Study on the Enantioselective Degradation of Imazethapyr in Soil by CE

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Abstract

A method was developed for the separation of imazethapyr enantiomers using capillary electrophoresis and large volume injection. Optimized buffer conditions were found using 6% hydroxypropyl- β -cyclodextrin as the chiral selector at pH 11 with an injection time of 20 s (0.5 psi). The limits of detection (LOD, S/N = 3) were 0.22 and 0.23 mg L⁻¹ for the two imazethapyr enantiomers (imazethapyr-I and imazethapyr-II) respectively. The relative standard deviation was less than 5%. This method was successfully used in the study of enantioselective degradation of this herbicide in field soil and the results suggested that imazethapyr-I degraded at a higher rate when compared with imazethapyr-II.

Keywords

Capillary zone electrophoresis
Enantioselective degradation
Imazethapyr
Soil

herbicidal activity [3, 4]. Ramezani and colleagues studied the photodegradation of imazaquin and found that no enantioselective degradation has been observed in water [4]. Imazethapyr shows excellent activity against annual and perennial grass and broadleaved weeds [5].

Capillary electrophoresis (CE) is an important, rapid and versatile technique for the separation and determination of chiral herbicides [3]. A wide range of chiral selectors are added to the running buffer in order to achieve chiral separation. Commonly used additives include cyclodextrins (CDs), macrocyclic glycopeptide antibiotics, crown ethers and proteins [6]. In the present study, a CD derivative was selected for the analysis of enantioselective degradation of imazethapyr in field soil.

Introduction

Many pesticides are chiral compounds and consist of two or more enantiomers, which may differ in biological activity, toxicity, and environmental fate [1]. Several racemic pesticides have been replaced by one isomer in the attempt to

decrease the release of inactive isomers into the biosphere. In recent years, enantioselective degradation of various herbicides in soil have been described [2].

Imidazolinone herbicides are chiral compounds and widely used for broad-spectrum weed control and previous studies reported on enantioselective

Materials and Methods

Chemicals

All the reagents, except imazethapyr, were of analytical grade. Imazethapyr (98%) was purchased from Jingmei Chemical Industry Company (Hebei, China). Hydroxypropyl- β -cyclodextrin

Table 1. Characteristics of the proposed CE method under optimized conditions

	<i>a</i>	<i>b</i>	<i>r</i> ²	Linear Range (mg L ⁻¹)	LOD (mg L ⁻¹)	LOQ (mg L ⁻¹)	RSD (%) (<i>n</i> = 6)	Recovery (%) (15 mg kg ⁻¹ soil)	Recovery (%) (5 mg kg ⁻¹ soil)
Imazethapyr-I	852.64	711.59	0.999	0.49–14.77	0.22	0.56	2.39	87.81	83.61
Imazethapyr-II	835.52	751.20	0.999	0.51–15.23	0.23	0.58	2.54	88.32	83.75

Calibration curves are expressed as regression lines ($y = ax + b$), where y is the ratio of the peak area of enantiomeric compound, x is enantiomer concentration (mg L⁻¹), a is slope, b is intercept, and r^2 is the correlation coefficient

Fig. 1. Degradation of imazethapyr in field experiments. **a** Capillary electropherograms of imazethapyr degradation after day 1 and 11, respectively. For experimental conditions see “Experimental”. **b** Degradation of imazethapyr over the period of 30 days showing decreased concentration and ER values. Peaks: 1 = imazethapyr-I, 2 = imazethapyr-II

(HP- β -CD) was purchased from Acros Organics (Fair Lawn, NJ, USA).

Apparatus and CE Separation Condition

CE separation was carried out on a Beckmann P/ACE MDQ CE system with a UV detector at 214 nm (Beckman, Fullerton, CA, USA). A fused silica capillary (Yongnian, Hebei, China), 50 μ m i.d., total length of 60 cm (50 cm to detector), was used. Before first use, the capillary was flushed with 1 M NaOH for 10 min, ultrapure water for 10 min, and finally with the running buffer for 10 min. Between runs the capillary was flushed with ultrapure water for 3 min. The running buffer was a 25 mM phosphate solution containing 6% HP- β -CD (pH 11). Injection samples were prepared by diluting the stock solution of imazethapyr (1000 mg L⁻¹ in methanol) with water containing 6% HP- β -CD. Pressure injections were performed at 0.5 psi and injection time was 20 s. Separation voltage was 20 kV and temperature was controlled at 25 °C.

Sample Treatment

The soil samples were collected from a *Setaria faberi* field located at Qinghe, Beijing. During the flourishing period, imazethapyr was sprayed thoroughly at 0.2 g m⁻². Soil samples (15 g) were randomly collected at a depth of about 1–15 cm from the surface soil on days 0, 1, 4, 7, 11, 15 and 30, respectively. The soil samples were sieved (2 mm) and mixed with 20 mL methanol and then ultrasonicated for 30 min. After filtration the soil phase was extracted twice with fresh solvents. The filtrate was combined and concentrated on a rotary evaporator to near dryness. For analysis, the residue was filtered through a 0.45 μ m filter and dissolved in 2 mL ultrapure water containing 6% HP- β -CD.

Results and Discussion

Method Development

HP- β -CD is chemically modified with hydroxypropyl groups which results in

good aqueous solubility and it was anticipated to achieve ideal separation of imazethapyr enantiomers.

The pH value is one of the most important factors for CE separations and considering that imazethapyr has three p*K*_a values of 2.1, 3.8 and 10.5, we studied the pH from 3 to 12 during separation. Two optimized pH values were observed at pH 6.5 and 12, respectively. When the pH was above 4, the imazethapyr enantiomers only partially separated. Increased pH values improved interactions between enantiomers and HP- β -CD, resulting in improved separation with a maximum resolution at pH 6.5. From pH 6 to pH 9, the resolution of the enantiomers decreased, but it was subsequently observed to increase again from pH 9 to pH 12, which was probably based on the p*K*_a of 10.5 and increased ionization. Ultimately, pH 11 was chosen for the separation based on the fact that the observed current was considered too high at pH 12.

The resolution was observed to be poor when sample matrix and buffer were identical. When the sample matrix did not contain any electrolytes, resolution was found to increase to 1.5. To enhance the detection, a 20 s injection time was selected.

Method Validation

For imazethapyr-I and imazethapyr-II, the limits of detection (LOD, S/N = 3) were determined to be at 0.22 and 0.23 mg L⁻¹ and the limits of quantification (LOQ, S/N = 3) were 0.56 and 0.58 mg L⁻¹, respectively (Table 1). Recoveries, RSD and calibration curves for both imazethapyr enantiomers are also shown.

Degradation of Imazethapyr in Soil

The enantiometric ratio (ER) was defined according to literature [3] to evaluate the enantioselective degradation. Figure 1 shows that imazethapyr-I appeared to degrade faster than imazethapyr-II, and ER slowly decreased over time from 0.97 (day 1) to 0.58 (day 30), which indicated enantioselective degradation of both enantiomers.

Ramezani and co-workers [4] pointed out that abiotic degradation of imidazolinone herbicides is likely to be slow in the environment. It is known [1–3] that different soils contain different fungi, bacteria and actinomycetes, which have been described to be the key factor for

the bio-degradation of herbicides in soil. Here, the enantioselective degradation of imazethapyr in *Setaria* field soil may have also been caused by similar principles.

Conclusion

A sensitive, rapid and reliable CE method was applied to the separation of imazethapyr enantiomers using HP- β -CD as the chiral selector. The fact that imazethapyr-I was observed to degrade more rapidly under the soil conditions studied, led to the conclusion that enantioselective degradation was present.

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