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Analysis of residues of prometryne and acetochlor in soil–water system by solid-phase extraction and gas chromatography/mass spectrometry

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ABSTRACT

A highly sensitive and simple analytical method was developed for analyzing the binary mixed pesticides of prometryne and acetochlor in soil–water system by gas chromatography/mass spectrometry (GC/MS). The sample solution was first purified by C_{18} solid-phase extraction column, which was leached by acetone. The leachate was enriched to 1.0 mL by pressure blowing concentrator and then analyzed by GC/MS. The linear calibration curves were showed in the range of 1–15 μg/mL with a correlation coefficient of 0.9991. The average recoveries ($n = 5$) were between 95.3 and 115.7%, with relative standard deviations ranged from 1.71 and 7.95%. The limits of detection of Prometryne/Acetochlor were up to 0.06 and 0.17 μg/mL, respectively. This method provides a reliable approach to examine and evaluate the residues of prometryne and acetochlor in the soil–water system.

Keywords: Soil; Prometryne; Acetochlor; Solid-phase extraction; Gas chromatography-mass spectrometer

1. Introduction

Pesticides are used widely in agriculture to protect plants from disease, weeds, and insect damage, but also bring an abundance of environmental problems at the same time [1]. They present a certain risk in the environment and especially in the soil. Soil is one of the most important environmental materials that influences and has been influenced by plants, naturally also serves as one of the most important sources of pollution [2]. There are a few reports that 60% of

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pesticide-spraying entered into soils. Therefore, the research in pesticides of soil is increasingly important compared with other environmental contaminants, because they can be present at higher levels in soil than the parent pesticides themselves [3–6].

Prometryne/Acetochlor (PA) is a binary mixtures of pesticides of triazine herbicide named prometryne and amides herbicide named acetochlor [7], with low toxicity, prominent efficacy, and a wide spraying range and a high spraying frequency. It can not only expand the weed control spectrum, but also reduce the resistance of drugs [8]. There are a wide range of applications of PA in dry land and paddy fields [9]. Adsorption and desorption of PA in soil is critical for its properties of exchange in soil and water [10–14]. The development of an effective analytical method for the residues of PA in soil–water system is desirable. It is particularly important in the study of the environmental behavior of PA in soil–water system [15]. The well-known methods for analysis of PA usually are gas chromatograph and high-performance liquid chromatography as the quality control of PA on production line [16–18]. Even numerous methods for analysis of pesticide residues in soil have been developed [19–22], there are few reports on the analytical methods to simultaneously detect the residues of PA in soil–water system, only a few reports on analysis of acetochlor or prometryne in the food, water, and soil, respectively [23–26]. In this study, we combined pre-extraction by C_{18} and gas chromatography-mass spectrometry (GC/MS) for simultaneous detection of PA in the soil matrix, which provide a simple and highly sensitive analytical method in soil–water system. This method can be used for the future study in the behavior of PA in transport and exchange in soil and water.

2. Materials and methods

2.1. Materials

Shimadzu GC/MS-QP-2010, including automatic sampler, WBI-2010 injection port, quadrupole mass analyzer of Shimadzu, working software of GC/MS solution; chromatographic column was Rtx-5MS (30 m × 0.25 mm × 0.25 μm); all reagents are analytical reagent; ultrapure water (18.12 MΩ·cm, AKP); florisil solid-phase extraction (SPE) column, C_{18} SPE column (Angilent, 500 mg/6 mL). The standards of prometryne and acetochlor are from Environmental Protection Scientific Research Monitor Institute of the Ministry of Agriculture, China.

The soil samples were collected from the vegetable field of Dounan, Yunnan Province. The samples were dried in air, then evenly mixed and pestled, sifted 1 mm, and their potential of hydrogen (pH), content of organic matter and particle size distribution were measured, respectively. The results are shown in Table 1.

Table 1
Physical and chemical properties of soil

Sampling site	Vegetable field of Dounan
Organic matter (%)	3.06
pH	7.32
Cation-exchange capacity (mmolkg^{-1})	47.03
Water content (%)	7.06
Sand content (%)	15.52
Viscous force (%)	11.26
Particles (%)	24.08

2.2. Methods

2.2.1. Standard solution preparation

The standard stock solution was prepared by dissolving 25 mg PA in 25 mL pure water. The prepared standard stock solution was stored in the refrigerator.

2.2.2. Sample extraction

Ten gram soil samples ($d < 1$ mm) was added into 250-mL beaker. Then, 100 mL water was added to the same beaker flask, oscillating for 24 h under the constant temperature of 25℃. They were centrifuged at 3,000 rpm. The supernatant was collected as soil/water solution.

According to ratio, the solution was made up of the standard stock solution of PA and soil/water solution.

2.2.3. Sample purification

The SPE column was first activated by 5 mL methanol and 5 mL ultrapure water, and then, it was added to the ready-to-use solution, until the base liquid flow ended by gravity column. It was leached with 5 mL acetone and concentrated to 1.0 mL by pressure blowing concentrator (under 35℃), then filtrated with microporous membrane ($d < 0.45$ μm). The solution was ready for analysis by GC/MS.

2.2.4. Chromatograph conditions

The pesticides were analyzed on a Shimadzu GC/MS-QP2010 instrumentation equipped with WBI-2010 injection device and an Rtx-5MS capillary column

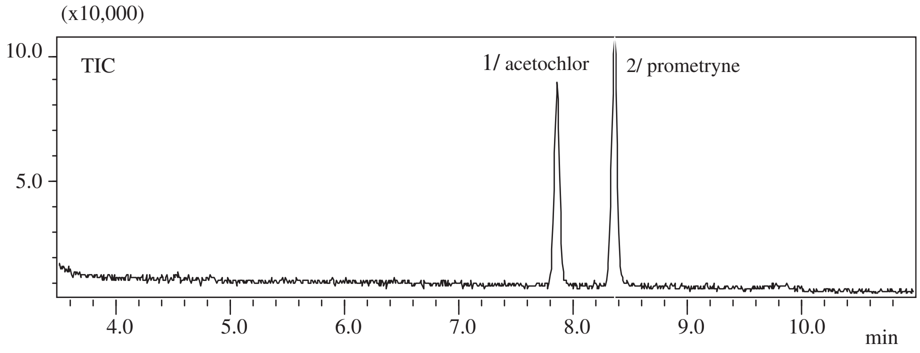

Fig. 1. TIC of prometryne and acetochlor by GC/EI/MS.

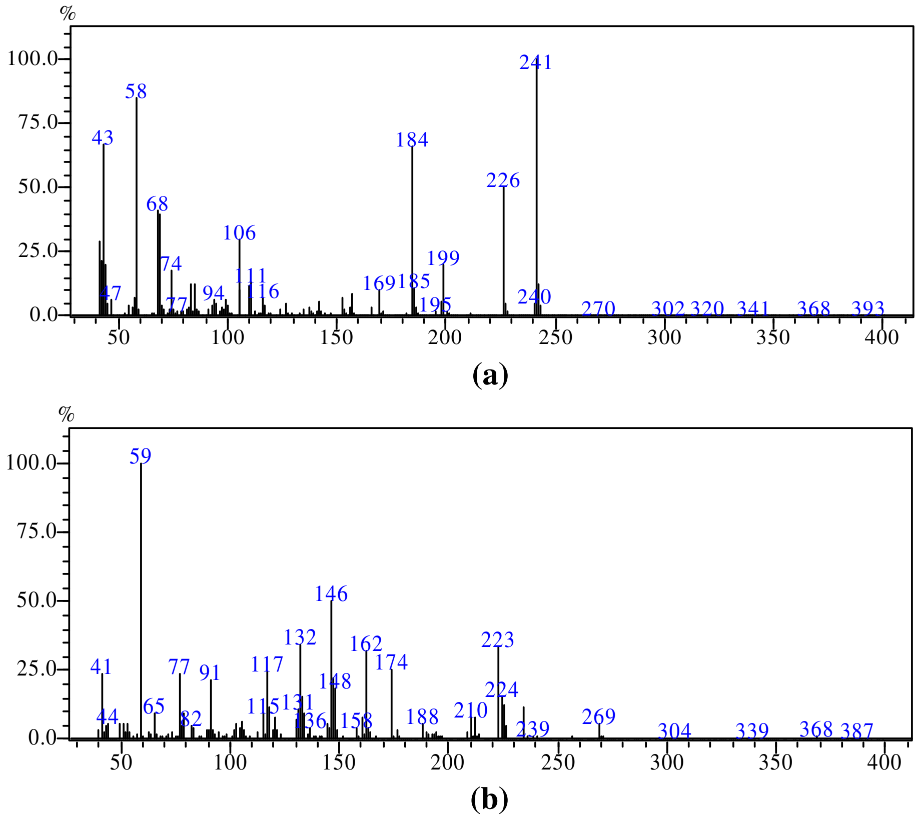

Fig. 2. The mass spectrum of prometryne (a) and acetochlor (b) by GC/EI/MS-SCAN.

(30 m × 0.25 mm × 0.25 μm). Injector temperature was 250℃. Column temperature program was 190℃ for 2 min, 2℃/min up to 200℃ for 4 min. Carrier gas was helium (0.8 mL/min), and the purging flow was 5 mL/min. The injection was carried out in split (20:1), and the injection volume was 1 μL. The quadruple mass spectrometer was operated in the electron impact ion mode. Ion source temperature and interface temperature were all set at 200℃. The mass spectrometer was operated in an ionizing energy of 0.7 kV.

Table 2
The quantitative ions and reference ions of prometryne and acetochlor

	Prometryne	Acetochlor
Mol. wt.	241.4	269.8
Quantitative ion	241 (100)	59 (100)
Reference ion (Ⅰ)	58 (51.5)	146 (85)
Reference ion (Ⅱ)	184 (34.9)	223 (65.8)

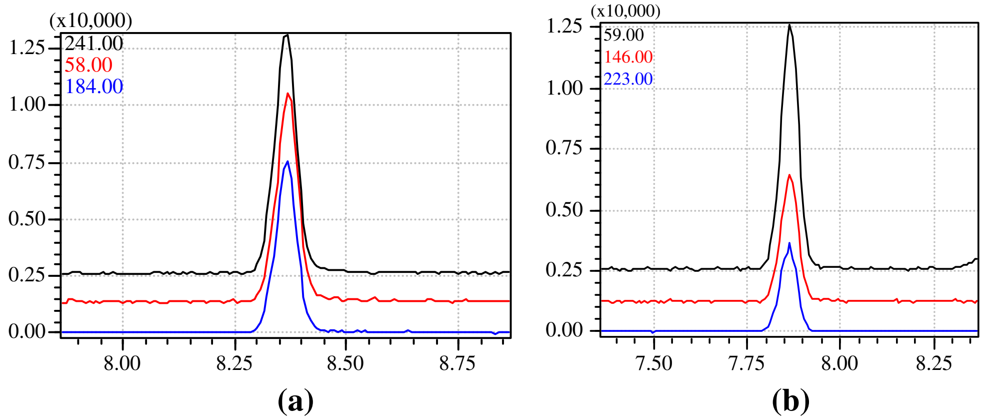

Fig. 3. The MC of prometryne (a) and acetochlor (b).

Scan interval was 0.2 s. Ion detection mode was selected ion monitoring.

3. Results and discussion

3.1. Chromatographic conditions optimization of experimental condition

3.1.1. Columns

According to the structure and polarity of prometryne and acetochlor, we compared the separation efficiency of four capillary columns through Rtx-1701, Rtx-1MS, Rtx-50MS, and Rtx-5MS, we found Rtx-5MS with good separation efficiency. The peak resolution was much better.

3.1.2. Solvents

In this experiment, the solvents were chloroform and acetone, and the solubility of them was good for prometryne and acetochlor. The results showed that the purity of chloroform was a predominant influence to analysis. When acetone was used as a solvent, the chromatogram peak was better.

3.1.3. Selection of characteristic ions

Selective ion scan was used to improve the signal-to-noise ratio. In all scanning mode, the total ion flow chromatograms (TIC), and the mass spectrum diagram of various compounds are shown in Figs. 1 and 2. The characteristic ions of prometryne and acetochlor could be confirmed according to Fig. 2, and Table 2 presents the three characteristic ions (1 of quantitative ion, 2 of reference ions). The quality chromatograms (MC) (Fig. 3) were obtained by scanning the target compounds during the chosen period of the three characteristic ions. The qualitative and quantitative analysis was determined by the retention time, characteristic ions, and relative abundance. Peak areas of ions were quantified by external standard methods (Fig. 4).

3.2. Sample pretreatment process

Florisil and C_{18} SPE small columns were chosen. Under the same conditions, the recovery was determined (Table 3). The recovery of the two kinds of pesticides on C_{18} column was superior to Florisil column. The recovery of prometryne was lower, but it could meet the requirements of pesticide residue analysis. So the C_{18} column was chosen.

3.2.1. Selection of elution agents and volume

Acetone, ethyl acetate, and methanol were selected as the solvent elution. The results are shown in Table 4. From Table 4, we found ethyl acetate was the elution, and the deviation was larger, and the devia-

Table 3
Recoveries of the different extraction columns

Pesticides	C_{18} column				Florisil column			
	1	2	3	Average recovery rate (%)	1	2	3	Average recovery rate (%)
Prometryne	79.5	83.4	85.6	82.8	64.4	68.1	63.7	65.4
Acetochlor	96.1	96.7	97.6	96.8	76.1	77.2	76.9	76.7

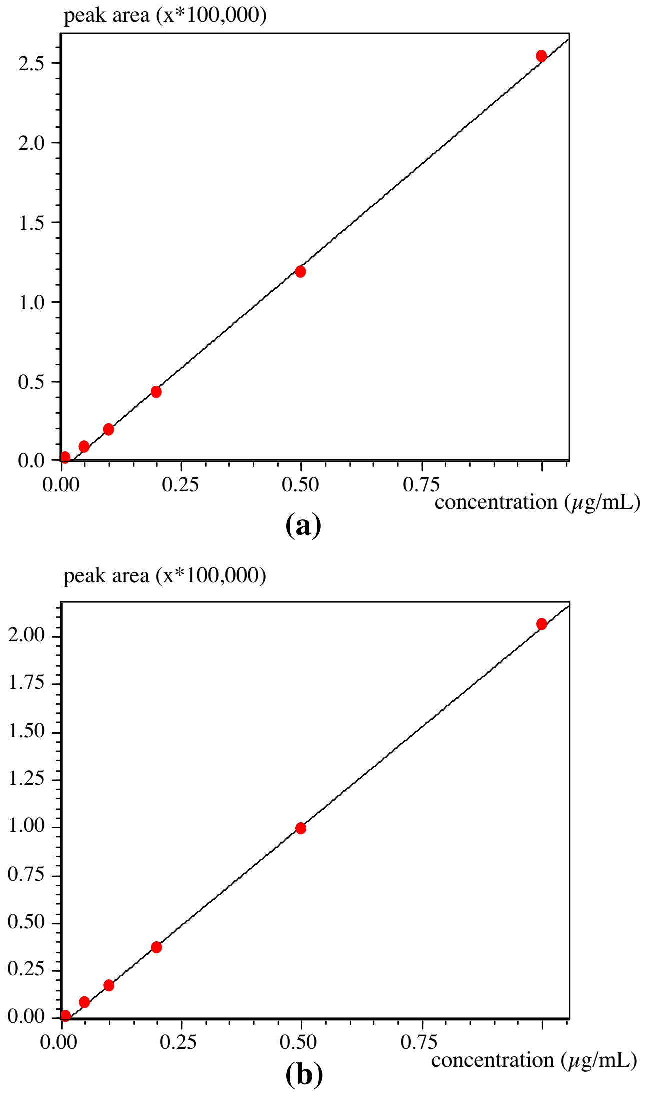

Fig. 4. The calibration curve of prometryne (a) and acetochlor (b).

Table 4
Recovery of different elution solvents

	Prometryne	Acetochlor
Acetone		
Recovery (%)	82.8	96.1
RSD (%)	4.04	0.7
Ethyl acetate		
Recovery (%)	96.2	86.3
RSD (%)	9.8	10.7
Methanol		
Recovery (%)	93.8	6.3
RSD (%)	77.9	4.8

Table 5
Linear equations, correlation coefficient, and limit of detection

	Prometryne	Acetochlor
Linear equation	$Y = 539.4395X - 106.9414$	$Y = 604.3669X - 447.871$
Correlation coefficient (r)	0.9991	0.9991
Detection limit (μg/ mL)	0.06	0.17

tion is due to more impurities and interference factors in the process of elution. Acetone was selected as the solvent elution. We compared the leaching effect of acetone with 2, 4, and 6 mL, respectively. The results showed that these two kinds of pesticides can be cleaned up within 4 mL. So, we chose 4 mL as the elute volume.

3.3. Detection limit

Different concentrations of pesticide in soil/water solution were prepared and followed by extraction, enrichment, and purification. The minimum detection limit of the method was calculated according to the method of triple noises. The results are shown in Fig. 4 and Table 5.

3.4. Recovery and precision

The recovery experiment of prometryne and acetochlor was done at three concentration levels of 15, 3, and 1 μg/mL in soil–water system fluid. Each concentration level was determined in parallel five times. Set a blank control. The recovery is the average of sample determined in parallel five times. The precision was expressed by relative standard deviation (RSD) of sample size in five. The results of recovery rate and precision are shown in Table 6. The results show that the recovery is from 95.26 to 115.70%, the RSD is from 1.71 to 7.95%, and both of them have good accuracy and reproducibility.

Table 6
Add recovery and precision

	Prometryne	Acetochlor
Added concentration (ug/mL)	15, 3, 1	14.1, 2.8, 1
Recovery (%)	100.9, 101.8, 109.2	101.6, 95.3, 115.7
RSD ($n = 5$) (%)	4.28, 2.39, 7.59	1.71, 4.23, 8.17

4. Conclusions

We developed an effective approach combined SPE and GC/MS method to determine PA in the soil–water system. The method can be used to simultaneously detect the residues of prometryne and acetochlor in the soil–water system. After extracted and purified by the solid-phase columella C_{18}, the matrix interferences could be removed effectively. Through the optimization of analytical condition and scanning ion, this method provides high sensitivity, precision, and accuracy for analysis of Prometryne-Acetochlor. This approach can be useful for the future study in PA behavior of transport and exchange in soil and water.

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