig. 2.

the migration time for the two compounds. This is probably due to on-column exclusion of matrix interferences during the CE separation and due to some interferences having longer migration times than the two herbicides as evidenced by a peak eluting after primisulfuron (Fig. 4). The water and soil samples were quantitated, through peak area response, against a 10 μg/ml and 2 μg/ml combined standard of primisulfuron and triasulfuron, respectively. The recoveries of primisulfuron and triasulfuron in water and soil samples are reported in Table 2. The results show excellent recoveries (≥90%) for the two compounds in both water and soil matrices using the extraction procedure outlined in Sections 2.5 and 2.6.

4. Conclusions

This work demonstrates the use of capillary electrophoresis for analysis of primisulfuron and triasulfuron in water and soil samples at the ppb level. The reported method is simple, rapid and yields excellent recoveries for the two herbicides.

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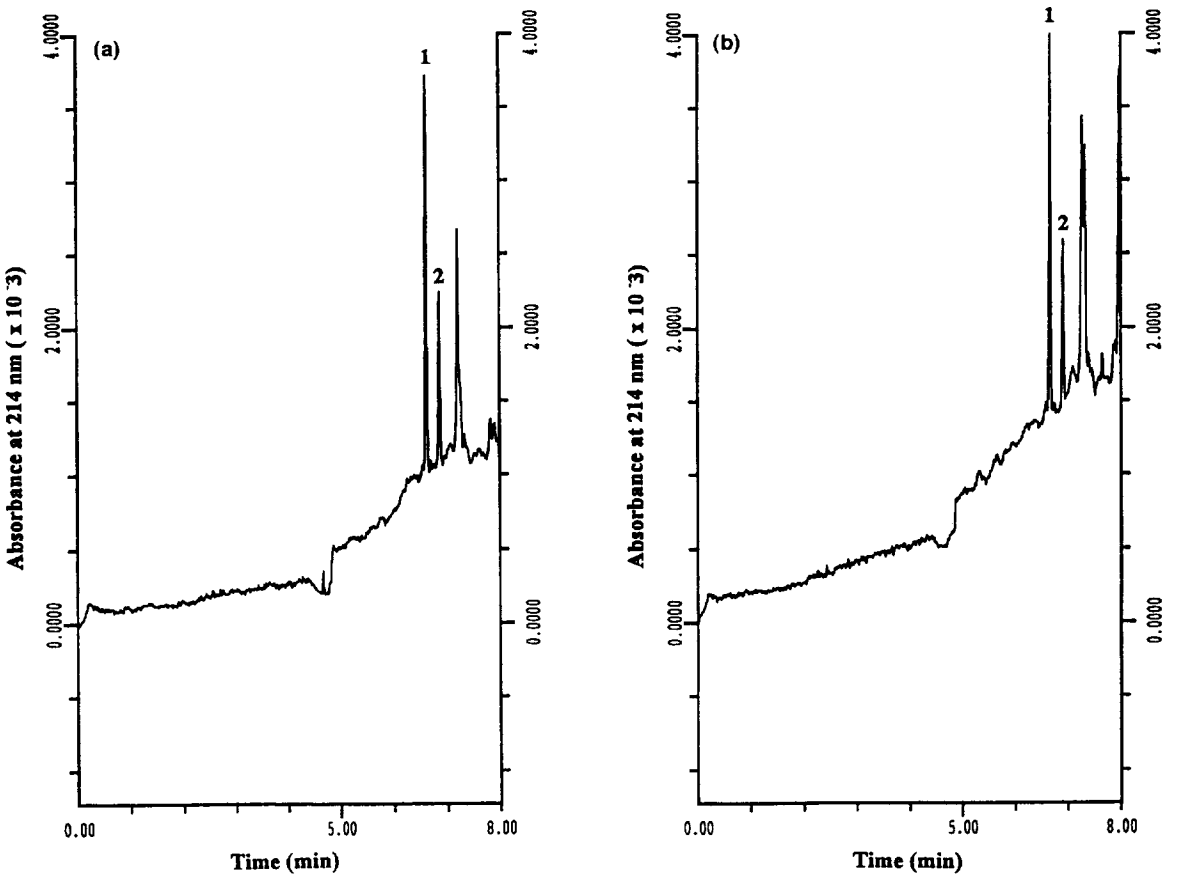

Fig. 4. Electropherograms of (a) sandy loam soil and (b) clay loam soil fortified with 50 μg/kg primisulfuron and triasulfuron followed by extraction: (1) triasulfuron, (2) primisulfuron. Analysis conditions are the same as described in the legend to Fig. 2.

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Table 2
Percent recovery of fortified water and soil samples

Matrix	% Recovery (±S.D.)	
	Triasulfuron	Primisulfuron
Deionized water[a]	101±2	90±5
Lake water[b]	106±3	97±3
Sandy loam soil[c]	95±4	96±6
Clay loam soil[c]	90±4	90±7

[a] Average of three samples; [b] average of nine samples; [c] average of five samples.

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