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Analysis of Chlorpyrifos in Water, Soil and Cabbage Samples by Solid Phase Microextraction and Gas Chromatography/Mass Spectrometry

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The feasibility of solid phase microextraction combined gas chromatography/mass spectrometry for determination of organo phosphorus pesticide chlorpyrifos in the water, soil and cabbage samples is evaluated. Solid phase microextraction analyses were carried out with polydimethylsiloxane and polyacrylate fibers. The chlorpyrifos was extracted with direct solid phase microextraction by inserting the fiber through the cap and exposing it to the sample for 1 h. The extraction efficiency of polydimethylsiloxane fiber is 1.5 times in the water and 2 times in the soil comparing to polyacrylate fiber. Good linearity ($r > 0.9985$) is observed in the 0.05-10 mg L^{-1} concentration range in the water sample, the limit of detection using the proposed method in the water was 0.05 mg L^{-1}; linearity range ($r > 0.9982$) was better in the 0.01-5 mg kg^{-1} concentration range in the soil sample, the limit of detection was 0.01 mg kg^{-1}; linearity range in the cabbage sample ($r > 0.9979$) was better also in the 0.01-5 mg kg^{-1} concentration range, detection limit of chlorpyrifos in the cabbage was 0.01 mg kg^{-1}. Experimental results confirmed the usefulness of the proposed method.

Keywords: Organophosphate insecticide, SPME, GC/MS.

INTRODUCTION

Chlorpyrifos (*O*,*O*-diethyl-*O*-3,5,6 trichloro-2-pyridyl phosphorothioate) is a moderate toxicity organophosphate insecticide and was widely used for insect pest control in the agriculture and family [1]. It had low water solubility and weak polarity. In order to develop super and safe crops, chlorpyrifos substituting for the very toxic organophosphate insecticide and its application amount increased year after year. Chlorpyrifos was broad-spectrum pesticide and was widely used for insect control in the soil and on grain, cotton, fruit, nut, as well as lawns and ornamental plants, especially on the vegetable crops [2]. Its application amount was very massive, the residual time of the pesticide in the leaves was not very long, but the time of existing in the soil was longer, so it could prevent soil insect effectively. The application amount of chlorpyrifos in the environment is so massive that public concerns on vegetable and environment safety have been rising. By the investigation, in field trials of rice, maize and soybean, the highest residues were 3.23, 0.114 and 0.102 mg kg^{-1} respectively [3]. There was report that chlorpyrifos had chronic toxicity on the human and it did harm on the nervous system of children [4] and also induce DNA damage [5], the embryonic malformations for rhinella arenarum and alteration of polyamine metabolism were caused by chlorpyrifos pollution [6], Consequently it is very significant that monitoring the residue of chlorpyrifos in the environment.

According to the previous studies, there were many methods for the determination of chlorpyrifos residues, such as ultraviolet spectrophotometry [7], enzyme membrane biosensor [8], high performance liquid chromatography [9] and gas chromatography [10]. In this study, chlorpyrifos has been monitored by GC/MS and this is a high sensitivity and high accuracy method.

There are several traditional sample preparation methods for the determination of organophosphorus pesticide (OPPs) in the water, soil and others samples, such as liquid-liquid extraction and solid phase extraction [11-15]. But these procedures are mostly time consuming and require a large amount of toxic organic solvent. At present, the new technology of pesticide residues in the world mainly includes: solid phase micro extraction [16], solid phase extraction [17], pressurized fluid extraction [18], accelerated solvent extraction [17], supercritical fluid extraction [19], gel permeation chromatography [20], *etc*. For supercritical fluid extraction and accelerated solvent extraction, the employed experimental apparatus is relatively expensive, which limits its application in the analytical field of pesticide residue. These new sample pretreatment

techniques are developing in the direction of rapid, precision, environmental protection, miniaturization and technology union, so more and more technical support for the qualitative and quantitative analysis of pesticide has been provided.

Nowadays many new technologies of analysis of pesticide residue have been developed rapidly; SPME is a convenient alternative to other extraction methods because it is rapid, easily automated and integrates extraction, concentration and sample introduction into a single step without use of solvent, which is generally known as the optimal experimental method to conventional extraction method. There are two main extraction methods of SPME, including direct immersion solid phase microextraction (DI-SPME) and headspace-solid phase microextraction (HS-SPME). Generally, the HS-SPME approach can reduce the complex matrix effects [21], because the fiber is not directly contacted with the samples and at the same time only volatile and semi-volatile organic compounds can be released into the headspace.

The main objects of this study was to test the effectiveness of the SPME method combined with gas chromatography/mass spectrometry for the determination of organophosphorus pesticides chlorpyrifos in the water, soil and cabbage samples.

EXPERIMENTAL

Acetone was analytical grade and was redistilled in an all-glass system prior to use. Chlorpyrifos (purity 99.5 %) was obtained from Dikma (California, USA). First the working standard solution of chlorpyrifos with the concentration of 100 μg mL^{-1} was made up by acetone and then the concentration of 0.1, 0.5, 1, 5 and 10 μg mL^{-1} was made up by dilution method.

GC/MS analysis of chlorpyrifos: The analyses of chlorpyrifos were carried out by the Clarus 500 GC/MS (Perkin Elmer USA) in the splitless mode at an injector temperature of 250 °C. The column was an Elite-5MS (Perkin Elmer) capillary column (containing 5 % diphenyl and 95 % dimethylpolysiloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). The oven temperature was programmed from an initial temperature of 80 °C (1.0 min hold) to 280 °C at a rate of 10 °C/min, maintained at 280 °C for 10 min. Electron ionization with an electron energy of 70 eV was used. The ion source temperature of the mass spectrometer was 250 °C. Scanning was from 40 to 550 u. The transfer line temperature was 250 °C. Quantitative analysis was performed by using selected ion monitoring (SIM) mode with the characteristic ion at *m/z* 197.

Solid phase micro extraction procedure of chlorpyrifos in the water: The residue of chlorpyrifos in the water was extracted by the direct SPME. Analysis of water was carried out by placing 3 mL water with the chlorpyrifos in the screw-capped glass flasks with Teflon-lined septa. 0.3 g sodium chloride was added in the water. The fibers (100 μm polydimethylsiloxane, 85 μm polyacrylate, Dikma) were inserted in the glass flasks and exposed it to the water for 0.5 h at the 70 °C in the magnetic stirrers (previously optimized using univariate experiment), the fiber was then retracted and transferred to the injector port of the gas chromatography/mass spectrometry where compounds were thermally desorbed for 5 min. Chlorpyrifos was detected by GC/MS under the condition described above. Suitable chlorpyrifos was added in the water and so its concentration in the water reached concentration range of 0.05-10 μg mL^{-1}, each concentration was set with three repeats.

Solid phase microextraction procedure of chlorpyrifos in the soil: The residue of chlorpyrifos in the soil was analyzed by the D-SPME and the HS-SPME analysis respectively. Analysis of soil was carried out by placing 3 g soil in screw-capped glass flasks with Teflon-lined septa. The soil moisture content was adjusted to 10 % by adding water. Suitable standard solution of chlorpyrifos was added in the soil and so its concentration reached concentration range of 0.01-5 mg kg^{-1}, each concentration was set with three repeats and then soil samples were maintained for 1 h to allow for equilibration. The fiber was inserted in the glass flasks and exposed it to the soil for 1 h at the 70 °C; the fiber was then retracted and transferred to the injector port of the gas chromatography/mass spectrometry where compounds were thermally desorbed for 5 min and then chlorpyrifos was analyzed by GC/MS under the condition described above.

Solid phase microextraction procedure of chlorpyrifos in the cabbage: The residue of chlorpyrifos in the cabbage was analyzed by the direct SPME and the headspace SPME analysis also. Cabbage (3 g) was placed in the screw-capped glass flasks with Teflon-lined septa. A certain amount of chlorpyrifos was added in the cabbage and its concentration reached concentration range of 0.01-5 mg kg^{-1}, each concentration was set with three repeats and samples were maintained at the room temperature for 1 h to allow for equilibration. The polydimethylsiloxane fiber was inserted in the glass flasks and exposed it to the cabbage for 1h at the 70 °C until reaching adsorption equilibrium. The fiber was then retracted and transferred to the injector port of the gas chromatography/mass spectrometry where compounds were thermally desorbed for 5 min.

RESULTS AND DISCUSSION

Monitoring condition of chlorpyrifos by GC/MS and the linearity range and its sensibility: Exploring the monitoring condition of chlorpyrifos by gas chromatography/mass spectrometry, at the beginning of the experiment, the column was maintained at 250 °C and remaining for 25 min. The TIC of chlorpyrifos standard solution was very bad and only the concentration of chlorpyrifos than 1 μg mL^{-1} was detected, at this condition, it would have an effect on the determination of low residue in the water and soil samples. But using the procedure temperature method, it would overcome this disadvantage, so in this experiment, we chose procedure temperature method to detect chlorpyrifos in the different samples. The oven temperature was programmed from an initial temperature of 80 °C (1.0 min hold) to 280 °C at a rate of 10 °C min^{-1}, maintained at 280 °C for 10 min, the Fig. 1 shows the TIC of chlorpyrifos standard solution at this condition, from the Fig. 1, we can see that the characteristic ion of chlorpyrifos was 197, its remaining time was 16.87 min.

The series standard solution was 0.1, 0.5, 1.0, 5.0 and 10 mg L^{-1}, under the analytical condition above, using automatic sampling, the figure was plotted by peak area as vertical coordi-

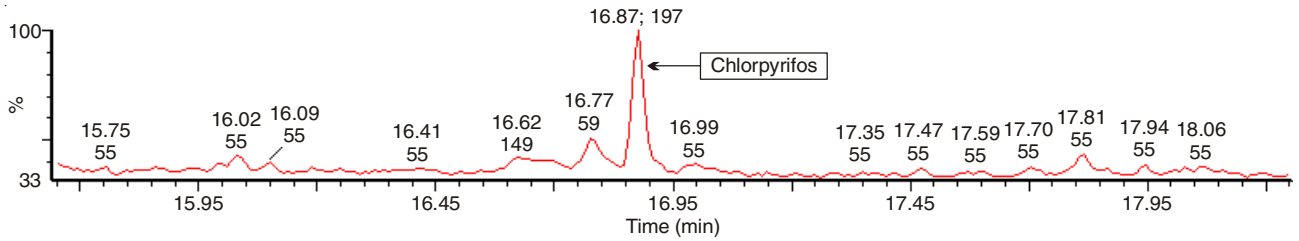

Fig. 1. Total ion chromatogram (TIC) of chlorpyrifos standard solution with 0.5 μg mL^{-1}

nates and injection amount as abscissa, the Fig. 2 was standard curve of chlorpyrifos. From the Fig. 2, its linear equation was y = 14.133x – 1.3445, the correlation coefficient was 0.9994, the linear range of chlorpyrifos was between 1.0×10^{-10} g and 1.0×10^{-8} g, LOD was 0.25×10^{-10} g, the linear range was wider and its sensibility was better, which could satisfy the determination of the test samples.

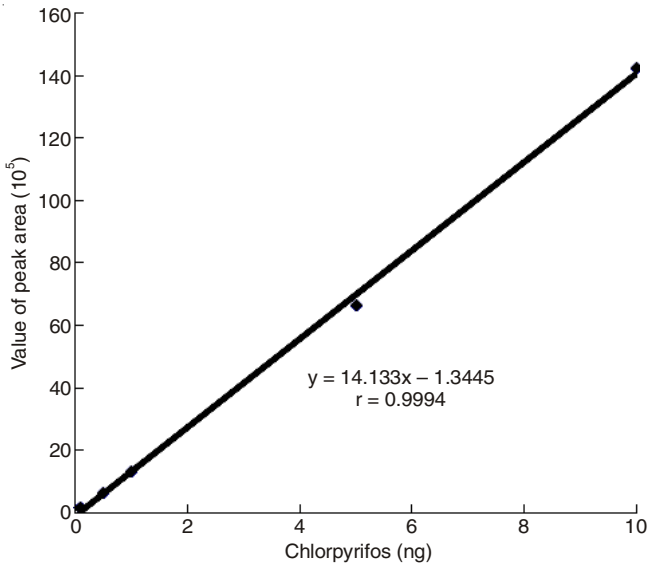

Fig. 2. Standard curve of chlorpyrifos

Evaluation of SPME fibers: In order to compare the extracting result of the two different SPME fibers, the two fibers were used in the experiment: one was the 100 μm polydimethylsiloxane (PDMS) fibre, the most common non-polar phase coating; the other was an 85 μm polyacrylate (PA) fiber, a polar coating phase. Triplicate analyses were made at each fiber and the results obtained are shown in Fig. 3. Fig. 3 shows the chlorpyrifos amounts extracted with the two fibers from the water and soil (the concentrations of chlorpyrifos were 1.0 mg L^{-1} and 1.0 mg kg^{-1} respectively). The results showed that the polydimethylsiloxane fiber was able to extract a higher amount of chlorpyrifos than the polyacrylate fiber, the extraction efficiency of polydimethylsiloxane fiber is 1.5 times in the water and 2.0 times in the soil comparing to polyacrylate fiber. Because chlorpyrifos belong to weak polar compound, the polydimethylsiloxane fiber was the more suitable to abstract it than the polyacrylate fiber, there were some differences with the result of the reference [18], so the polydimethylsiloxane fiber was chosen to test in this study.

Adsorption-concentration curve of chlorpyrifos in the water, soil and cabbage: The analysis of chlopyrifos was implemented by the direct SPME in this study. Fig. 4(a) was

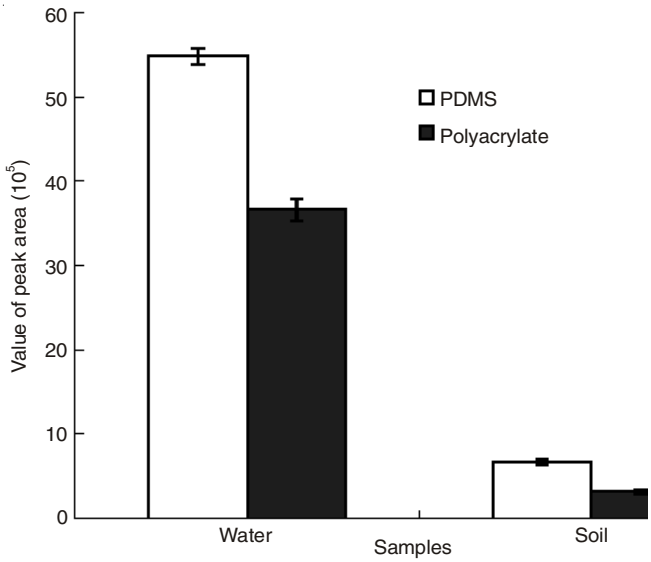

Fig. 3. Chlorpyrifos amounts extracted by the polydimethylsiloxane and polyacrylate fibers from the water and soil sample with the direct solid phase microextraction

the adsorption-concentration curve of chlorpyrifos in the water. From the Fig. 4(a), it was known that the linearity range between the peak area and chlorpyrifos was very well and the correlation coefficient was 0.9985. The values of the relative standard deviation (RSD) varied between 0.16 and 9.5 % and are within the range of accepted values in the pesticide analysis (less than 20 %). Fig. 5(a) was the total ion current of chlorpyrifos with the concentration of 0.1 μg mL^{-1} in the water extracted by SPME. The remain time of chlorpyrifos was 16.86 min at this determination condition and it was very feasible that chorpyrifos in the water was extracted using the D-SPME with the fiber polydimethylsiloxane from the response signal.

The different extracting ways were used in the soil experiment: HS-SPME and D-SPME. It was proved that the result was not well using the headspace SPME from the soil. At this determination condition, chlorpyrifos was not detected, Castro *et al.* [22] reported that chlorpyrifos determined from soil and plants by headspace SPME procedure, there was some discrepancy in this test with the result of the reference. The analysis of chlopyrifos was implemented by the D-SPME in this study. Fig. 4(b) was the adsorption-concentration curve of chlorpyrifos in the soil. From the Fig. 4(b), it was known that the linearity range between the peak area and chlorpyrifos was very well and its correlation coefficient was 0.9982, the value of the relative standard deviation (RSD) was less than 4.7 %. Fig. 5(b) was the total ion current of chlorpyrifos with the concentration of 0.01 μg/g in the soil extracted by SPME. The remain time of chlorpyrifos was 16.84 min at this determi-

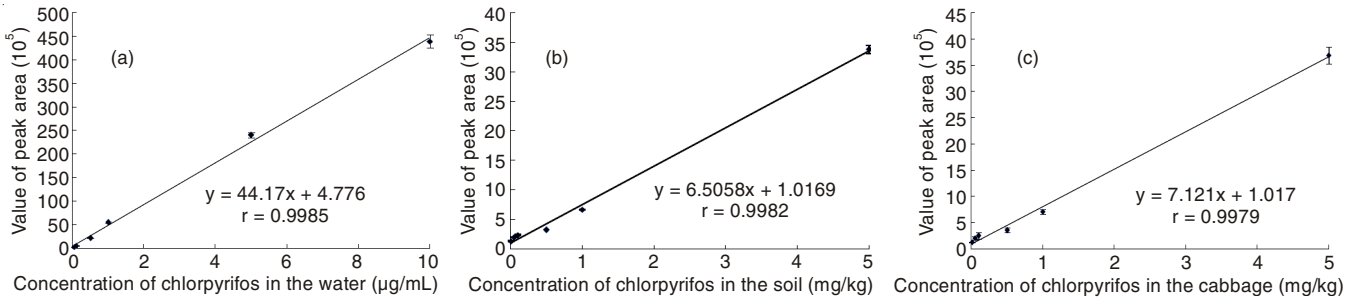

Fig. 4. Adsorption concentration curve of chlorpyrifos in (a) water, (b) soil and (c) cabbage

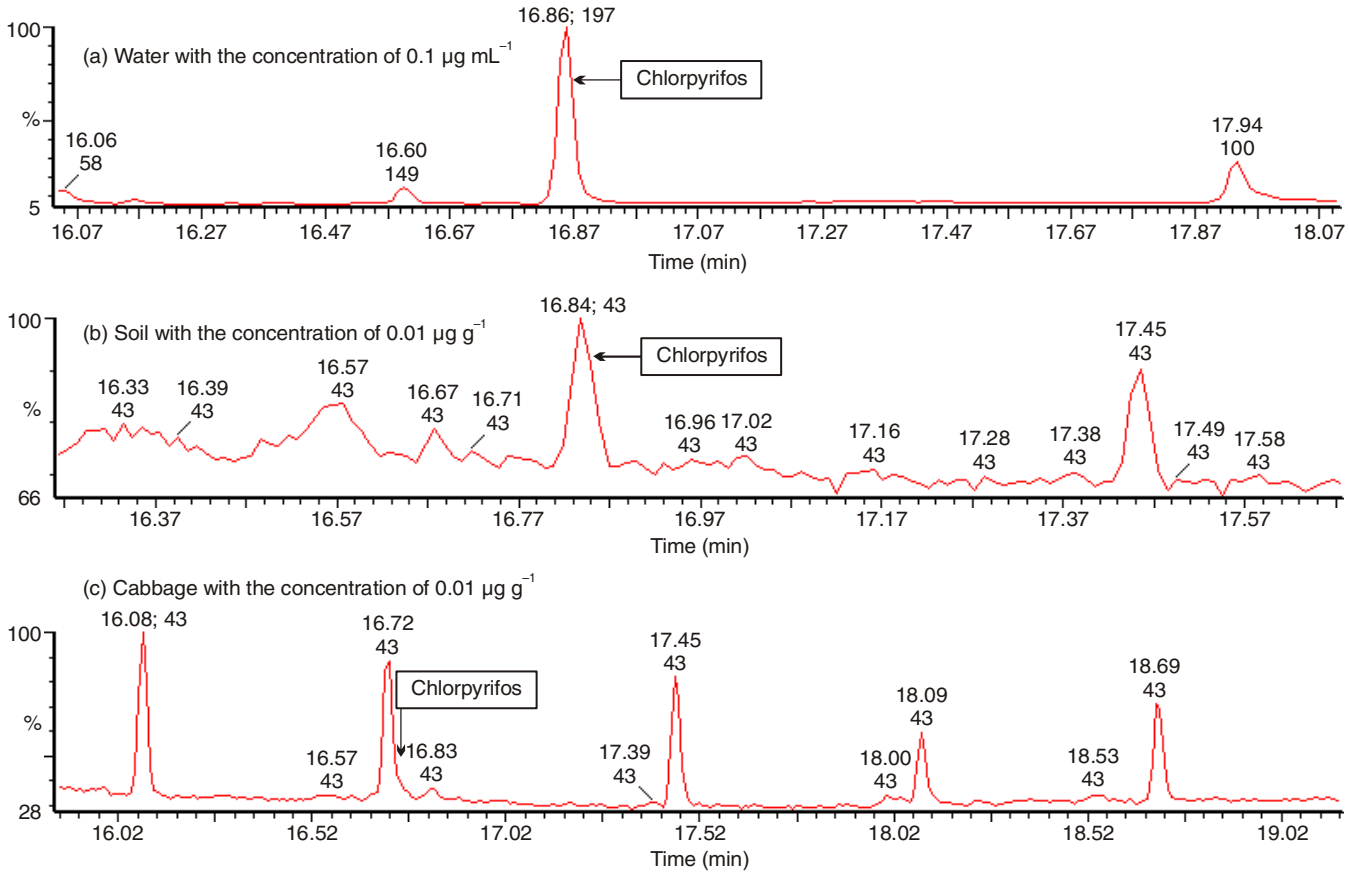

Fig. 5. Total ion current (TIC) of chlorpyrifos with different concentration in the water, soil and cabbage extracted by SPME

nation condition, but its characteristic ion was covered by others organic pollutants in the soil.

The method of the extraction of chlorpyrifos from the cabbage was the same as that of the soil. It was proved that the extracting result was not satisfactory using the headspace SPME from the cabbage, at this extraction condition, the chlorpyrifos was not monitored by GC/MS. The analysis of chlopyrifos was implemented by the direct SPME in this experiment. Fig. 4(c) was the adsorption-concentration curve of chlorpyrifos in the cabbage. It was known that the linearity range between the peak area and chlorpyrifos concentration was very well and the correlation coefficient was 0.9979, the value of the relative standard deviation (RSD) was less than 15.5 %, which could meet the requirements of pesticide residue analysis. Fig. 5(c) was the total ion current of chlorpyrifos with the concentration of 0.01 μg/g in the cabbage extracted by SPME. The remain time of chlorpyrifos was 16.83 min at this determination condition, but its characteristic ion was covered by organic pollutants in the cabbage.

Conclusion

Using the column programmed temperature gas chromatography, the monitoring condition of chlorpyfifos by gas chromatography/mass spectrometry was confirmed. Comparing the extracting result of the two different SPME fibers, the 100 μm polydimethylsiloxane fiber owned higher extraction rate than the 85 μm polyacrylate fibre. The adsorption-concentration curves of chlorpyrifos in the water, soil and cabbage were very well and the correlation coefficient was more than 0.9979, the value of the relative standard deviation (RSD) was less than 15.5 %, which could meet the requirements of pesticide residue analysis. It was very feasible and precise that using the D-SPME with the fiber polydimethylsiloxane to determinate chlorpyrifos residue in the water, soil and cabbage.

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