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Simultaneous Determination of Nine Trace Organophosphorous Pesticide Residues in Fruit Samples Using Molecularly Imprinted Matrix Solid-Phase Dispersion Followed by Gas Chromatography

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ABSTRACT: How to determine trace multipesticide residues in fruits is an important problem. This paper reports a molecularly imprinted polymer (MIP) that was prepared using 4-(dimethoxyphosphorothioylamino)butanoic acid as the template, acrylamide as the functional monomer, and ethylene glycol dimethacrylate (EGDMA) as the cross-linker. The novel imprinted polymer was characterized by static and kinetic adsorption experiments, and it exhibited good recognition ability and fast adsorption−desorption dynamicd toward trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion. Using this imprinted polymer as sorbent, matrix solid-phase dispersion coupled to gas chromatography for simultaneous determination of nine trace organophosphorus pesticide residues was first presented. Under the optimized conditions, the LOD (S/N = 3) of this method for the nine organophosphorus was 0.3−1.6 μg kg^{-1}; the RSD for three replicate extractions ranged from 1.2 to 4.8%. The apple and pear samples spiked with nine organophosphate pesticides at levels of 20 and 100 μg kg^{-1} were determined according to this method with good recoveries ranging from 81 to 105%. Moreover, this developed method was successfully applied to the quantitative detection of the nine organophosphorus pesticide residues in orange samples.

KEYWORDS: *molecular imprinting, matrix solid-phase dispersion, multipesticide residues, gas chromatography*

INTRODUCTION

Organophosphorus pesticides generally act as cholinesterase inhibitors because of their fast biodegradation, low bioaccumulation, and broad target spectrum[1] and have been widely used in agricultural production. However, their extensive use also gives rise to pesticide residues on the plant, which are harmful to human health because of their potential mutagenicity and carcinogenics properties.[2] Therefore, it is of great significance to develop an accurate and reliable analytical method to prevent their uncontrolled effects on environmental pollution and human health.

In the past decades, a lot of screening methods have been used for the determination of organophosphorus pesticides such as spectrophotometry, atomic absorption spectrometry (AAS),[3] thin layer chromatography (TLC),[4,5] chromatography−mass spectrometry, [6] capillary electrophoresis (CE),[7] and biosensor and immunoassay methods.[8] Gas chromatography coupled to mass spectrometry (GC-MS) is the first-choice technique for the determination of organophosphorus pesticides in foodstuffs because of its high sensitivity. However, it requires expensive equipment investment, which is not an option for every laboratory. Gas chromatography (GC) is one of the most classical techniques but it has high limits of detection, which are insufficient for analysis of trace pesticide residues.[9] Therefore, an effective separation and preconcentration procedure is usually needed prior to GC analysis.

The traditional pretreatment methods in pesticide residue analysis include oscillation extraction, liquid−liquid extraction (LLE), solid-phase extraction (SPE), Soxhlet extraction, and ultrasonic extraction. These methods not only require lots of organic solvents, causing environmental pollution, as well as lots of time but also have low reliability. In recent years, many new pretreatment technologies have been reported, for example, supercritical fluid extraction (SFE),[10] solid-phase microextraction (SPME),[11] stir bar sorptive extraction (SBSE),[12] matrix solid-phase dispersion (MSPD),[13] and dispersive liquid−liquid microextraction (DLLME).[14,15] Among them, MSPD is a patented process, first reported in 1989, for conducting simultaneous disruption and extraction of solid and semisolid samples.[16] Application of MSPD in food analysis can greatly reduce the analysis time. Furthermore, it requires less solvent. Thus, the cost per analysis can be decreased.[17] With these advantages, MSPD has been widely used to extract and concentrate the target, as well as to improve the sensitivity of analysis. Currently, the commercial MSPD sorbent materials are florisil or C_{18} bonded silica gel. They have no specific recognition toward a target, which will lead to poor purification efficiency and result in matrix interferences to analysis. Therefore, preparation of a kind of MSPD phase sorbent with good absorption and high selectivity is crucial and necessary.

The molecular imprinting technique is one of the most ideal and promising methods to prepare functional materials. With high specific recognition ability and far greater physiochemical stability,[18] the resulting molecularly imprinted polymers (MIPs) have been extensively applied in separation,[19] sensor,[20] catalysis,[21] enzyme mimics, and biomimetic immunoassays.[22] The use of MIPs as a MSPD sorbent is one of their most exciting applications, which will provide a simple and effective

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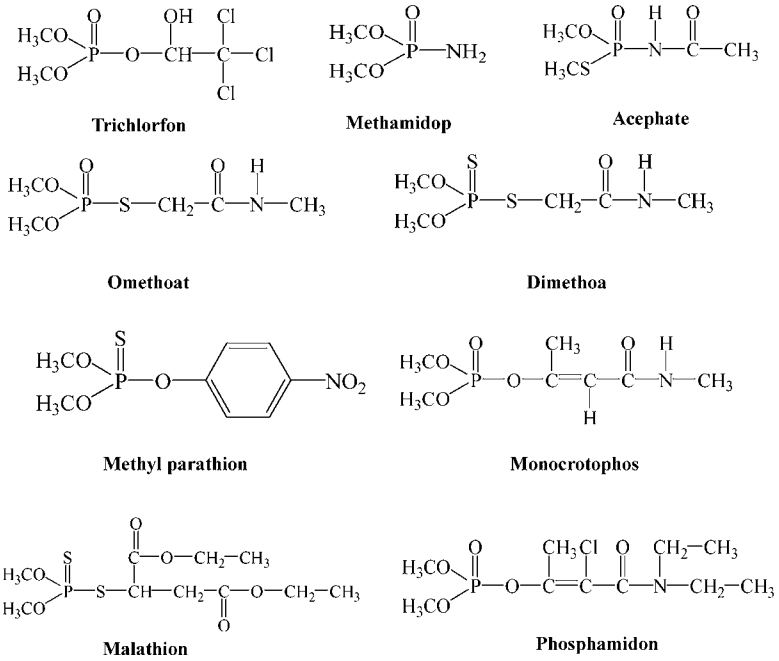

Figure 1. Chemical structures of trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion.

pretreatment method for complicated samples. However, MIPs prepared by the traditional method can only selectively recognize the template molecule, and their adsorption capacities toward other analytes are low.[23] Thus, their applications in the multiresidue analysis have been greatly limited.

As previous study has shown, 4-(dimethoxyphosphorothioylamino)butanoic acid has the common functional groups and structure of organophosphorus pesticides and has been used as the hapten to immunize animals to obtain antibodies that can selectively recognize multipesticides.[24] In this study, a new MIP that can selectively recognize nine organophosphorus pesticides (trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion) (Figure 1) was synthesized using 4-(dimethoxyphosphorothioylamino)butanoic acid as the template. By using the MIP as sorbent, an effective and sensitive method of molecularly imprinted matrix solid-phase dispersion (MIMSPD) coupled to GC (MIMSPD-GC) for the determination of multipesticide residues was developed. The factors affecting the preconcentration and the detection sensitivity of the method are optimized in detail. The applicability of the presented method is also evaluated. The present study is the first work to describe a methodology for the simultaneous separation and determination of nine trace organophosphorous pesticide residues in real samples based on MIMSPD enrichment. To our knowledge, MIPs against nine organophosphorous pesticides have not been reported before.

EXPERIMENTAL PROCEDURES

Materials and Reagents. The apple, pear, and orange samples were purchased from the market of Taian (Shandong, China) in November 2012. Trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion were obtained from the Institute for the Control of Agrochemicals of Ministry of Agriculture (Beijing, China) with purity >99%. *O,O*-Dimethyl phosphorochloridothioate and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich Co., Ltd. (USA). 4-Aminobutyric acid was purchased from TCI Development Corp. (Shanghai, China). Acrylamide (AM) was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Methacrylic acid (MAA) and 2,2-azobis(isobutyronitrile) (AIBN) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China), and they were purified before use. Doubly deionized water (DDW) was used throughout the study. All reagents were of the highest available purity and at least of analytical grade.

Instruments. Analysis of organophosphate pesticides was performed using a 2010 gas chromatograph (Shimadzu, Japan) equipped with a flame photometric detector and PC-based data system to control data acquisition and instrument conditions. The separation was conducted on an RTX-1 capillary column (30 m × 250 μm i.d. × 0.1 μm film thickness). Nitrogen was used as the carrier gas at the constant flow rate of 1.0 mL min^{-1}, and the injection volume was 1.0 μL. The injection port temperature was held at 180 °C at the split mode with the split ratio of 2:1. The detector temperature was held at 250 °C. The oven temperature was programmed as follows: 50 °C held for 1.0 min, and then the temperature was increased to 200 °C at a rate of 20 °C min^{-1} and held for 10 min; finally, the temperature was raised to 240 °C at 40 °C min^{-1} and maintained for 10 min.

A UV-2450 ultraviolet spectrometer (Shimadzu, Japan) was also used in this study. The UCT SPE column (30 mL) was purchased from Pribo Lab Pte. Ltd. (Singapore).

Synthesis of the 4-(Dimethoxyphosphorothioylamino)-butanoic Acid. In this study, the 4-(dimethoxyphosphorothioylamino)butanoic acid was synthesized following the method of Zhang et al.[24] First, 0.103 g of 4-aminobutyric acid (1.0 mmol) was dissolved in 10 mL of NaOH (2.5 mol L^{-1}). After 30 min of stirring in an ice bath, 1.215 mL of *O,O*-dimethyl phosphorochloridothioate was added to the mixture. Then, 2.5 mol L^{-1} NaOH was added dropwise into the solution until the pH reached 10. After another 6.0 h of stirring at room temperature, the mixture was washed by diethyl ester to remove the impurities, and the pH value of the reaction solution was then adjusted to 2.0 by the addition of 1.0 mol L^{-1} HCl. Finally, the mixture was extracted by diethyl ester (3 × 25 mL), and the organic layer was combined and dried by Na_2SO_4. The product was obtained by rotary evaporation.

MIP Preparation. The MIP was prepared as follows: 0.227 g of 4-(dimethoxyphosphorothioylamino)butanoic acid (1 mmol) was dissolved in 5.0 mL of acetonitrile. The solution was mixed with

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0.213 g of AM (3 mmol) and then stirred for 30 min. When 1.585 g of EDGMA (8 mmol) and 50 mg of AIBN were added, the mixture was magnetically stirred for 15 min until fully homogenized. The reaction solution was treated with ultrasound for 15 min, purged by nitrogen for 15 min, and incubated in a water bath at 60 °C for 24 h. After that, the rigid polymer was crushed and sieved with a 200-mesh screen. The polymer particle was first washed sequentially by 200 mL of methanol/acetic acid (4:1, v/v) for 24 h, followed by 200 mL of methanol for 12 h, to be free of templates (Figure 2). Finally, the product was dried in a vacuum oven at 40 °C for 24 h.

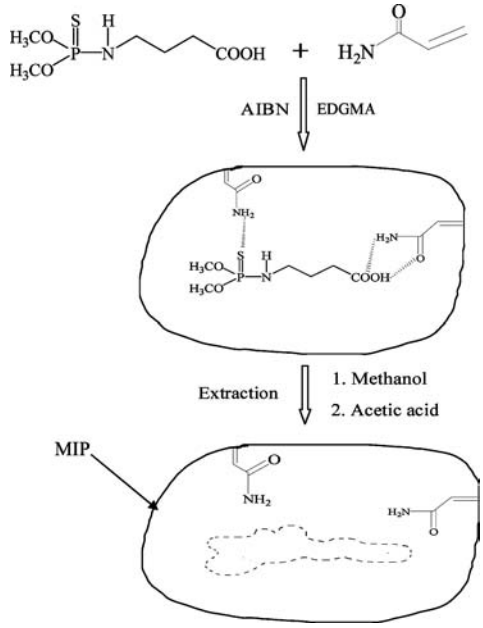

Figure 2. Schematic representation of the molecularly imprinted polymer used in this study.

In comparison, the nonimprinted polymer (NIP) was simultaneously prepared in the same way but without the addition of the template.

MIP Characterization. To evaluate the adsorption capacity of MIP, 20 mg of MIP or NIP was separately added to a 50 mL volumetric flask, and then 10 mL of aqueous solution containing trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion at 300 mg L^{-1} was added. The mixtures were vigorously shaken for 240 min at room temperature with a horizontal baker and then centrifuged at 4000 rpm for 15 min. Supernatant was measured by UV spectrometry at 200, 225, 220, 225, 210, 215, 214, 190, and 280 nm, separately. The adsorption capacity (Q) was calculated. Furthermore, the adsorption isotherms of the MIP toward trichlorfon and acephate were also investigated. When 20 mg of MIP or NIP was added, 10 mL of aqueous solution containing trichlorfon and acephate at various concentrations (100−500 mg L^{-1}) was added. After 240 min of shaking, the supernatant was measured at 200 and 220 nm, separately. Their adsorption capacities were calculated.

The uptake kinetics of MIP toward trichlorfon and acephate were examined as follows: 20 mg of MIP and 10 mL of a 300 mg L^{-1} trichlorfon and acephate aqueous solution were added to a 50 mL volumetric flask. After 5, 30, 60, 90, 120, 180, and 240 min of shaking at room temperature, the adsorption capacity was determined, respectively.

MIMSPD-GC Procedure. Two grams of sample (previously ground) and 0.5 g of MIP were placed into a glass mortar and blended together using a glass pestle. Thus, the sample was completely dispersed onto the MIP material. When blending was completed, the mixture was packed into an empty UCT SPE column. When the MIMSPD cartridge was first rinsed with 30 mL of hexane, the target analytes adsorbed on the MIP sorbent were then eluted with 5.0 mL of methanol/acetic acid (95:5, v/v). The effluents were collected into test tubes, condensed to dryness under a gentle flow of nitroge, and then accurately redissolved with 0.2 mL of dichloromethane. After filtration with a 0.22 μm filter membrane, 1.0 μL of the filtrate was injected into the GC for analysis.

Sample Preparation. To check the accuracy of the MIMSPD-GC method, the fortified fruit sample was prepared, which was analyzed by GC before spiking. Briefly, 2.0 g of apple or pear sample was separately weighed into a 100 mL conical flask and spiked with 2.0 mL of mixed standard solution (0.02 or 0.1 mg L^{-1}) containing 0.04 or 0.2 μg of nine organophosphorous pesticides. After a 4.0 h incubation, the spiked samples were extracted and analyzed according to the MIMSPD-GC procedure. The GC signals were recorded.

RESULTS AND DISCUSSION

Adsorption Ability Characterization. The adsorption capacity (Q) of the MIP or NIP was calculated according to the following equation:[25]

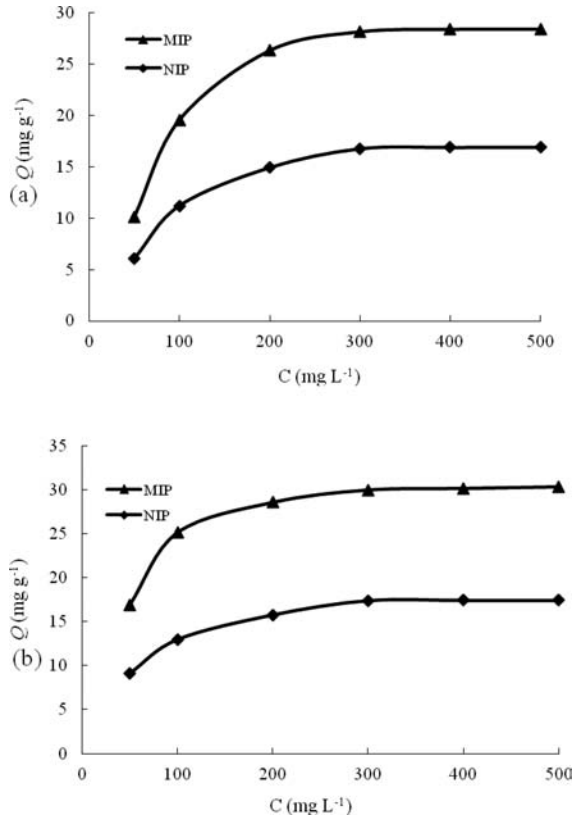

Figure 3. Adsorption isotherms of the imprinted and nonimprinted polymers toward trichlorfon (a) and acephate (b) at 100−500 mg L^{-1}.

$$Q = (C_0 - C_1)V/M \quad (1)$$

In eq 1, C_0 and C_1 are the concentrations of the target molecule in solution before and after absorption, respectively; V is the volume of the solution, and M is the mass of the polymer.

The adsorption capacities of MIP toward trichlorfon, malathion, acephate, methamidophos, omethoate, dimethoate, phosphamidon, monocrotophos, and methyl parathion are evaluated. Their adsorption capacities were 28.40, 33.51, 30.11, 35.20, 26.51, 19.90, 9.04, 13.43, and 13.23 mg g^{-1}, respectively. The MIP had high adsorption ability toward the nine organophosphate pesticides, and the adsorption capacity

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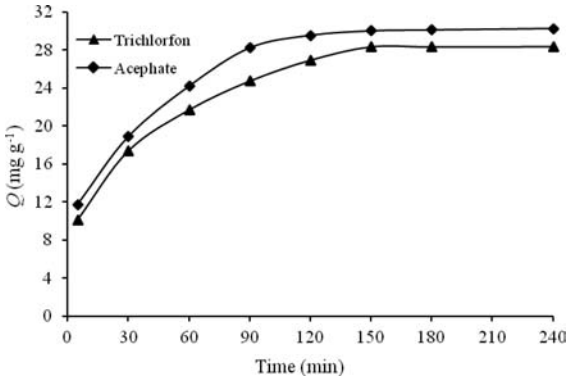

Figure 4. Kinetic uptake plots of the imprinted polymer toward trichlorfon and acephate at 300 mg L^{-1}.

toward methamidophos was higher than those of the other eight pesticides because it has smaller structure.

The adsorption isotherms of MIP and NIP toward the trichlorfon and acephate at 100−500 mg L^{-1} were investigated (Figure 3). The results showed that the binding capacity of imprinted or nonimprinted polymer increased with the increasing concentration of trichlorfon (Figure 3a) and acephate (Figure 3b). The adsorption capacity of MIP was >1.5 times higher than that of NIP at the concentration of 500 mg L^{-1}. It was concluded that the prepared MIP can selectively recognize these nine organophosphate pesticides in an aqueous environment.

This phenomenon could result from the imprinting effect and the difference in structures. During the polymerization process, the template molecule of 4-(dimethoxyphosphorothioylamino)butanoic acid was incorporated with the functional monomer of EDGMA and copolymerized. Subsequent removal of the template molecule resulted in imprinted cavities having structure, size, and spatial arrangement that were complementary to the 4-(dimethoxyphosphorothioylamino)butanoic acid. It is known that 4-(dimethoxyphosphorothioylamino)-butanoic acid has the common functional groups and structure of organophosphorus pesticides. The structures of these nine organophosphate pesticides are all similar to that of 4-(dimethoxyphosphorothioylamino)butanoic acid. Thus, the novel imprinted polymer should have high adsorption capacity toward them. However, the NIP had no such imprinted cavities and specific binding sites. Our results also indicated that the structure of the template has an important effect on the selective ability of MIP.

The uptake kinetics of MIP toward trichlorfon and acephate at 300 mg L^{-1} concentration were also examined. As shown in Figure 4, the MIP had fast uptake kinetics. After a 30 min period of shaking, the adsorption capacities toward trichlorfon and acephate were 17.41 and 18.93 mg g^{-1}, respectively, which were 61.30 and 62.41% of the saturated adsorption capacity. The adsorption almost reached the adsorption equilibrium within 180 min.

With good adsorption capacity and fast uptake kinetics, MIP is suitable for use as a sorbent in the pretreatment procedure to quickly extract the multiorganophosphorous pesticide residues in food samples.

MIMSPD Conditions Optimization. To achieve the good precision and sensitivity for the MIMSPD-GC method, the MIMSPD conditions, such as elution solvent and volume and the proportion of the polymer and matrix, were optimized.

In the MIMSPD procedure, selection of a solvent that can effectively elute the target analytes from the MIMSPD cartridge is very important. Different elution solvents of dichloromethane, ethyl acetate, acetone, acetonitrile, and methanol were investigated in this study. As shown in Table 1, best recoveries for all pesticides were obtained when the MIMSPD cartridge was eluted by methanol. It was known that acetic acid can increase the eluting strength, weaken the binding of template to the imprinted polymer, and release the template from the imprinted cavity more quickly. The addition levels of acetic acid were investigated from 1 to 10% (v/v), and the best result was obtained when 5% acetic acid was added. Therefore, a mixture of methanol/acetic acid (95:5, v/v) was selected as elution solvent for the further experiment.

Various volumes (1.0−10.0 mL) of methanol/acetic acid (95:5, v/v) were also tested in the MIMSPD process. It was found that the recoveries of the nine organophosphate pesticides increased with the elution solvent volume increasing. The chromatographic peak areas increased quickly as the eluent volume increased from 1.0 to 4.5 mL and then hardly changed in the range of 4.5−10.0 mL. Thus, the optimal elution solution was 5.0 mL of methanol/acetic acid (95:5, v/v).

The influence of MIP addition level on the extraction efficiency was also investigated. Different proportions (4:1, 2:1, 1:1, 1:2, 1:4, and 1:8, m/m) between the MIP and sample were studied. Results indicated that good recovery was obtained when the proportion was 1:4, and the impurity peak became higher when the proportion was 1:8. Therefore, 0.5 g of MIP and 2.0 g of fruit sample were blended in the MIMSPD procedure.

Analytical Parameters of MIMSPD-GC Method. The analytical figures of the presented MIMSPD-GC method for the simultaneous determination of nine organophosphate pesticides were evaluated under optimal conditions. Enrich-

Table 1. Influence of Different Elution Solutions on the Recoveries (Percent) of Nine Pesticides

	elution solutions				
pesticide	dichloromethane	ethyl acetate	acetone	acetonitrile	methanol
trichlorfon	35	0	11	4	70
malathion	77	57	69	74	92
acephate	46	17	34	24	77
methamidophos	38	18	29	27	79
omethoate	59	30	41	60	85
dimethoate	50	36	37	55	73
phosphamidon	54	33	58	47	80
monocrotophos	24	12	26	40	71
methyl parathion	39	19	30	44	76

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Table 2. Equation, Linearity (R^2), and LOD of the MIMSPD-GC Method

pesticide	equation	R^2	LOD (μg kg^{-1})	MRL China	MRL EU
trichlorfon	$y = 3828670x + 54567$	0.985	0.3	100	500
malathion	$y = 6450658x + 44236$	0.9987	0.6	2000	
acephate	$y = 1846474x + 3535$	0.9995	1.2	200	20
methamidophos	$y = 3918925x + 12815$	0.991	0.4		10
omethoate	$y = 2675490x + 22640$	0.998	0.5		
dimethoate	$y = 3831077x + 5936$	0.9999	0.3	1000	20
phosphamidon	$y = 923222x + 19594$	0.9827	1.6		50
monocrotophos	$y = 1620740x - 15848$	0.9969	0.7		
methyl parathion	$y = 3402563x + 104624$	0.9814	0.5		200

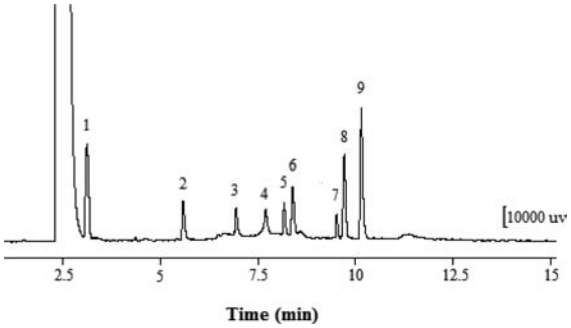

Figure 5. Gas chromatograms of apple sample spiked with nine organophosphorous pesticides at a level of 20 μg kg^{-1} and preconcentration by a MIMSPD procedure. Peaks: 1, trichlorfon; 2, methamidophos; 3, acephate; 4, omethoate; 5, monocrotophos; 6, dimethoate; 7, phosphamidon; 8, methyl parathion; 9, malathion.

ment factors between 4.2 and 9.8 were obtained by comparing the slopes of the linear portion of the calibration curves before and after preconcentration. The limit of detection (LOD) (S/N = 3) of this method for the nine organophosphorous pesticides was in the range of 0.3−1.6 μg kg^{-1} (Table 2). The linear ranges of the calibration graph were all between 0.001 and 10.0 mg L^{-1} with good correlation coefficients of >0.981.

Applicability of the MIMSPD-GC Method. To evaluate the applicability of the MIMSPD-GC method, the apple and pear samples spiked with nine organophosphate pesticides at 20 and 100 μg kg^{-1} levels were extracted and analyzed (Figure 5). For each concentration, triple measurements were performed, and good recoveries between 81 and 105% were obtained (Table 3). The peak area precision (RSD) for five replicate extractions of spiked samples was 1.2−4.8%. These results indicated that the developed method had high accuracy and precision.

The developed method was applied for the extraction and determination of nine pesticide residues in orange samples. Trichlorfon, acephate, methamidophos, omethoate, dimethoate, phosphamidon, and monocrotophos were not found in orange samples, which indicated that these seven organophosphorus pesticides may be not widely applied in orange cultivation. Methyl parathion and malathion were quantitatively detected with different levels of 0.016 and 0.024 mg L^{-1}. According to the "Japanese Positive List System" and the World Health Organization, the MRLs for organophosphorous pesticides in primary agricultural products are 0.01−8.0 mg L^{-1}. In China, methyl parathion has been forbidden to be sprayed in fruit trees. Therefore, more efforts should be devoted to the control of pesticide residues in primary agricultural products.

Table 3. Recoveries of Nine Organophosphate Pesticides in the Spiked Fruit Samples (Mean ± RSD, $n = 3$)

sample	pesticide	contents in sample (μg kg^{-1})	spiked level = 20 μg kg^{-1} detected content (±SD, μg kg^{-1})	spiked level = 20 μg kg^{-1} recovery (%)	spiked level = 100 μg kg^{-1} detected content (±SD, μg kg^{-1})	spiked level = 100 μg kg^{-1} recovery (%)
apple	trichlorfon	0.8	18.8 ± 0.4	90 ± 2	90.7 ± 2.0	90 ± 2
apple	malathion	26.0	45.7 ± 0.6	99 ± 3	124.6 ± 2.7	99 ± 3
apple	acephate		17.8 ± 0.6	89 ± 3	92.7 ± 2.5	93 ± 3
apple	methamidophos		20.9 ± 0.3	105 ± 2	100.4 ± 2.2	100 ± 2
apple	omethoate		17.5 ± 0.4	88 ± 2	88.9 ± 3.2	89 ± 4
apple	dimethoate		18.3 ± 0.6	92 ± 4	82.1 ± 3.3	82 ± 4
apple	phosphamidon		19.2 ± 0.7	96 ± 4	89.5 ± 2.8	89 ± 3
apple	monocrotophos		18.0 ± 0.6	90 ± 3	98.1 ± 3.5	98 ± 4
apple	methyl parathion		17.4 ± 0.5	87 ± 3	86.8 ± 2.1	87 ± 2
pear	trichlorfon		18.0 ± 0.9	90 ± 5	90.0 ± 3.6	90 ± 4
pear	malathion	8.5	28.0 ± 0.5	97 ± 2	103.7 ± 1.9	95 ± 2
pear	acephate		17.3 ± 0.6	86 ± 3	91.0 ± 2.9	91 ± 3
pear	methamidophos	24.0	22.1 ± 0.8	98 ± 4	105.2 ± 4.3	81 ± 4
pear	omethoate		19.1 ± 0.3	95 ± 2	91.0 ± 1.1	91 ± 1
pear	dimethoate		17.9 ± 0.2	90 ± 1	89.3 ± 3.8	89 ± 4
pear	phosphamidon		18.8 ± 0.2	94 ± 1	101.7 ± 2.0	102 ± 2
pear	monocrotophos		19.8 ± 0.8	99 ± 4	96.0 ± 2.5	96 ± 3
pear	methyl parathion		17.6 ± 0.6	88 ± 4	84.6 ± 1.4	85 ± 2

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Merits of the Developed Method. On the basis of the MIP sorbent, the present method has sufficient sensitivity for the determination of trace multipesticide residues in samples to meet export regulations. The LOD of this method was much lower than the MRLs of the European Union (EU) and China (Table 2). Therefore, the use of MIMSPD can improve the precision of the GC method and lower the LOD because of its good adsorption ability and selectivity. More importantly, without sample extraction and loading procedures, about 70 min of analysis time was reduced in this method compared with the traditional SPE. Thus, the cost per analysis of the MIMSPD-GC method was reduced.

On the basis of these results, this study established a methodology for the preparation of a MIP that can selectively recognize many structural analogues. Moreover, we will provide a new tool for the rapid determination of multipesticide residues in the complicated food samples.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

AAS, atomic absorption spectrometry; TLC, thin layer chromatography; CE, capillary electrophoresis; GC-MS, gas chromatography−mass spectrometry; LC-MS, liquid chromatography−mass spectrometry; GC, gas chromatography; LC, liquid chromatography; LLE, liquid−liquid extraction; SPE, solid-phase extraction; SFE, supercritical fluid extraction; SPME, solid-phase microextraction; SBSE, stir bar sorptive extraction; MSPD, matrix solid-phase dispersion; DLLME, dispersive liquid−liquid microextraction; MIPs, molecularly imprinted polymers; MIMSPD, molecularly imprinted matrix solid phase dispersion; MIMSPD-GC, molecularly imprinted matrix solid phase dispersion coupled to gas chromatography; EGDMA, ethylene glycol dimethacrylate; AIBN, 2,2-azobis-(isobutyronitrile); AM, acrylamide; MAA, methacrylic acid; DDW, doubly deionized water; NIP, nonimprinted polymer; *Q*, adsorption capacity; LOD, limit of detection; RSD, peak area precision; MRL, maximum residue limit

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