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Molecularly Imprinted Polymer as Sorbent for Solid-Phase Extraction Coupling to Gas Chromatography for the Simultaneous Determination of Trichlorfon and Monocrotophos Residues in Vegetables

Junhong Xin · Xuguang Qiao · Zhixiang Xu · Jie Zhou

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Abstract In this study, a molecularly imprinted polymer (MIP) was prepared using the mixture of trichlorfon and monocrotophos as the mixed template. The imprinted polymer was characterized and exhibited good recognition ability and fast adsorption–desorption dynamic toward the trichlorfon and monocrotophos. Using this imprinted polymer as sorbent, a new method of molecularly imprinted solid-phase extraction coupled to gas chromatography for the simultaneous determination of two organophosphate pesticides residues was developed. Under optimal condition, the linear range was 0.005–10.0 mg/l. At a loading flow rate of 2.0 ml/min for loading 100 ml, the detection limits were 0.28 μg/l for trichlorfon and 0.090 μg/l for monocrotophos, the peak area precision (RSD) for five replicates was 4.23–4.50 %. The blank rape samples spiked with two organophosphate pesticides at 0.05 and 0.1 mg/l levels were determined by this method with recoveries ranging from 89.41 % to 95.12 %. Moreover, this method was successfully applied to the quantitative detection of the trichlorfon and monocrotophos residues in leek samples.

Keywords Molecular imprinting · Mixed template · Organophosphate pesticides · Solid-phase extraction · Gas chromatography

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Introduction

Organophosphate pesticides can effectively control the insects and weeds in agriculture to improve the productivity and quality of the crop. However, their wide use also gives rise to the pesticides residues on the plant which are harmful to human health because of their potential mutagenics and carcinogenics properties (Mathieu et al. 2007). To prevent these uncontrolled effects on environmental pollution and human health, the development of a detection method with high sensitivity is very necessary.

In the past decades, a lot of screening methods have been reported for the determination of organophosphorus compounds such as chromatography (Shen et al. 2007; He and Lee 2006; Xu et al. 2010; Li et al. 2010; Berijani et al. 2006; He et al. 2009), chromatography–mass spectrometry (Su et al. 2011; García-López et al. 2010; Pang et al. 2006; Sun et al. 2011; John et al. 2010), electrochemiluminescence (Chen et al. 2008), biosensor and immunoassay methods (Wang et al. 2011; Sun and Wang 2010; Lee et al. 2006). Among them, immunoassay method is fast and inexpensive, but the antibody is relatively unstable and the antibody production is particularly complicated. Gas chromatography–mass spectrometry (GC/MS) and liquid chromatography–mass spectrometry (LC/MS) are the most sensitive; however, they require expensive equipment investments which are not obtained for every laboratory. GC and LC are the most common methods except their high limit of detections (typically 10–500 μg/kg), which is insufficient for direct determination of trace pesticide residues. Therefore, a simple separation and preconcentration step is needed prior to chromatography analysis of trace pesticide in complicated samples.

The commonly used pretreatment methods in pesticide residues analysis include solid-phase extraction (SPE),

liquid–liquid extraction (LLE), matrix solid-phase dispersion extraction, solid-phase microextraction (SPME), supercritical fluid extraction, and column chromatography. With many advantages, SPE has been recognized as the most efficient pretreatment technique to enhance the concentration of target, as well as to improve the sensitivity of analysis. However, the commercial solid-phase extraction material is C_{18}-bonded silica gel. The interaction between adsorbent and target in this system is nonspecific, which leads to poor purification efficiency. Furthermore, it is difficult to remove the interference of matrix, and the cost is high (Fang et al. 2006; Wang et al. 2008). Therefore, it is critical and necessary to develop a new sorbent with high specificity.

One of the most interesting and promising methods for preparation of functionalized materials is the molecular imprinting technology. The resulting molecularly imprinted polymers (MIPs) not only possess high selectivity and specificity for recognition of the target but also exhibit far greater mechanical and thermal stability. MIPs have been applied in the separation, sensor, catalysis, enzymes mimics, and biomimetic immunoassays (Turiel and Martin-Esteban 2004; Bui and Haupt 2010; Wang et al. 2006, 2009; Surugiu et al. 2001; Urraca et al. 2007; Martin-Esteban 2004). The use as sorbent for SPE is one of the most exciting applications of MIPs (Xu et al. 2010; Turiel and Martin-Esteban 2004; Marinah et al. 2007; Han et al. 2005; Wang et al. 2007; Francesco et al. 2005), which has provided a simple and effective method in the complicated sample cleaning up prior to analysis.

The applications of MIPs in the extraction of organophosphate pesticides have been reported (Xu et al. 2010; Zhu et al. 2005; Yan et al. 2007). However, the traditional MIPs are prepared using single template molecule. They have specific recognition of the template. Their adsorption capacities toward the structural analogues are very low (nonspecific adsorption). The organophosphate pesticide residues in agricultural products are often multiple. More importantly, simultaneous determination of a group of the analytes can shorten analytical time and economize the cost (Jing et al. 2010). The preparation of MIPs that can selectively recognize multicomponent is a challenging subject.

In this study, a MIP that can simultaneously identify the trichlorfon and monocrotophos (Fig. 1) was prepared. Using this material as sorbent, a method of molecularly imprinted SPE coupled to GC (MISPE-GC) for the determination of two organophosphate pesticides was developed. The factors affecting the preconcentration of the analytes and the detection sensitivity of the method are discussed in details. The applicability of the presented method is also evaluated.

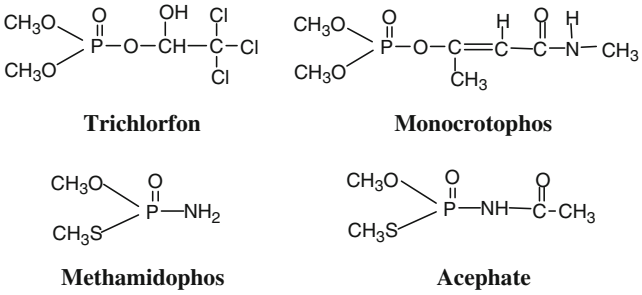

Fig. 1 Chemical structures of trichlorfon, monocrotophos, methamidophos, and acephate

Material and Methods

Chemicals and Materials

The rape and leek samples were purchased from the market of Taian in April 2011 (Shandong, China). Trichlorfon, methamidophos, acephate, and monocrotophos were obtained from the Institute for the Control of Agrochemicals of Ministry of Agriculture (Beijing, China) with purity above 99 %. Methacrylic acid (MAA) and 2,2-azobis (isobutyronitrile) (AIBN) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China), and they were purified before use. Ethylene glycol dimethacrylate (EGDMA) was supplied by Sigma-Aldrich (USA). Chromatography grade acetone was obtained from YongDa Chemical Reagent (Tianjin, China). Doubly deionised water (DDW) was used throughout the study. All the other solvents used in this study were of analytical grade.

The C_{18} SPE column (Strata SCX, 200 mg/3 ml) was purchased from Phenomenex (Torrance, CA, USA).

Instruments

A Shimadzu 2010 gas chromatograph equipped with a flame photometric detector was used for the separation and determination of organophosphate pesticide residues. The separation was conducted on an RTX-1701 capillary column (30 m×250 μm i.d.×0.25 μm film thickness). Nitrogen was used as the carrier gas at the constant flow rate of 1.0 ml/min, and the injection volume was 1.0 μl. The injection port temperature was held at 200 °C at the split mode with the split ratio of 10:1. The detector temperature was held at 250 °C. The temperature program was used as follows: 90 °C held for 1 min, then increased the temperature to 150 °C at a rate of 30 °C/min and held for 3 min. After that, the temperature was increased to 170 °C at 1.0 °C/min and held for 2 min. Finally, the temperature was heated to 250 °C at 30 °C/min and held for 4 min. Thus, a complete cycle was finished with a run time of 35 min.

FT-IR spectra (4000–400 cm^{-1}) in KBr were recorded using a Vector 22 spectrometer (Bruker). A 721 ultraviolet

(UV) spectrometer and a 20.0 kV on a SS-35 scanning electron microscope (Shimadzu, Kyoto, Japan) were also used in this study.

Methods

MIP Preparation

The MIP was prepared as follows: 0.2575 g trichlorfon (1 mmol) and 0.2232 g monocrotophos (1 mmol) were dissolved in 3.0 ml chloroform. The solution was mixed with 0.6886 g MAA (8 mmol) and kept stirred for 30 min. Then 3.9644 g EDGMA (20 mmol) and 100 mg AIBN were added, the mixture was magnetically stirred for 15 min until fully homogenized. After purging with nitrogen for 15 min, the reaction solution was incubated in a water bath at 58 °C for 24 h. After that, the rigid polymer was crushed and sieved with a 200-mesh screen. The imprinted polymer was firstly washed sequentially by 200 ml of methanol/acetic acid (9:1, v/v) for 8 h, followed by 200 ml methanol for 8 h to be free of templates. Finally, the product was dried in a vacuum oven at 60 °C for 24 h.

The nonimprinted polymer (NIP) was prepared following the same procedure except for the addition of the mixed-template molecules.

MIP Characterization

The adsorption capacity of the MIP toward the template was tested. MIP or NIP (20 mg) was separately added to 10 ml aqueous solution containing trichlorfon at various concentrations in a 50-ml volumetric flask. The mixture was vigorously shaken for 4 h at room temperature with a horizontal shaker and then centrifuged (4000 rpm) for 15 min. The unextracted trichlorfon in the supernatant was determined by UV spectrometry at 190 nm, and the adsorption capacity (Q) was calculated.

To investigate the selective recognition of the MIP, the adsorption capacities of MIP toward trichlorfon, monocrotophos, and structural related compounds of methamidophos and acephate were determined at 300 mg/l concentration. The unextracted four organophosphate pesticides in the supernatants were measured by UV spectrometry at 190, 219, 190, and 192 nm, respectively.

The dynamic adsorption of the prepared polymer was tested. For this purpose, 20 mg of imprinted polymer was added to 10 ml 300 mg/l of trichlorfon aqueous solution in a 50-ml volumetric flask. After being shaken for 5, 30, 60, 90, 120, 180, and 240 min at room temperature, the adsorption capacity was determined, respectively.

MISPE-GC Procedure

To investigate the applicability of the MIP sorbent for the extraction of trace organophosphate pesticides in foods, an empty SPE column was packed with 100 mg MIP. The molecularly imprinted solid-phase extraction (MISPE) cartridge was firstly rinsed with 6.0 ml methanol and DDW, followed loading 100 ml of mixed standard aqueous solution containing 0.05 mg/l richlorfon, monocrotophos, methamidophos and acephatefour at a flow rate of 2.0 ml/min. Thus, these four organophosphate pesticides were concentrated onto the functionalized sorbent. When the samples loading was finished, the target analytes adsorbed on the MISPE microcolumn were eluted by 2.0 ml portions of methanol/water/acetic acid (95:5:2, v/v/v). The effluents were collected into a test tube and condensed to dryness

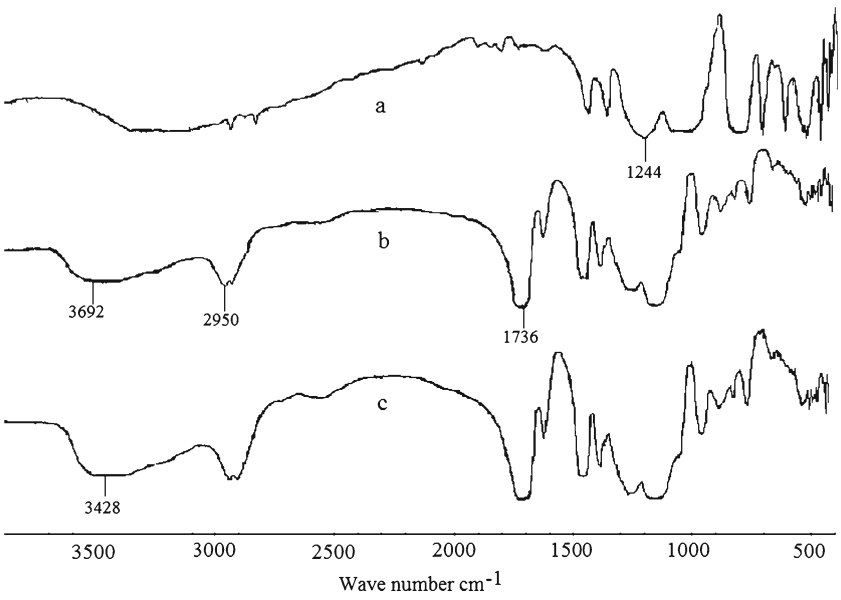

Fig. 2 FT-IR spectra of **a** trichlorfon, **b** imprinted polymer after extraction of the template, and **c** nonimprinted polymer

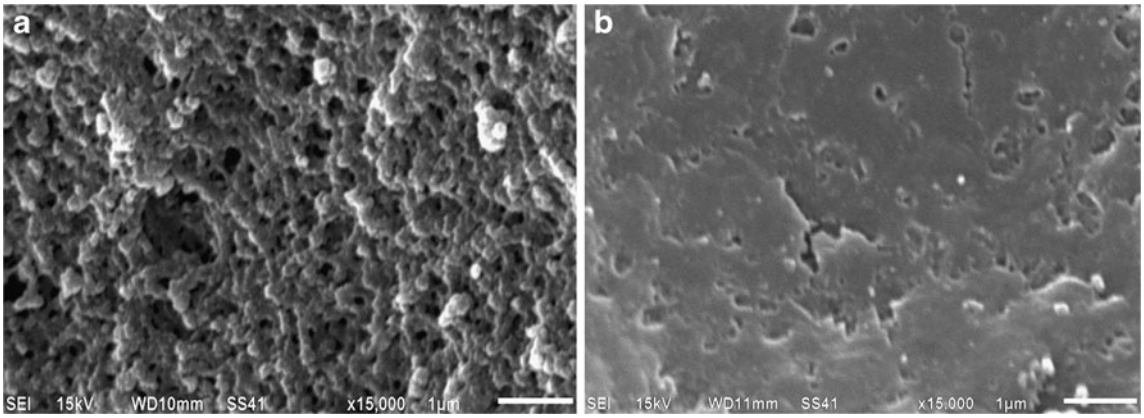

Fig. 3 Scanning electron micrographs of imprinted polymer (**a**, ×15000) and nonimprinted polymer (**b**, ×15000)

under a gentle flow of nitrogen, and then accurately redissolved with 0.2 ml acetone. After being filtered, 1.0 μl of the filtrate was injected into GC for analysis. Finally, the MISPE column was rinsed with 6.0 ml of methanol/acetic acid (9:1, v/v) for the next sample preconcentration.

For comparison with the MIPSE cartridge, the same procedure was used by the NIP or C_{18} SPE column for the extraction of the standard mixed solution containing four organophosphate pesticides.

Sample Preparation

To check the accuracy of the developed MISPE-GC method, 2.0 g of rape samples, which were determined to be free of trichlorfon and monocrotophos, were separately weighed into a 100 ml conical flask and then spiked with 1.0 ml of trichlorfon and monocrotophos mixed standard solution (5.0 or 10.0 mg/l). After being incubated for 1 h, the spiked samples were ultrasonicated with 3×10 ml DDW for 30 min. Finally, the resulting extractions were filtered for the MISPE-GC procedure, and the GC signals were recorded.

To detect the trichlorfon and monocrotophos in leek samples, 2.0 g leeks were weighed into a 100 ml conical flask and extracted according to the above process. The resulting extractions were filtered for the MISPE-GC procedure, and the trichlorfon and monocrotophos levels were calculated.

Results and Discussion

FT-IR Spectra Analysis

The FT-IR spectra of trichlorfon, imprinted polymer after extraction of the template and nonimprinted polymer are compared in Fig. 2.

For the FT-IR spectrum of the trichlorfon (a), the observed feature around 1224 cm^{-1} indicated a P = O stretch. For the imprinted polymer (b) and nonimprinted polymer (c), the feature around 1736 cm^{-1} indicated the C = O stretch. The feature of 3692 cm^{-1} for the imprinted polymer (b) was –OH group, and the shift in the position of this stretch could be attributed to the interaction between the P = O group of organophosphate pesticide and the –OH group

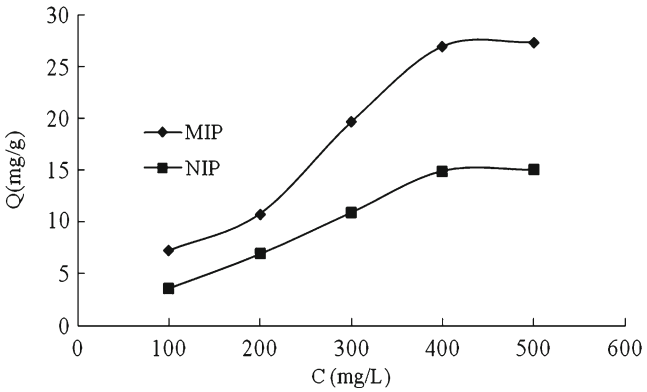

Fig. 4 Adsorption isotherms of the imprinted and nonimprinted polymers toward trichlorfon at 100–500 mg/l

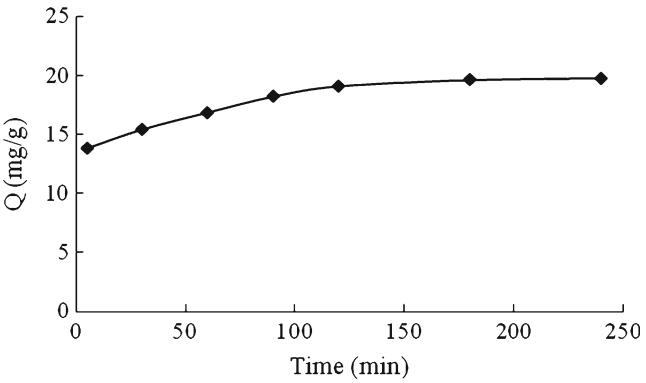

Fig. 5 Kinetic uptake plot of the imprinted polymer toward trichlorfon at 300 mg/l

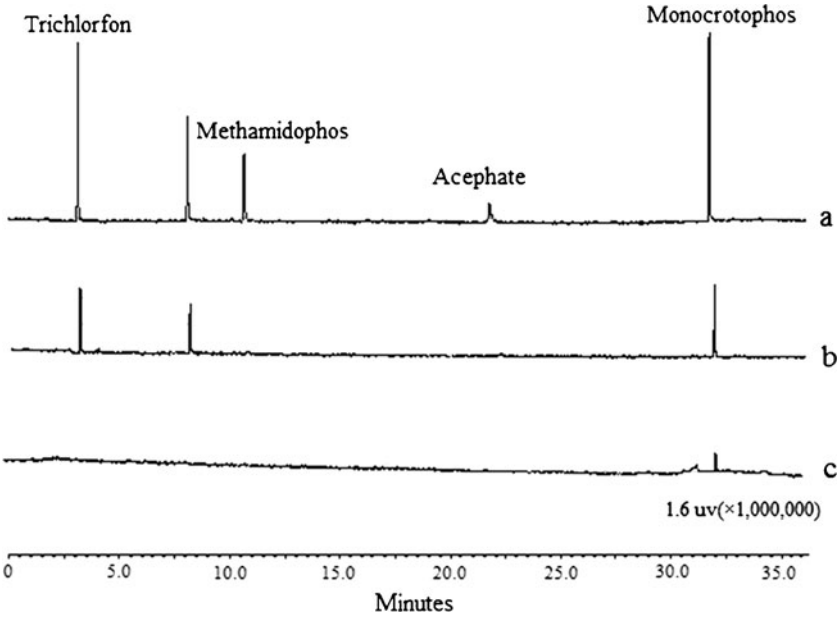

Fig. 6 Gas chromatograms of four organophosphate pesticides after solid-phase extraction of 100 ml 0.05 mg/l mixed standard aqueous solution at a flow rate of 2.0 ml/min using **a** imprinted polymer, **b** nonimprinted polymer, and **c** C_{18} as sorbent

of MAA (Xu et al. 2010; Zhu et al. 2006), which indicated that the mixed-template had reacted with the functional monomer of MAA, and the imprinted polymer had been synthesized.

The imprinted and nonimprinted polymers showed similar locations and appearances of the major bands, which indicated that the template had been removed from the imprinted polymer after extraction.

Scanning Electron Micrograph Analysis

The structures of the imprinted and nonimprinted polymers were visualized by the scanning electron microscope (SEM). As shown in Fig. 3, many cavities existed on the surfaces of imprinted polymers (a) and nonimprinted polymers (b), and more cavities were obviously observed on the imprinted polymers. For the nonimprinted polymer, it can be speculated that its nonspecific adsorption might result from these cavities.

Adsorption Ability Characterization

The isothermal adsorption experiments of the imprinted and nonimprinted polymers toward trichlorfon at 100–500 mg/l are depicted in Fig. 4. The results showed that the binding capacity of imprinted or nonimprinted polymer was increased with the increasing of trichlorfon concentration. MIP had a higher adsorption ability toward trichlorfon than the NIP, and the adsorption capacity of the MIP (27.38 mg/g) was more than 1.8-fold that of NIP (15.04 mg/g) at 500 mg/l concentration.

The selective ability of the MIP was also investigated. The respective adsorption capacity of MIP toward trichlorfon, monocrotophos. and structural related compounds of methamidophos and acephate at 300 mg/l was 19.67, 16.27, 6.23, and 5.45 mg/g respectively. This demonstrated that the MIP can recognize the structural differences between the mixed templates and their analogues in aqueous phase. This finding might result from the imprinting effect, the difference of the molecular interactions and structures. During polymerization step, the mixed templates were incorporated with the functional monomer. Subsequent removal of the template molecule resulted in imprinted cavities having structure, size and spatial arrangement complementary to both trichlorfon and monocrotophos. Furthermore, the novel imprinted polymer had higher adsorption capacity toward trichlorfon than the monocrotophos. This might because that the trichlorfon has smaller structure than the monocrotophos (Fig. 1), so trichlorfon can be easily absorbed into the imprinted cavities during adsorption process.

Table 1 Analytical parameters of the developed MISPE–GC method (mean ± SD)

Pesticides	Linear range (mg/l)	Detection limit, μg/l (S/N=3)	RSD, % (n=5)	Enrichment factors	Sample consumption, ml
Trichlorfon	0.005–10.0	0.28	4.50	142	100
Monocrotophos	0.005–10.0	0.090	4.23	318	100
Methamidophos				76	100
Acephate				65	100

Table 2 Recoveries of two organophosphate pesticides in the spiking rape samples (mean ± RSD, n=3)

Samples	Spiked level (mg/l)		Recovery (%)	
	Trichlorfon	Monocrotophos	Trichlorfon	Monocrotophos
Rape	0.05	0.05	89.41±3.44	94.13±3.49
Rape	0.10	0.10	90.43±2.50	95.12±3.13

The uptake kinetics of MIP toward trichlorfon was also examined at 300 mg/l concentration. As shown in Fig. 5, the prepared MIP had fast uptake kinetics. After shaking for 5 min, an adsorption capacity of 13.88 mg/g was obtained, which was 71.34 % of the saturated adsorption capacity, and the adsorption almost reached equilibrium within 120 min. This is an obvious advantage of MIP for its application as sorbent in SPE to quickly extract of the multiorganophosphate pesticides in food samples.

MISPE Condition Optimization

To achieve the highest precision and sensitivity for the MISPE-GC method, the MISPE conditions including eluent composition and volume, the pH of the sample solution, the sample loading flow rate and time, were optimized.

Different eluents were investigated to identify the effect on the desorption of two organophosphate pesticides from the imprinted sorbent cartridges after loading of 100 ml of mixed standard aqueous solution at a flow rate of 2.0 ml/min. It was found that when methanol was used as the eluent, no signal was observed in the chromatograms. Some of the trichlorfon and monocrotophos could be eluted from the imprinted cartridges by methanol/water at ratio of 90:10 (v/v). Most of them could be desorbed from the imprinted cartridges by a solution of methanol/water (95:5, v/v). Acetic acid can weaken the binding of template to the imprinted polymer and release the template from the imprinted cavity more quickly (Stafiej et al. 2007). The addition levels of acetic acid were investigated from 0.5 % to 3 % (v/v), and the best result was obtained when 2 % acetic acid was added. Therefore, a mixture of methanol/water/acetic acid (95:5:2, v/v/v) was selected as the eluent in this study.

Various volumes (0–3.0 ml) of methanol/water/acetic acid (95:5:2, v/v/v) was also tested in the MISPE process. It was found that the chromatographic peak areas of two organophosphate pesticides increased quickly as the eluent volume increasing from 0 to 1.8 ml, and then hardly changed in the range of 1.8–3.0 ml. Accordingly, an eluent volume of 2.0 ml was selected to ensure the complete stripping of the adsorbed trichlorfon and monocrotophos from the imprinted functionalized column.

For absorbing 100 ml of mixed standard aqueous solution containing 0.05 mg/l trichlorfon and monocrotophos, different sample loading flow times of 30–120 min were studied. The results indicated that the chromatographic peak area increased as it increasing from 30 to 50 min, and then leveled off in the range of 50–120 min. Based on above results, 2.0 ml/min of the loading flow rate and 50 min of sample loading time were chosen as the experimental condition in the following studies.

The pH of the sample solution is an important factor in the MISPE process. Organophosphate pesticides are more stable in acid condition, and the influence of sample pH on the molecularly imprinted extraction of 0.05 mg/l trichlorfon and monocrotophos mixture was tested in the range of 3.0–7.8 at a sample flow rate of 2.0 ml/min for 50 min. The results showed that two organophosphate pesticides could be effectively adsorbed onto the imprinted sorbent-packed column in the pH range of 5.0–7.0. Outside this pH range, the chromatographic peak area was decreased. The maximum chromatographic peak was achieved at the pH of 6.5. Therefore, the sample solution pH of 6.5 was chosen for the further studies.

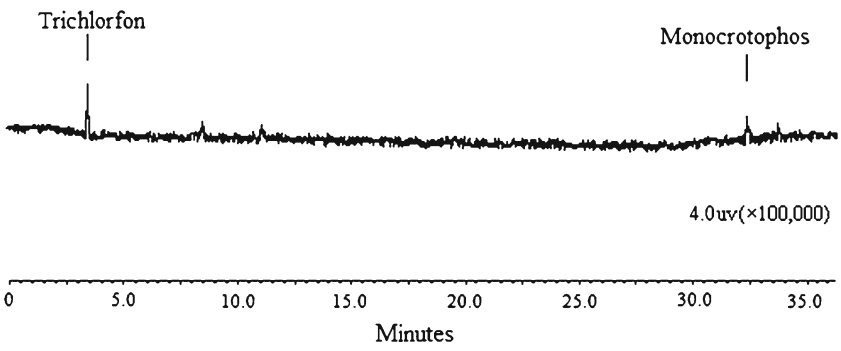

Fig. 7 Gas chromatograms of the trichlorfon and monocrotophos residue in the leek sample after MISPE process

Merits of the MISPE–GC Method

The selectivity of the imprinted polymer sorbent in the SPE process was tested by loading 100 ml of mixed standard aqueous solution containing 0.05 mg/l four organophosphate pesticides at a sample flow rate of 2.0 ml/min (Fig. 6). In comparison to chromatogram (b), the signals of richlorfon and monocrotophos were obviously appeared in the chromatogram (a). These results indicated that the richlorfon and monocrotophos were selectively adsorbed onto the MIP sorbent (Fig. 6a), and the selectivity of the MIP sorbent toward the two organophosphate pesticides was higher than that of the NIP sorbent.

The selectivity of the MISPE was also investigated by comparing with the C_{18} SPE. It was found that the C_{18} cartridges had little concentrations on the trichlorfon, monocrotophos, methamidophos, and acephate, and their chromatographic peaks were all low (Fig. 6c). Therefore, the imprinted polymer cartridge had a higher selectivity toward trichlorfon and monocrotophos, and a better concentration on the methamidophos and acephate than the C_{18} SPE column (Fig. 6a).

Furthermore, the working life of the novel imprinted polymer was also tested. It had a reusability of more than 50 times without loss of sensitivity, and the cost per analysis of this developed MISPE–GC method was impressively reduced. Thus, this imprinted polymer was more suitable to be used as an effective SPE sorbent for the separation and extraction of multiorganophosphate pesticide residues prior to chromatography analysis.

Analytical Parameters of MISPE–GC Method

The analytical parameters of the presented MISPE–GC method for the simultaneous determination of two organophosphate pesticides were evaluated under optimal experimental conditions (Table 1). The enrichment factors, which obtained by the slope of the linear portion in comparison with the direct injection of 1.0 μl standard sample solution, were 142 for trichlorfon and 318 for monocrotopho, respectively. at a flow rate of 2.0 ml/min for loading 100 ml, which were higher (more than twofold to fourfold) than those for methamidophos (76) and acephate (65). The detection limits (S/N = 3) of the MISPE–GC method for trichlorfon and monocrotophos were 0.28 and 0.090 μg/l, respectively. The linear ranges of the calibration graph were all between 0.005 and 10.0 mg/l. The peak area precision (RSD) for five replicate extractions of 0.05 mg/l standard aqueous solution were 4.23 % for trichlorfon and 4.50 % for monocrotophos.

Applicability of MISPE–GC Method

To evaluate the accuracy of the MISPE–GC method, the blank rape samples spiked with trichlorfon and monocrotophos at 0.05 and 0.1 mg/l levels were extracted and analyzed by this method, as shown in Table 2. For each concentration, triple measurements were performed, and high recoveries ranging from 89.41 % to 95.12 % were achieved.

The developed method was applied to the extraction and determination of target pesticide residues in leek samples, which is depicted in Fig. 7. The trichlorfon and monocrotophos were quantitatively detected with different levels of 0.030 and 0.023 mg/kg, and both the results were higher than the maximum residue level of organophosphate pesticides in “Japanese Positive List System” (10 μg/kg). Therefore, more efforts should be devoted to the control of pesticide residues in primary agricultural products.

Conclusion

In this study, a MIP for simultaneous recognition of trichlorfon and monocrotophos was prepared. Besides, a new method of MISPE–GC was introduced. The detection limits of the developed method were 0.28 μg/l for trichlorfon and 0.090 μg/l for monocrotophos, and the linear range was 0.005–10.0 mg/l. With high precision and sensitivity, this method has been demonstrated to be suitable for the screening and analyzing of trace multiorganophosphate pesticide residues in foods.

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