



## Analytical Methods

## Molecularly imprinted calixarene fiber for solid-phase microextraction of four organophosphorous pesticides in fruits

Jing-Wen Li, Yu-Long Wang, Shan Yan, Xiu-Juan Li<sup>\*</sup>, Si-Yi Pan

Key Laboratory of Environment Correlative Dietology (Ministry of Education), College of Food Science &amp; Technology, Huazhong Agricultural University, Wuhan 430070, China

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## ABSTRACT

Calixarene was used as a functional monomer to fabricate a molecularly imprinted polymer (MIP) by sol-gel technique for solid-phase microextraction (SPME) of parathion-methyl and its structural analogs. The MIP-coated fiber possessed excellent thermal and chemical stability as well as high extraction capacity. Its selectivity and possible recognition mechanism were investigated. The similarities in molecular shape and functional group play a key role in the selective recognition of the imprinted material. Any changes to the structure of the template would decrease the imprinting factor. A comparison of MIP-SPME was made with liquid-liquid extraction coupled with gas chromatography for the determination of organophosphorus pesticides (OPPs) in fruits. Much lower limits of detection and better recoveries were achieved by SPME in spiked apple and pineapple samples. The experiment demonstrates that the proposed method using the calixarene MIP fiber was more suitable for selective determination of trace OPPs in those fruit samples.

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## 1. Introduction

Molecularly imprinted polymers (MIPs) are attractive synthetic materials with artificial receptor-like binding sites able to specifically rebinding a target molecule and its structural analogous compounds (Martín-Esteban, 2013; Wen, Chen, Li, Liu, & Chen, 2014). Recently, great attention has been paid to the development of MIPs for solid-phase microextraction (SPME) (Manbohi, Shamaeli, & Alizadeh, 2014; Zhang, Zeng, Wang, & Chen, 2013; Zhao, Guan, Tang, Ma, & Zhang, 2015). Once the testing object is decided, the most straightforward task is to choose the proper monomer whose substituent groups would directly determine the interaction types and the number of binding sites. Up to now, the most frequently used functional monomer in MIP-SPME is methacrylic acid, which can easily establish strong hydrogen bond with imprinted molecules. However, it is essential to match the functionality of the template with that of the functional monomer in a complementary

fashion to maximize complex formation and further increase the imprinting effect.

Calixarenes are cavity-shaped cyclic molecules made up of phenol units linked via alkylidene groups, and have aroused great interest for their host-guest chemistry. Several kinds of calixarene-based sol-gel SPME fibers had been prepared previously in our laboratory (Li, Ye, Huo, & Zeng, 2010; Li, Zeng, & Zhou, 2004; Li et al., 2004; Ye et al., 2009). The fibers exhibited high sensitivity and selectivity to aromatic compounds mainly owing to  $\pi$ - $\pi$  and inclusion interactions. What's more, these coatings showed excellent thermal and chemical stability. By modifying with functional groups, the polarity and selectivity of calixarenes could be further enhanced.

Few reports have been found on the use of calixarenes for MIPs. Lu, He, He, and Zeng (2004) prepared MIPs with 25,27-diallyl-26,28-dihydroxylic calix[4]arene for the recognition of acetanilide. The phenyl moiety of acetanilide may go into the hydrophobic cavity of calix[4]arene, which increased the selective recognition properties of acetanilide-imprinted polymers. Li, Wang, Guan, Zhang, and Hu (2005) reported an electrochemical sensor for the determination of parathion using

<sup>\*</sup> Corresponding author.E-mail addresses: [lixj78@126.com](mailto:lixj78@126.com), [lixjujuan@mail.hzau.edu.cn](mailto:lixjujuan@mail.hzau.edu.cn) (X.-J. Li).

*p*-tert-butylcalix[6]-1,4-crown-4 as a functional monomer. The structural analogs did not interfere obviously with the electrochemical response of parathion. Faizal, Kikuchi, and Kobayashi (2009) developed a polymer membrane targeted to  $\alpha$ -tocopherol containing calix[4]resorcinarenes, and an imprinting factor (IF, the ratio of extraction ability of the MIP fiber to non-imprinted polymer (NIP) fiber) of 1.85 was obtained. These studies demonstrate that calixarenes are promising functional monomers for MIPs due to their special hydrophobic cavity with plentiful  $\pi$  electrons.

Parathion-methyl, one of the most important representatives of substituted aromatic organophosphorus pesticides (OPPs), is frequently applied against sucking and chewing insects in fruits and vegetables. The residue, however, becomes a potential threat to human beings by bioaccumulation. Countries over the world have established the maximum residue limit (MRL) for parathion-methyl in food. In China, the MRL in most fruits and vegetables is between 10 and 20  $\mu\text{g kg}^{-1}$  according to GB 2763-2014, which is consistent with that established by the European Union (European Union, 2013). Therefore, the sensitive detection of parathion-methyl residue is generally necessary for food safety. However, unlike the typical template molecules containing amino, hydroxyl, azine or carboxyl, parathion-methyl has no such groups, which is disadvantageous to build strong interactions with conventional functional monomers such as methacrylic acid.

In this study, 5,11,17,23-tetra-*tert*-butyl-25,27-dicyanomethoxyl-26,28-dihydroxy calix[4]arene (C[4]) was firstly synthesized and introduced for preparation of MIP-SPME fiber targeted for parathion-methyl by sol-gel technique. The characteristics and extraction efficiency of the fiber were evaluated. Its selectivity and possible recognition mechanism were investigated. After optimization of some parameters influencing MIP-SPME extraction, the novel MIP-coated fiber combined with SPME-gas chromatography (GC) method has been successfully developed for simultaneous monitoring of four residual OPPs in apple and pineapple samples. Meanwhile, liquid-liquid extraction (LLE) coupled with GC was applied for comparison.

## 2. Experimental

### 2.1. Reagents, standards and materials

Individual stock standard solutions of parathion, fonofos, fenitrothion, fenthion, ethion and sulfotep at a concentration of 100  $\mu\text{g mL}^{-1}$  in acetone were purchased from Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China). Parathion-methyl (99.0%) was purchased from Helishun Technology Ltd. (Beijing, China). Diethyl phthalate (DEP) (99%) was obtained from Fluka (Sigma-Aldrich, Steinheim, Germany). The stock solutions of parathion-methyl and DEP were prepared in methanol at a concentration of 1  $\text{mg mL}^{-1}$  and stored at 4 °C in a refrigerator. A mixed stock solution containing parathion-methyl (0.05  $\text{mg mL}^{-1}$ ), parathion (0.015  $\text{mg mL}^{-1}$ ), fonofos (0.005  $\text{mg mL}^{-1}$ ) and fenitrothion (0.03  $\text{mg mL}^{-1}$ ) was prepared according to the responses of different pesticides in nitrogen phosphorus detector (NPD). Diluting the stock solution serially with methanol yielded working standard solutions.

C[4] was synthesized and kindly provided by Professor Haibing Li at the Central China Normal University. Hydroxy-terminated silicone oil (OH-TSO), poly(methylhydrosiloxane) (PMHS), tetraethoxysilane (TEOS) and 3-(2-cyclooxypropoxyl) propyltrimethoxysilane (KH-560) were obtained from Wuhan University Silicone New Material Co., Ltd. (Wuhan, China). Trifluoroacetic acid (TFA) was purchased from Shanghai Chemical Factory, China. Potassium bromide (KBr) was spectroscopically pure and other reagents were of analytical grade, and all of them

were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Apple and pineapple were randomly purchased from a local market (Wuhan, China). 100 g of fruits were homogenized along with 100 mL of distilled water using a juice extractor (Philips China Co., Guangzhou, China). The samples were then placed in separate amber glass bottles and stored in a freezer at 4 °C until analysis.

### 2.2. Instruments and chromatographic conditions

Experiments were conducted with a SP-6890A capillary GC system (Shandong Lunan Ruihong Chemical Engineering Instrument Co., Ltd., Tengzhou, China) equipped with a capillary split/splitless injector system and an NPD system. Separations were performed on a SE-54 capillary column (30 m  $\times$  0.32 mm  $\times$  0.33  $\mu\text{m}$ , Lanzhou ATECH technologies Co., Ltd., Lanzhou, China) using ultrapure nitrogen (99.999%) as the carrier gas at a linear velocity of 12–15  $\text{cm s}^{-1}$ . Online data collection and processing were carried out with a chromatopac model N2000 (Hangzhou Mingtong Technology Co., Ltd., Hangzhou, China). The injector and detector temperatures were set at 250 °C and 260 °C, respectively. The oven temperature was programmed from 60 °C held for 3 min, to 180 °C at ramp rate of 15 °C  $\text{min}^{-1}$ , held for 5 min, and finally heated at 5 °C  $\text{min}^{-1}$  to 220 °C held for 3 min.

A magnetic stirrer DF-101S (Zhengzhou Greatwall Scientific Industrial and Trading Co., Ltd., Zhengzhou, China) was employed to stir the sample during extraction. A laboratory-made SPME fiber syringe was used to transfer the extracted analytes to the GC injector for analysis. The commercial available polydimethylsiloxane (PDMS, 100  $\mu\text{m}$ ), polyacrylate (PA, 85  $\mu\text{m}$ ), PDMS/divinylbenzene (PDMS/DVB, 65  $\mu\text{m}$ ) and DVB/carboxen/PDMS (DVB/CAR/PDMS, 50/30  $\mu\text{m}$ ) coated fibers were purchased from Supelco (Bellefonte, PA, USA). The morphological evaluation of the prepared fiber was performed with a JSM-6390LV scanning electron microscope (JEOL, Tokyo, Japan). The infrared absorption spectra were obtained with a Nicolet Nexus 470 FT-IR spectrometer (Thermo Nicolet, USA). The thermal stability of the coating was analyzed by thermogravimetric analysis (TGA, Netzsch, Germany) under nitrogen atmosphere, over the temperature of 50–600 °C at a heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.3. Fiber preparation

The MIP-coated SPME fibers were fabricated by sol-gel molecular imprinting technique with C[4] as a functional monomer and parathion-methyl as a template molecule. The sol solution was prepared as follows: 30 mg of C[4] and 11.2 mg of parathion-methyl were dissolved in 600  $\mu\text{L}$  of dichloromethane in a polypropylene tube. This solution was stored for 12 h at room temperature. And then 90 mg of OH-TSO, 10 mg of PMHS, 100  $\mu\text{L}$  of TEOS, 50  $\mu\text{L}$  of KH-560 were added and mixed thoroughly by ultrasonic agitation for 5 min. An 80- $\mu\text{L}$  volume of TFA containing 5% water was sequentially added to the resulting solution with ultrasonic agitation for another 5 min. The mixture was then centrifuged at 12,000 rpm for 8 min and the top clear sol solution was moved to another tube for fiber coating. The pre-treating and coating of fused-silica fibers were the same as Li, Zeng, Gao, and Li (2004). The fibers were then placed in a desiccator at room temperature for 48 h and then conditioned at 150 °C, 200 °C, and 250 °C under nitrogen for each 1 h in the GC injector, successively. The final thickness of the fiber coating was 50  $\mu\text{m}$ . The NIP-coated fiber and blank fiber were also prepared following the identical procedures without the addition of parathion-methyl, parathion-methyl and C[4], respectively.

#### 2.4. Headspace SPME (HS-SPME) procedures

Each day prior to analysis, the fibers were conditioned in the GC injection port to ensure no residual contamination occurred. In a typical assay, 2  $\mu\text{L}$  of standard solution, 4 mL of distilled water (or 2 g of sample solution with 2 mL of water) and 1.6 g of NaCl were placed into a 10-mL glass vial containing a magnetic stirring bar. To avoid sample evaporation, the vial was tightly capped with a PTFE stopper and an aluminum cap. Extraction was performed by exposing the coated fiber to the headspace of the vial at 70  $^{\circ}\text{C}$  for 30 min under a stirring rate of 600 rpm. After a suitable extraction time, the fiber was withdrawn into the needle, and the needle was removed from the sample vial and immediately inserted into the GC injector for thermal desorption at 250  $^{\circ}\text{C}$  for 8 min. All the determinations were performed in triplicate except extra explanations. The average values and their standard deviations (SD) were reported.

#### 2.5. LLE procedure

Four OPPs in apple and pineapple samples were extracted and purified according to the Agricultural Standard of China NY/T 761-2008 (<http://down.foodmate.net/standard/sort/5/15091.html>). Briefly, a portion of 25 g of chopped sample was weighed into a homogenizer, followed by adding 50 mL of acetonitrile, and then the mixture was vigorously shaken for 2 min and filtrated by filter paper. The filtrate with the volume of 40–50 mL was collected in a 100-mL measuring cylinder with stopper. Subsequent phase separation was facilitated by adding 6 g of NaCl and shaking for 1 min. After standing for 30 min, 10 mL of acetonitrile solution from the upper layer was suctioned out and put into a beaker and then evaporated to near dryness in water bath under 80  $^{\circ}\text{C}$  with a stream of nitrogen. Less than 5 mL of acetone was applied to flush the beaker for 3 times, and the solutions were totally transferred to a 15-mL centrifuge tube. Finally the solution was diluted to 5 mL with acetone and mixed thoroughly by utilizing a vortex mixer. If the sample solution was not clear, a membrane filtration procedure was conducted before GC analysis.

### 3. Results and discussion

#### 3.1. Characterization of the prepared fibers

The scanning electron microscope (SEM) was employed to assess the morphology of the MIP-coated fiber (Fig. 1S). Fig. 1SA–B shows that the surface of the coating was covered with a large number of raised nubbins, which increased the surface area of the fiber. As exhibited in Fig. 1SC, a loose structure was observed in the internal coating, which was beneficial for the mass transfer during absorption and desorption.

Fig. 2S exhibits the IR adsorption spectra of NIP and MIP (after removing the template) coatings. The same spectra of the two coatings indicated a complete remove of the template.

The thermal stability of the MIP coating was explored by TGA. As revealed in Fig. 3S, a good stability from room temperature to 300  $^{\circ}\text{C}$  with a weight loss lower than 5% was observed and an obvious mass loss occurred at 380  $^{\circ}\text{C}$ , which can be assigned to the maximum practicable temperature of the sol-gel MIP-SPME fiber. The thermal property of the coating was further evaluated by placing the fiber in the GC injector for 30 min at 250, 270, 290, 310 and 330  $^{\circ}\text{C}$ , successively. The fiber was then used to extract OPPs from aqueous samples, and the results were given in Fig. 4S. There was no apparent change by comparison of the peak areas at 250  $^{\circ}\text{C}$  with those at 330  $^{\circ}\text{C}$ . Moreover, no crack was found on the surface of the fiber. Accordingly, the C[4] imprinted fiber had high thermal stability, much higher than those prepared by co-polymerization methods (He et al., 2010; Hu et al., 2012; Zhang, Xu, Lim, & Lee, 2012). Apart from the sol-gel technique, the contribution of C[4] also improved the thermostability of the coating (Li, Zeng, Gao, & Li, 2004; Li, Zeng, & Zhou, 2004).

The chemical stability was performed by immersing the MIP-coated fiber in methanol, acetone, benzene, water, 0.1 M HCl and 0.1 M NaOH separately for 0.5 h under the stirring speed of 600 rpm. Subsequently, the fiber was applied to extract OPPs from spiked water samples. As illustrated in Table 1S, there was no statistically significant differences ( $P \leq 0.05$ ) in extraction efficiency. The tested fiber also retained good surface quality without any

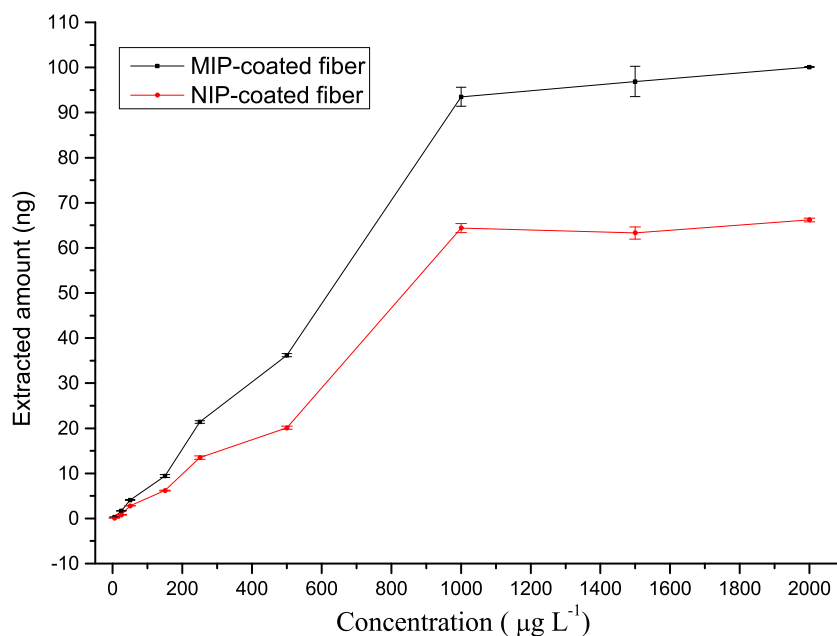
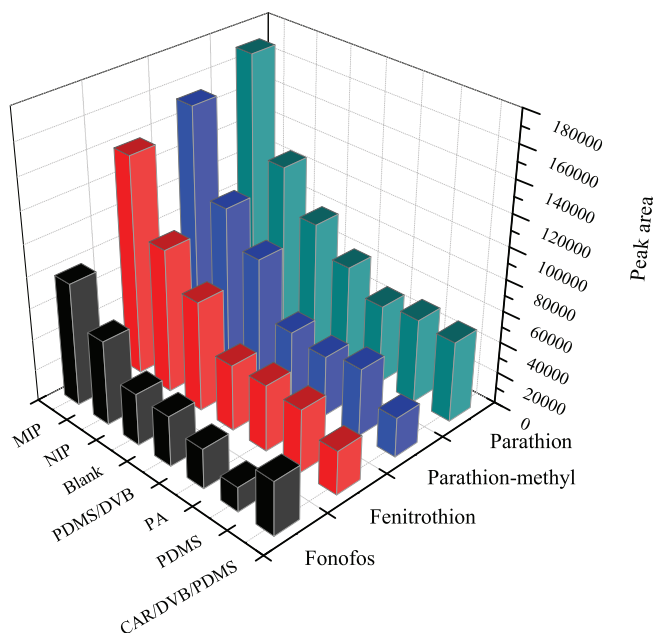


Fig. 1. Extracted amount (Average  $\pm$  SD,  $n = 3$ ) curves of parathion-methyl by the MIP and NIP fibers in spiked water samples.



**Fig. 2.** Extraction capability of the prepared fibers and the commercial fibers in spiked water samples. The concentrations of OPPs were the same as in Fig. 4S.

**Table 1**  
Chemical structures of the tested compounds and their IFs.

Compound	Structure	IF <sup>a</sup>
Parathion-methyl		1.63
Parathion		1.40
Fenitrothion		1.37
Fonofos		1.44
Fenthion		1.48
Nitrobenzene		2.24
Sulfotep		1.18
Diethion		1.07
DEP		0.93

<sup>a</sup> SPME conditions were the same as in Table 1S.

peeling-off and swelling problems. The results indicated that the fiber was inherently stable in organic and inorganic solvents.

Five fibers with an approximate thickness of 50  $\mu\text{m}$  were randomly selected to investigate the fiber-to-fiber reproducibility for the analysis of OPPs. The relative standard deviations (RSDs) in the range of 2.24–6.67% for extraction yields were achieved, proving that preparation of the fiber by the proposed method was highly reproducible.

### 3.2. Extraction capacity

A series of aqueous parathion-methyl solutions were used to investigate the extraction capacity of the MIP and NIP-coated fibers. Fig. 1 displayed the profiles of the amounts extracted versus the concentrations of parathion-methyl. The amounts of parathion-methyl rose rapidly along with the increase of the concentration in the range of 5–1000  $\mu\text{g L}^{-1}$  for both fibers. After that, the extraction was near saturation. At the concentration of 2000  $\mu\text{g L}^{-1}$ , the extraction capacity was 66.2 ng for the NIP fiber while it was 100.1 ng for the MIP fiber. Such different capacities probably originated from dissimilar extraction mechanisms. For the MIP-coated fiber, there was specific adsorption due to the pre-determined recognition sites able to selectively rebind parathion-methyl. While for the NIP-coated fiber, the extraction was non-selective. Compared with those in the literature (Hu, Hu, & Li, 2007; Zhang et al., 2012), the extraction capacities of these sol-gel fibers are higher while the IF is similar or even lower. It's also because of the sol-gel process. The large surface area and porous and loose structure of the sol-gel coatings provide plentiful adsorption sites for analytes. Thereinto, there are more non-specific sites compared with other coating techniques.

The blank fiber (without C[4]) and commercial PDMS, PA, PDMS/DVB and CAR/DVB/PDMS fibers were used for further investigation. As shown in Fig. 2, the three home-made fibers displayed much better extraction ability than those of the commercial fibers thanks to the outstanding material properties of sol-gel process. Moreover, the extraction performance of MIP and NIP-coated fibers was superior to that of the blank fiber due to the introduction of C[4], which contributed to the bonding force between the coatings and target analytes by providing  $\pi$ - $\pi$  interactions, hydrophobic interactions and inclusion interactions and hence resulted in high affinity for these OPPs.

### 3.3. Selectivity and recognition mechanism

The compounds in Table 1 were selected to study the selectivity and recognition mechanism of the MIP-coated fiber. The template molecule was composed of three parts, namely nitro, phenyl and phosphorothioate groups. Since the cavity of C[4] is hydrophobic, phenyls are more likely to go inside than nitro and phosphorothioate groups. Due to this reason, fonofos and fenthion could form stronger inclusion interactions than parathion, parathion-methyl and fenitrothion. However, parathion-methyl still achieved the highest IF among them because it was the imprinted molecule, and also the cyano in C[4] could interact with nitro and phosphorothioate groups to improve the imprinting effect. Any changes to the structure of the template molecule would decrease the IF. For example, the methyl in phosphorothioate is extended to ethyl for parathion, and a methyl is attached to the benzene ring for fenitrothion, and both of the small changes declined the selectivity. Nitrobenzene was an exception. It contains two parts and has the smallest molecule volume as well as the lowest steric hindrance, which help it to occupy most of the recognition sites. As reference compounds, DEP, diethion and sulfotep were not recognized by the coating due to the large molecule volume and poor structural similarity. The results supported the presumption that similarities in molecular shape and functional group play a key role in the selective recognition of imprinted materials. Fig. 3 illustrates the interactions between the template molecule and MIP coating.

### 3.4. Optimization of SPME conditions

In this work, headspace extraction was performed in pineapple sample. Fig. 4 shows the effects of extraction temperature and time, salt addition and desorption time on the extraction efficiency



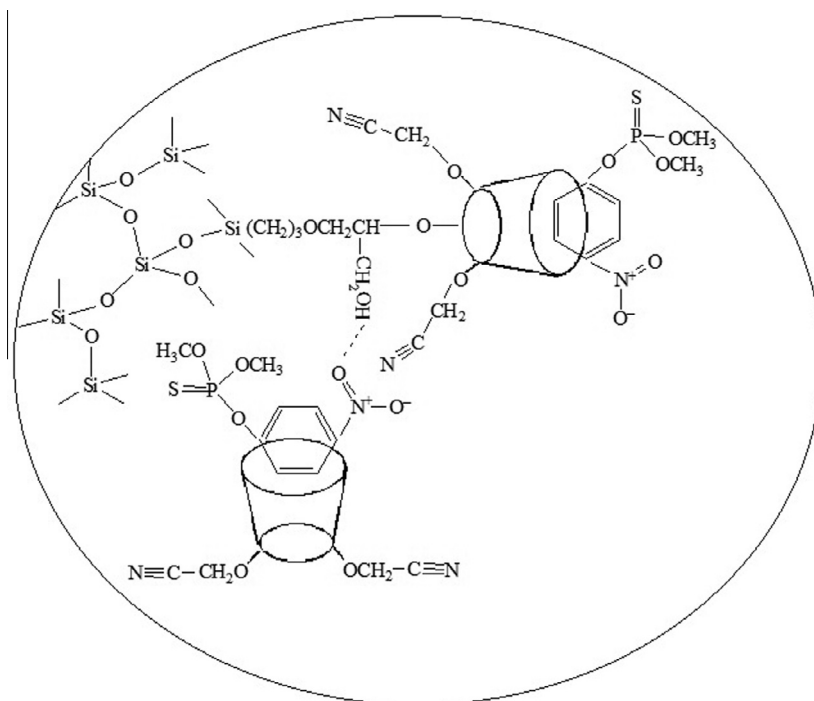


Fig. 3. A schematic illustration of the interaction mechanism between the MIP coating and analytes.

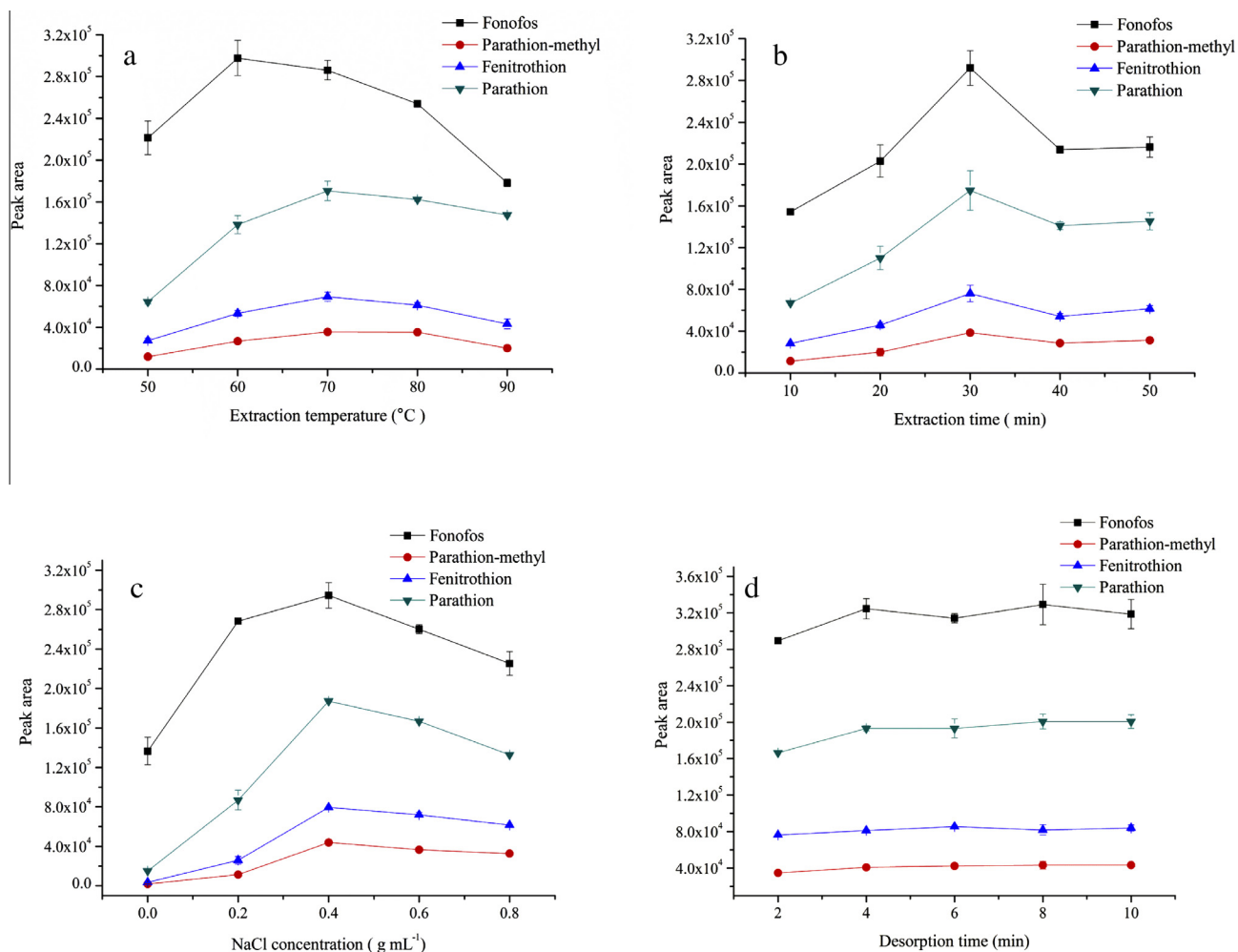


Fig. 4. Optimization of the SPME conditions (Average  $\pm$  SD,  $n = 3$ ). (a) Extraction temperature; (b), extraction time; (c), salt concentration; (d), desorption time.

of four OPPs. In Fig. 4a, three OPPs reached the highest extraction amounts at 70 °C while the optimum temperature for fonofos was 60 °C because of its low molecular weight and high partition coefficient (*n*-octanol and water). The extraction was also greatly affected by extraction time and NaCl addition as shown in Fig. 4b–c. All of the OPPs obtained the highest extraction efficiency when the adsorption time was 30 min and NaCl was 0.4 g mL<sup>-1</sup>. The examination of desorption time revealed that the OPPs could be almost desorbed after 4 min. To avoid possible carryover, the desorption time was set at 8 min.

### 3.5. Method validation and comparison

Table 2 summarized the linear ranges, correlation coefficients, limits of detection (LODs) and RSDs obtained by the proposed method using the MIP-coated fiber in spiked pineapple samples. Wide linear ranges and good correlation coefficients ( $R^2 > 0.997$ ) were achieved for all of the compounds studied. The precision of the method was satisfactory with RSDs in the range of 3.4–7.0%. The LODs, ranged from 0.0019 to 0.065 µg kg<sup>-1</sup>, were lower than those reported in the literature by other SPME fibers (Fytianos, Raikos, Theodoridis, Velinova, & Tsoukali, 2006; Lambropoulou & Albanis, 2003; Menezes Filho, dos Santos, & Pereira, 2010). MIPs targeted for methyl parathion or parathion were applied to electrochemical sensors with different functional monomers (Li et al., 2005; Xue et al., 2014; Yang, Sun, Zhou, Shi, & Jin, 2009; Zhao, Zhao, & Zeng, 2013), but the LODs obtained were higher than the value in this study. In the meantime, extraction of pesticides from the sample and/or enrichment of the analytes are required before determination, which complicated the procedure. In contrast, SPME encompasses sampling, extraction, preconcentration and

introduction of the analytes into a single uninterrupted process, which is easy to operate and avoids contamination of the matrix.

In order to make a direct comparison, LLE technique was performed according to the Agricultural Standard of China NY/T 761–2008. As shown in Table 2, the detectable concentrations of LLE were rather higher than those of SPME in this study. The LOD for fonofos, parathion-methyl, fenitrothion and parathion was 100, 26, 810 and 33 times bigger than that obtained by SPME, respectively. The experiment demonstrated that the proposed method was more suitable for trace-level analysis. What's more, considering the reduced operation procedures and free organic solvent consumption, the HS-SPME technique offered distinct advantages for the determination of OPPs in fruit samples.

The MIP-SPME/GC-NPD method was applied for the determination of pesticide residues in apple and pineapple samples. The results showed that the tested fruit samples were free of OPPs contamination.

A recovery experiment was then used to evaluate the accuracy of the SPME- and LLE-based methods, and the results were shown in Table 3. The recoveries of four OPPs in spiked apple and pineapple samples ranged from 84.0% to 109.0% by HS-SPME with most of them around 100%, but ranged from 71.9% to 98.9% by LLE. Clearly, SPME possessed better recoveries owing to its sensitivity and simplicity, which reduced the loss of analytes during the extraction process. In addition, the accuracy was higher than those given by other SPME methods (Abdulra'uf & Tan, 2015; Menezes Filho et al., 2010), probably thanks to the good selectivity of the MIP-coated fiber.

Fig. 5 displayed the typical chromatograms of spiked pineapple samples by MIP and NIP-coated fibers. In comparison with those of the NIP-coated fiber, the extraction amounts of parathion-methyl

**Table 2**  
Comparison of HS-SPME and LLE for the determination of OPPs in pineapple samples.

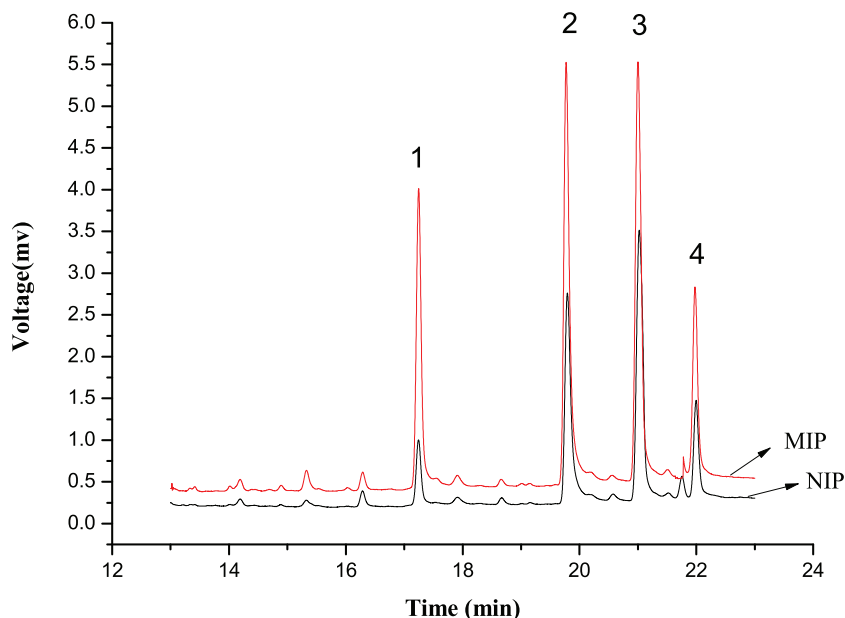
Compound	HS-SPME				LLE			
	Linear range (µg kg <sup>-1</sup> )	$R^2$	LODs <sup>a</sup> (µg kg <sup>-1</sup> )	RSD <sup>b</sup> (%, <i>n</i> = 5)	Linear range (µg kg <sup>-1</sup> )	$R^2$	LODs (µg kg <sup>-1</sup> )	RSD (%, <i>n</i> = 5)
Fonofos	0.2–1000	0.9992	0.0051	5.8	5–5000	0.9999	0.51	13.4
Parathion-methyl	2–1000	0.9973	0.065	3.4	50–50,000	0.9990	1.68	6.3
Fenitrothion	0.12–1000	0.9992	0.0019	6.6	30–30,000	0.9994	1.54	5.8
Parathion	0.6–1000	0.9996	0.037	7.0	15–15,000	0.9999	1.22	3.5

<sup>a</sup> Limits of detection were estimated on the basis of 3:1 signal-to-noise ratio.

<sup>b</sup> Spiking level: fonofos, 10 µg kg<sup>-1</sup>; parathion-methyl, 100 µg kg<sup>-1</sup>; fenitrothion, 60 µg kg<sup>-1</sup>; parathion, 30 µg kg<sup>-1</sup>.

**Table 3**  
Spiking levels and recoveries obtained by SPME and LLE in fruits.

Pesticide	Recovery (% , <i>n</i> = 3)				
	HS-SPME			LLE	
	Spiking levels (µg kg <sup>-1</sup> )	Pineapple	Apple	Spiking levels (µg kg <sup>-1</sup> )	Apple
Fonofos	1	84.0 ± 2.4	105.4 ± 7.1	100	71.9 ± 7.9
	2	109.0 ± 2.2	96.9 ± 2.4	50	95.5 ± 4.1
	10	99.8 ± 2.3	100.1 ± 10.1	10	80.0 ± 6.3
Parathion-methyl	10	99.2 ± 1.4	104.2 ± 5.4	1000	93.8 ± 4.4
	20	100.4 ± 2.1	97.6 ± 7.3	500	98.9 ± 3.1
	100	99.9 ± 2.1	99.9 ± 4.8	100	90.8 ± 4.9
Fenitrothion	6	97.5 ± 8.1	103.2 ± 3.5	600	93.9 ± 3.9
	12	101.4 ± 7.0	98.2 ± 12.1	300	97.3 ± 3.0
	60	99.9 ± 9.9	100.0 ± 5.8	60	94.9 ± 4.6
Parathion	3	95.3 ± 10.3	95.5 ± 2.7	300	82.6 ± 6.1
	6	102.6 ± 8.8	102.5 ± 7.9	150	92.5 ± 7.4
	30	99.9 ± 12.7	99.9 ± 8.2	30	83.1 ± 5.2



**Fig. 5.** HS-SPME/GC chromatograms of the spiked pineapple samples. Peaks and spiking levels: 1, fonofos,  $10 \mu\text{g kg}^{-1}$ ; 2, parathion-methyl,  $100 \mu\text{g kg}^{-1}$ ; 3, fenitrothion,  $60 \mu\text{g kg}^{-1}$ ; 4, parathion,  $30 \mu\text{g kg}^{-1}$ .

and its analogs were significantly improved by the MIP-coated fiber whilst the interferences from sample matrix were partially eliminated.

#### 4. Conclusion

A novel water-compatible imprinted SPME fiber coated by sol-gel process using calixarene as a functional monomer was developed for the analysis of parathion-methyl and its analogs in apple and pineapple samples in conjunction with GC-NPD. The fiber exhibited attractive characteristics such as high extraction ability, good selectivity, and excellent thermal and solvent resistance. In comparison with LLE and other SPME-based methods, the MIP-SPME technique achieved rather lower LODs and better recoveries, proving its smart performance in trace-level analysis in complex matrices. The LODs were also greatly less than the maximum allowed limits of the EU for OPPs. Compared with other MIP preparation methods, the extraction capacities of the sol-gel fibers are high, but the IF is similar or even lower. As a result, the further work should be focused on improving the imprinting effect of sol-gel MIP coatings.

#### Compliance with ethics requirements

All the authors have no conflict of interests to declare. This article does not contain any studies with human or animal subjects.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2015.07.018>.

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