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Preparation, evaluation and application of molecularly imprinted solid-phase microextraction monolith for selective extraction of pirimicarb in tomato and pear

Jinfang Zhou, Chao Ma, Shu Zhou, Peili Ma, Fangrong Chen, Yue Qi, Huaixia Chen *

Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules & College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China

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ABSTRACT

A simple, rapid and sensitive method for the determination of pirimicarb in tomato and pear using polymer monolith microextraction (PMME) based on the molecularly imprinted polymer (MIP) monolith combined with high-performance liquid chromatography-photodiodes array detector (HPLC-PAD) was developed. By optimizing the polymerization conditions, such as the nature of porogenic solvent and functional monomer, the molar ratio of the monomer and cross-linker, an pirimicarb MIP monolith was synthesized in a micropipette tip using methacrylic acid (MAA) as the functional monomer, ethylene dimethacrylate (EGDMA) as the cross-linker and the mixture of toluene-dodecanol as the porogenic solvent. The MIP monolith showed highly specific recognition for the template pirimicarb. The monolith was applied for the selective extraction of pirimicarb in tomato and pear. Several parameters affecting MIP-PMME were investigated, including the nature and volume of extraction solvent, sample volume, flow rate and sample pH. Under the optimum PMME and HPLC conditions, the linear ranges were 2.0–1400 μg/kg for pirimicarb in tomato and pear with the correlation coefficient of above 0.999. The detection limits (s/n = 3) were both 0.6 μg/kg. The proposed method was successfully applied for the selective extraction and determination of pirimicarb in tomato and pear.

1. Introduction

Worldwide pesticide usage has increased dramatically during the last two decades which has resulted in the presence of their residues in fruit, vegetable and various environmental matrices [1,2]. Pirimicarb (Fig. 1), one of the most important representatives substituted N,N-dimethylcarbamate insecticides, was introduced in 1969 as selective insecticide and applied against aphids in fruit and vegetable culture. Inhibition of acetylcholinesterase is the basis for its insecticidal effect but causes toxicity for mammals including man as well [3]. It is suspected carcinogens and mutagens [4]. The Chinese safe maximum residue limits (MRLs) for pirimicarb in fruit and vegetable are 500 and 1000 μg/kg, respectively.

Usually, the complexity of food matrices and contaminants presented in food at low concentration levels require performance analysis only after some clean-up and preconcentration steps [5]. So, there is a considerable interest in developing new selective and sensitive methods for extracting and isolating components from complex food matrices.

The commonly used solid phase extraction (SPE) and liquid–liquid extraction (LLE) processes are complex, time consuming and low selectivity. Recently, a novel microextraction technique using polymer monolith microextraction (PMME) based on the molecularly imprinted polymer (MIP) technology have been described by Feng and co-workers [6]. In the paper, by using water-compatible MIPs as a specific PMME sorbents, fluoroquinolones in milk samples were selectively isolated and matrix interferences eliminated, which significantly enhanced PMME selectivity.

Molecular imprinting is a technique for the creation of artificial receptor-like binding sites with a "memory" for the shape and functional group positions of the template molecule. Non-covalent bonding, ionic interactions and hydrophobic interactions are usual used in the synthesis of molecularly imprinted polymer (MIP). Over the past decades, this technique has received considerable attention due to the potential applications in the fields of chromatographic stationary phases [7–10], solid-phase extraction [11–13], artificial antibody minics [14,15], catalysis [16,17], and biosensing [18,19]. Traditionally, the MIPs as SPE and HPLC materials have been prepared by bulk polymerization. However, the resulting polymer blocks must be crushed, grounded and sieved to desired size ranges for practical use. These tedious procedures maybe lead to the destruction of some interaction sites. MIP mono-

* Corresponding author. Tel.: +86 27 88662747; fax: +86 27 88663043.
E-mail address: hxch88@yahoo.com.cn (H. Chen).

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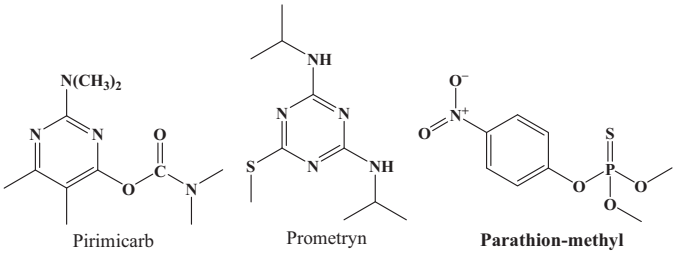

Fig. 1. Structural formula of pirimicarb, prometryn and parathion-methyl.

lith prepared by in situ synthesis with the ideal porous structure accelerates the rate of mass transfer and has good separation efficiency. MIP monolith has been applied to SPE [20–25] and liquid chromatography stationary phase [26–28].

Polymer monolith microextraction (PMME) is one type of solid-phase microextraction in which the polymer monolith is used as the sorbent [29–31]. This method integrates sample extraction, concentration and introduction into a single step. The polymer monolith shows stability in most conditions that has been applied for the determination of trace organic pollutants and drug in the environmental and biological samples. In contrast to in-tube SPME [32], this novel technique is free moving and requires only a simple instrument and manipulation. The combination of polymer monolith with MIP technology can be used as an extraction medium for achieving high extraction efficiency and selectivity of the analytes from complex matrices.

To date, several MIP sorbents using pirimicarb as the template have been reported [33–35]. However, the combination of the pirimicarb MIP with PMME has been obtained little attention.

In this study, pirimicarb imprinted polymer monolith was synthesized in a micropipette tip for the first time. The specific recognition of the MIP monolith for the template pirimicarb was evaluated. The MIP monolith was applied to the PMME process for the selective extraction of pirimicarb. The pirimicarb MIP monolith could be connected with syringes in different sizes simply without any other treatment. Various experimental parameters were optimized. The optimized method based on MIP-PMME combined with high-performance liquid chromatography (HPLC) was applied for the determination of pirimicarb in tomato and pear to evaluate the application of this method to real samples.

2. Experimental

2.1. Reagents and standards

Ethylene dimethacrylate (EGDMA) purchased from Acros (New Jersey, USA) was extracted with 5% aqueous sodium hydroxide and water, then dried over using anhydrous magnesium sulfate. 2,2′-azobisisobutyronitrile (AIBN) was obtained from Shanghai No. 4 Chemical Reagent Corp. (Shanghai, China) and recrystallized in anhydrous ethanol before use. Pirimicarb, parathion-methyl, prometryn were purchased from Dikma Technology Inc. (Beijing, China). 4-Vinylpyridine (4-VP) was obtained from Acros (New Jersey, USA). Methacrylic acid (MAA), acrylic acid (AA), toluene and dodecanol purchased from Fuchen Chemical Reagent Company (Tianjin, China) were distilled under vacuum prior to use. Methanol and acetonitrile (HPLC grade) were obtained from Tedia Company Inc. (Ohio, USA). Sodium chloride, phosphoric acid and other reagents used were all of analytical grade. The water used was purified on an Ultrapure Water System (Beijing, China).

The stock standard solution was prepared in methanol at a concentration of 5.82 mg/mL and stored at 4 °C in refrigerator. Working standard solutions of pirimicarb were prepared by appropriate dilution of the stock solution using deionized water.

20.0 g of chopped sample (tomato and pear) were weighed into a 50 mL glass beaker and mixed with 2.0 g of sodium chloride and 15.0 g of anhydrous sodium sulfate. Then, 30 mL of acetonitrile was added. Briefly, extraction was performed by sonication, followed by washing with acetonitrile (twice, 20 mL each) during filtration in buchner funnel. The three extraction fractions were collected to concentrate in rotator-evaporator at 40 °C until dryness. Then, it was reconstituted in 40 mL of water. Finally, the reconstituted solutions were stored at 4 °C and filtered through a 0.45 μm membrane filter prior to use.

2.2. Instrumentation

The chromatographic analysis was carried out on a Dionex Summit U3000 HPLC system equipped with a manual injector and a Photodiode Array Detector (PAD) (Dionex Technologies, USA). A personal computer equipped with a Chromeleon Chem-Station program for LC was used to process chromatographic data. A amethyst-C18 column (4.6 mm × 250 mm, 5 μm) from Sepax Technologies Inc. (Newark, USA) was connected with a guard column (cartridge 2.1 mm × 12.5 mm, 5 μm, Agilent Technologies, PaloAlto, CA, USA) filled with the same packing material. The mobile phase was a mixture of methanol–water (60:40, v/v) and the flow rate was 1.0 mL/min. The column temperature was set at 25 °C by a temperature controller (Nuohai Technologies, China). The UV detector was set at a wavelength of 246 nm for analytes. All injections were performed manually with a 20.0 μL sample loop. An LSP01-1A longer pump (Baoding Longer Precision Pump Co. Ltd., China) was used for pumping. 0.45 μm membrane was obtained from Xingya Scavenging Material Company (Shanghai, China). The microscopic morphology of the monolith was examined by a Model X-650 scanning electron microscope (Hitachi, Tokyo, Japan).

2.3. Preparation of molecularly imprinted monolith

The pirimicarb imprinted polymer monolith was prepared in a micropipette tip by in situ polymerization technique according to the optimized synthesis conditions in Section 3.1 and the previously reports [10,33]. Briefly, the template pirimicarb (0.042 mmol) was dissolved in 500 μL of porogenic solvents (toluene:dodecanol, 2:8, n/n) in a clean PE tube and mixed with MAA (0.25 mmol) as the functional monomer. The mixture was surged ultrasonically for 4 h. Then, 235 μL (1.25 mmol) of cross-linker EGDMA and 5.5 mg of initiator AIBN were added and degassed by ultrasonication for about 10 min. Next, 60 μL of the homogeneous solution was filled into a micropipette tip which had been sealed at one end. Subsequently, the other end of the pipette tip was sealed with silicon rubber. After polymerization at 60 °C for 27 h, the silicon rubber was removed. The resultant MIP monolith was washed with methanol to remove the template molecules. A reference, non-imprinted polymer monolith (NIP), was prepared simultaneously as the same procedure, including washing, but in the absence of the template molecule.

2.4. Preparation of the extraction device

As shown in Fig. 2, the pirimicarb imprinted polymer monolith could be connected with syringes in different sizes simply without any other treatment. A syringe infusion pump (Baoding Longer Precision Pump Co. Ltd., China) was employed for the delivery of sample solution, washing solution and desorption solvent.

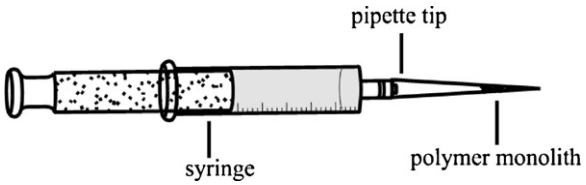

Fig. 2. Scheme of the novel PMME device.

2.5. MIP-PMME procedure

The MIP monolith was washing with 5.0 mL of methanol and 1.0 mL of water, respectively. Then, an aliquot of 5.0 mL homogeneous sample solution was loaded at a flow rate of 0.1 mL/min with the aid of an infusion pump. The MIP monolith was washed with 200 μL of water to remove the matrix interferences. Last, the analytes were eluted with 60 μL of ACN–water (8:2, v/v). The eluent solution in the PE tube was removed using a 100 μL HPLC microsyringe and injected into the HPLC system for analysis directly. All experiments were performed repeatedly and means of results were used in plotting of curves or in tables.

3. Results and discussion

In order to evaluate the extraction efficiency of MIP and obtain the optimized extraction conditions, enrichment factor (EF) and extraction recovery (ER) were used.

The enrichment factor was defined as the ratio between the analyte concentration in eluent (C_{elu}) and the initial concentration of analyte (C_0) within the sample.

$$EF = \frac{C_{elu}}{C_0}$$

The C_{elu} was obtained from calibration graph of direct injection of pirimicarb standard solution in ACN–water (8:2, v/v) mixed solvent.

The extraction recovery was defined as the percentage of the total analytes amount (n_0) which was extracted to the eluent (n_{elu}).

$$ER = \frac{n_{elu}}{n_0} \times 100 = \left[\frac{C_{elu} \times V_{elu}}{C_0 \times V_{aq}}\right] \times 100 = EF \times \left(\frac{V_{elu}}{V_{aq}}\right) \times 100$$

where V_{elu} and V_{aq} are the volumes of eluent and sample solution, respectively.

The imprinting factor (IF) was used to evaluate the recognition abilities of the MIP monolith.

$$IF = \frac{EF_{MIP}}{EF_{NIP}}$$

where the EF_{MIP} is the enrichment factor of pirimicarb extracted in MIP monolith and EF_{NIP} is the enrichment factor of pirimicarb extracted in NIP monolith under the same conditions.

3.1. Optimization of synthesis conditions

Several parameters were investigated to obtain higher specific recognition ability and extraction efficiency for the target analyte, such as the nature of porogenic solvent and functional monomer, the molar ratios of the monomer to cross-linker.

3.1.1. Selection of porogenic solvent

The selection of the porogenic solvent is significant for the preparation of the molecularly imprinted monolith. Porogenic solvent can make all components into one phase in the polymerization process, and played an important role in the morphology of the MIP monolith in terms of specific surface area and pore size. In the selection of porogenic solvent, some properties must be considered: (a) the porogenic solvent must be able to dissolve the template molecule, monomer, initiator and cross-linker. (b) The porogenic solvent should form large pores to ensure good flow-through properties of the polymer. (c) The polarity of the porogenic solvent should be lower in order to reduce the interferences during complex formation between the template molecule and the monomer. In this study, chloroform, acetonitrile, toluene and dodecanol as porogenic solvent were tested. The results showed that only the low polar mixture of toluene and dodecanol could satisfy the three properties. However, the rate of toluene and dodecanol also influenced the pore structure of polymer and led to the change of separation performance and column pressure. The investigation revealed that the mean pore size decreased with increasing the proportion of toluene. The monolith had too small pore diameter to allow the sample solution flow through when toluene reached 30% in the porogenic mixture. So, a balance had to be found between low backpressure of monolith and large surface area. Finally, 20% of toluene in the porogenic mixture was selected as the appropriate porogenic solvent.

Table 1
The effect of functional monomer on the IF of MIP monolith for pirimicarb.

Functional monomer	EF		IF
	MIP	NIP	
MAA	9.14	3.27	2.79
AA	5.73	3.69	1.55
MAA:4-VP, 1:1	10.27	8.71	1.17

3.1.2. Selection of functional monomer

To improve the recognition and selectivity property of MIP monolith, three different functional monomers were investigated, including MAA, AA, a mixture of 4-VP and MAA. Different functional monomers will construct different binding-site with template. The imprinting factors of different pirimicarb MIPs were compared in Table 1. It can be seen that, comparing with other functional monomers, MAA has the best imprinting recognition and extraction efficiency. So, in our further work, MAA was chosen as the functional monomer.

3.1.3. Effect of the molar ratios of the monomer and cross-linker

Increasing the amount of cross-linker can maintain the stability of the recognition sites and lead to high selectivity for the target. But, on the other hand, with increasing amount of cross-linker, the difficulty of mass transfer of analytes in MIP monolith increased. In this study, the molar ratios of the monomer to cross-linker ranged from 1:1 to 1:7 were investigated, respectively. The result revealed that when the ratio was lower than 1:3, the MIPs showed bad recognition ability. And, the backpressure is too high to allow the mobile phase to flow through the monolith when the ratio higher than 1:5. So, 1:5 was chosen as the optimized ratio of the monomer and cross-linker.

3.2. The characterization and specificity evaluation of the MIP monolith

The MIP monolith morphological structure was investigated by scanning electron microscope. As can be seen in Fig. 3, there were many macropores and flow-through channels inlaid in the network skeleton of pirimicarb imprinted monolith which provided flow paths through the column. Due to the size and density of the macropore network, the monolith had a high external porosity and, consequently, a large permeability and low column hydraulic resis-

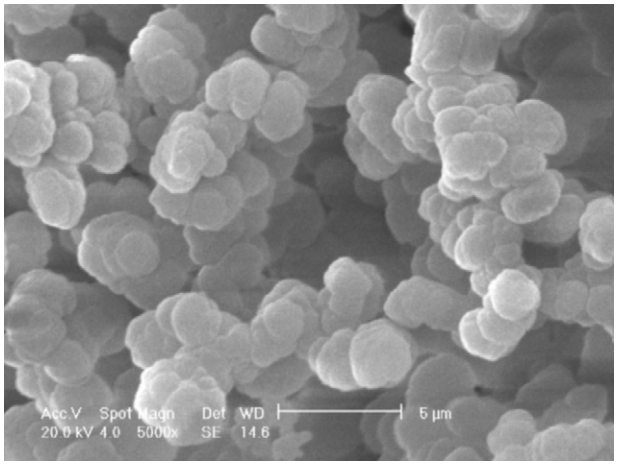

Fig. 3. SEM image of MIP monolith (magnification, 5000×).

tance. This pores allowed the mobile phase to flow through with low flow resistance.

Fig. 4 showed that the infrared spectrogram of pirimicarb imprinted monolith was different from that of pirimicarb and MAA.

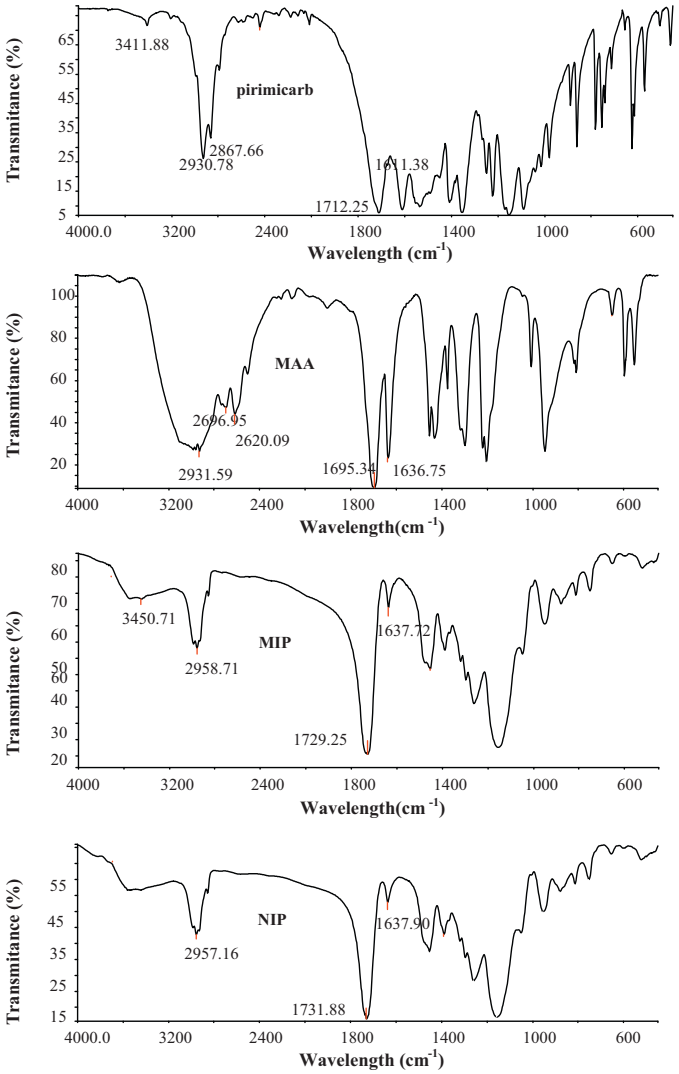

Fig. 4. FT-IR spectra of pirimicarb, MAA, MIP and NIP.

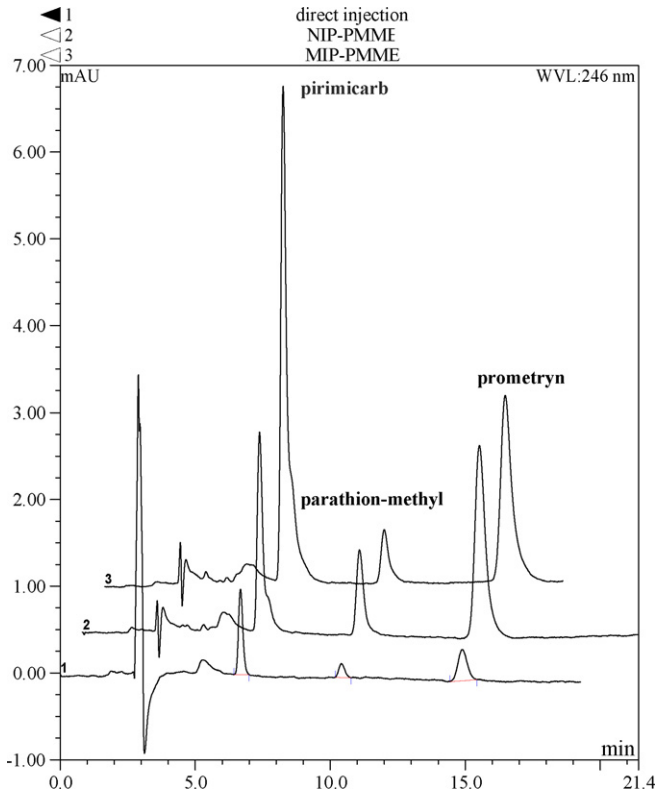

Fig. 5. HPLC chromatograms of mixed pirimicarb, prometryn and parathion-methyl standard solutions at concentration level 100 ng/mL. Sample injection was performed using: (1) direct injection; (2) NIP-PMME and (3) MIP-PMME. Extraction conditions: sample volume, 1 mL; eluent, 100 μL of methanol; sample flow rate, 0.1 mL/min. HPLC conditions: mobile phase, MeOH–water (70:30, v/v).

Comparing with the infrared spectrogram of MAA, the stretching vibration wide peak of 3000–3300 cm^{-1} and the peak of 1636 cm^{-1} became weak in the infrared spectrogram of the associated complexes. Comparing with the infrared spectrogram of pirimicarb, the peak of 3450 cm^{-1} appeared. The C=O stretch vibration peak of 1712 cm^{-1} shifted to that of 1729 cm^{-1}. These results showed that the polymers have been successfully synthesized. The NIP and MIP monoliths showed similar locations and appearances of the major bands. However, the stretching vibration peak of C=O at 1729 cm^{-1} of MIP monolith shifted and the intensity was higher than NIP monolith. The results indicated that the template molecules were assembled with monomer via the hydrogen-bonded interaction in preparing MIP monolith.

The MIP monolith was firstly in situ polymerized in a micropipette tip. The selectivity of MIP monolith is most likely because of hydrogen bone formation between the oxygen or nitrogen atoms of pirimicarb and MAA as the interaction for binding site construction [33].

In order to evaluate the selectivity of the MIP monolith, prometryn with similar structure to pirimicarb as the analogue and parathion-methyl as non-analogue were tested. For sampling, pirimicarb, prometryn and parathion-methyl standard solutions were mixed and diluted using deionized water at a final concentration of 100 ng/mL, 1.0 mL of the mixed solution was loaded on the MIP and NIP monoliths at a flow rate of 0.1 mL/min. 100 μL of methanol was used to elute analytes. The eluent was analyzed by HPLC directly. As shown in Fig. 5, the results indicated that the MIP had a higher affinity for pirimicarb than NIP. And, the MIP-PMME possessed higher extraction efficiency for prometryn than the NIP-PMME. This is due to the similar structure between prometryn and pirimicarb. The

Table 2
Recoveries, precisions, linear, LODs and LOQs of the MIP-PMME-HPLC method for pirimicarb in tomato and pear.

Matrix	Added (ng/kg)	Recovery (%)	RSD (%)		Regression equation	LOD (ng/kg)	LOQ (ng/kg)
			Intraday	Interday	r		
Tomato	20	105.3	4.2	7.6	$Y = 0.1045X + 0.3737$	0.6	2
	200	104.2	5.5	0.3			
	800	99.5	1.3	2.3	0.9999		
Pear	20	112.1	1.4	2.1	$Y = 0.1105X - 0.2513$	0.6	2
	200	101.9	7.2	7.2			
	1000	100.7	3.5	1.4	0.999		

data also showed that the retention of parathion-methyl on MIP was weaker than that on NIP. These results demonstrated the good selectivity of the synthesized MIP monolith for pirimicarb.

3.3. Optimization of MIP-PMME conditions

Several parameters associated with the MIP-PMME efficiency, such as the type and volume of eluent, the pH, flow rate and volume of sample solution, were optimized in this study. 50 ng/mL of the pirimicarb standard solution was used to perform the experiments.

3.3.1. Effect of eluent type

The selection of an appropriate eluent is of high important for the MIP-PMME process. Considering the consistency to the mobile phase used in liquid chromatography, the eluent is limited to solvents such as methanol, acetonitrile and purified water. 1.0 mL of 50 ng/mL pirimicarb standard solutions was used in the MIP-PMME system, and then different proportions of methanol with water, acetonitrile with water as eluent were tested. The results indicated that the mixture of ACN–water (8:2, v/v) as the eluent exhibited the highest EF and ER. The experimental results also showed that a certain amount of acetic acid in eluent could enhance the elution ability, but strong UV absorption of glacial acetic acid at 246 nm caused serious interference. Thus, an ACN–water mixture of 8:2 (v/v) was selected as the eluent.

3.3.2. Effect of sample pH

The sample pH is a significant factor, which may affect the molecule form of the analyte and closely relate to the interaction between analytes and the MIP monolith. The effect of the sample pH on the extraction efficiency for pirimicarb was investigated using several buffer solutions with pH 3.0–7.35. The results showed that pirimicarb underwent complete extracted at pH 5.56. The lower responses observed at lower pH may be attributed to the protonation of the amine group of pirimicarb molecules. These protonated charged molecules could not "fit" the binding sites, which led to that the pirimicarb molecules could not be adsorbed by the polymer. The decrease of the recovery at higher sample pH could be explained by the deprotonation of carboxyl in imprinted sites and the deprotonation charged imprinted sites could not adsorb analyte effectively. Thus, pH 5.56 was chosen as the optimum sample pH.

3.3.3. Effect of sample flow rate

The effect of sample flow rate (0.1–0.30 mL/min) has been investigated. The experimental results showed that EF and ER increased with decreasing the flow rate. This may be due to the plenitudinous mass transfer of the analyte from sample solution to MIP monolith at lower flow rate. In order to obtain better extraction efficiency, 0.1 mL/min was chosen as the optimized flow rate of sample solution in the following experiments.

3.3.4. Effect of sample volume

The effect of sample volume was monitored by loading pirimicarb standard solution (containing 50 ng/mL of the analyte) from 1.0 to 10.0 mL at a constant flow rate. The eluent volume (ACN–water, 8:2, v/v) was 0.1 mL. The results showed that EF of pirimicarb increased with the increasing of sample volume from 1.0 to 10.0 mL. This indicates that the extraction capacity was not reached even when 10.0 mL of sample solution was loaded. However, ER began to decrease when the sample volume increased. For obtaining higher EF and ER for pirimicarb, 5.0 mL of sample solution was selected in the MIP-PMME procedure.

3.3.5. Effect of eluent volume

In order to study the effect of eluent volume on the extraction efficiency, different volumes of eluent (ACN–water, 8:2, v/v) were tested. The experimental results showed that 60 μL eluent was sufficient to elute more than 85% analyte from the monolith. Moreover, further increasing the volume of the eluent was not preferred because EF decreased with the increasing of eluent volume. Thus, 60 μL of eluent volume was selected for subsequent work.

3.4. Evaluation of the method

Blank tomato and pear samples were spiked at range of 2.0–1400 μg/kg with the pirimicarb. Then, the spiked samples were analyzed by the proposed MIP-PMME-HPLC method. As shown in Table 2, the regression coefficients (r) of the calibration curves were greater than 0.999. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated at signal-to-noise ratios (S/N) of 3 and 10, respectively. The LODs of the method were 0.6 μg/kg for pirimicarb in tomato and pear, and the LOQs were 2 μg/kg for pirimicarb in tomato and pear, respectively. The LODs of the analyte in tomato and pear were both lower than the Chinese safe maximum residue limits.

The reproducibility of the method was determined by the within-day and between-day precisions at the concentration of 20, 200, 800 μg/kg in spiked tomato and 20, 200, 1000 μg/kg in spiked pear for pirimicarb, respectively. As shown in Table 2, the results showed that the intraday precisions (RSDs) were 1.3–5.5% for tomato and 1.4–7.2% for pear, while the interday precisions (RSDs) were 0.3–7.6% and 1.4–7.2%, respectively.

3.5. Real samples analysis

The chromatograms of spiked tomato and pear samples before and after treated by MIP-PMME were shown in Fig. 6. The results showed that pirimicarb was extracted effectively. And no interference from the samples matrix was observed after MIP-PMME process, which demonstrated the high selectivity of the MIP monolith for pirimicarb.

The developed MIP-PMME-HPLC method was applied for the determination of pirimicarb in tomato and pear samples to elucidate its applicability and reliability. Fresh tomoto and pear samples were collected from local supermarkets. The experimental results

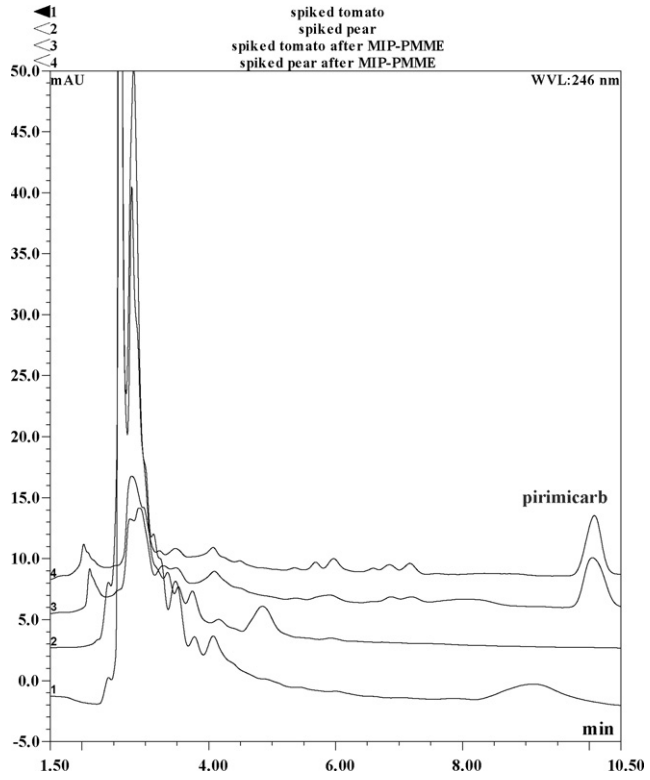

Fig. 6. HPLC chromatograms of pirimicarb in tomato and pear samples: (1) spiked tomato, (2) spiked pear, (3) spiked tomato after MIP-PMME and (4) spiked pear after MIP-PMME. Samples solutions of pirimicarb were spiked at 20 μg/kg. HPLC conditions: mobile phase, MeOH–water (60:40, v/v).

showed that three different batches of tomato and pear samples were free of pirimicarb contamination. To test the performance of the established method, the extraction recoveries were performed by fresh tomato and pear samples spiked with pirimicarb standard solution. For each concentration level, five replicate experiments with the whole analysis process were made. The recoveries of pirimicarb in the spiked tomato and pear samples were 99.5–105.3% and 100.7–112.1%, respectively.

4. Conclusion

A novel, durable pirimicarb MIP monolith was synthesized in a micropipette tip for the first time. The micromonolith could be connected with syringes in different sizes simply without any other treatment to perform PMME process.

A new method was developed for the sensitive, selective determination of pirimicarb in tomato and pear by combining MIP-PMME with HPLC-PAD. The optimum conditions of synthesis and extraction performance have been obtained. The experimental results revealed that this method provided high selectivity, lower solvent consumption, higher extraction efficiency and good linearity over the investigated concentration range. The performance of the procedure in the analysis of pirimicarb in tomato and pear samples was satisfactory.

Acknowledgements

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