Talanta 115 (2013) 920–927

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Sol–gel molecularly imprinted polymer for selective solid phase microextraction of organophosphorous pesticides

Yu-Long Wang, Yuan-Li Gao, Pei-Pei Wang, Huan Shang, Si-Yi Pan, Xiu-Juan Li *

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

ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form
21 June 2013
Accepted 28 June 2013
Available online 4 July 2013

Keywords:
Sol–gel
Molecularly imprinted polymer
Solid phase microextraction
Organophosphorous pesticides
Vegetable

ABSTRACT

A sol–gel technique was applied for the preparation of water-compatible molecularly imprinted polymer (MIP) for solid phase microextraction (SPME) using diazinon as template and polyethylene glycol as functional monomer. The MIP-coated fiber demonstrated much better selectivity to diazinon and its structural analogs in aqueous cucumber sample than in distilled water, indicating its potential in real samples. Thanks to its specific adsorption as well as rough and porous surface, the coating revealed rather larger extraction capability than the non-imprinted polymer and commercial fibers. In addition, the fiber exhibited excellent thermal (about 350 °C) and chemical stability (organic and inorganic). After optimization of several parameters affecting extraction efficiency, a method based on MIP-SPME combined with gas chromatography was developed for the determination of organophosphorus pesticides (OPPs) in vegetable samples. The limits of detection for the tested OPPs were in the range of 0.017–0.77 μg kg^{-1}. The proposed method was applied to evaluate OPPs in spiked cucumber, green pepper, Chinese cabbage, eggplant and lettuce samples, and recoveries of 81.2–113.5% were obtained by the standard addition method with three spiking levels in each kind of vegetable.

1. Introduction

Recently, the introduction of molecularly imprinted polymers (MIPs) [1–6] into solid phase microextraction (SPME) [7] coating materials has been attractive since Koster et al. [8] firstly reported the preparation and application of MIP-SPME fiber for the extraction of brombuterol from urine samples. But more researches on MIPs fibers have not been developed until Turiel et al. [9] reported a propazine imprinted fiber in 2007.

The vast majority of MIP-coated fibers, by far, are synthesized by the co-polymerization method, using methacrylic acid and its derivatives as monomers. Li and co-workers prepared a series of MIP-SPME fibers through multiple co-polymerization method [10–14]. The MIP-coated fibers possess high imprinting factors (the peak areas obtained by the MIP-coated fiber to the non-imprinted polymer (NIP) coated fiber ratio) from 3.4 to 5.8 for templates and low selectivity in the range of 1.1–5.4 for structural analogs [10,12]. However, these fibers traditionally demonstrate their best performance only in hydrophobic organic solvents, which renders limitation on application to aqueous conditions. The preparation yield and efficiency becomes another important problem yet to be solved as a result of only about 1–3 μm of thickness on the fiber obtained by a single coating procedure. The common repeated coating times, in correspondence, are up to 10, which therefore leads to lots of glass tubes, polymerization solution, and manual labor wasted during the preparation of a batch of fibers. Moreover, it is crucial to select polymerization time and porogen because some problems could also crop up with pulling the fragile fiber out of the semi-solid polymer. Monolith [9] is a good strategy for the preparation of MIPs fibers through in situ polymerization inside fused silica capillaries. The approach is fast and straightforward and the obtained fibers are porous, thermally stable and flexible enough to be placed in home-made syringes. But a fatal weakness is that it requires strict control of the concentration of cross-linkers [15]. Furthermore, the lifetime of the prepared fibers is as short as 50 times [16]. Anyhow, work should be in hand to develop new strategies for preparation and application of MIPs in aqueous environment.

The sol–gel technique provides a resourceful approach to synthesize hybrid organic–inorganic materials and can overcome the aforementioned difficulties. Numerous significant advantages of imprinted sol–gel process over MIPs [17], namely, easy preparation, high thermal and chemical stability, long lifetime, high surface area, various monomers, possibility to design the material structure and property by varying the proportion of the sol–gel solution, could not be disregarded. Indeed, coupling of sol–gel technique with MIPs in some extraction formats, such as solid phase extraction [18], has been carried out in recent years. But as far as we know, the utilization of sol–gel imprinted fibers for SPME has been

* Corresponding author. Tel.: +86 27 8728 2111; fax: +86 27 8728 8373.
E-mail addresses: lixj78@126.com, lixiujuan@mail.hzau.edu.cn (X.-J. Li).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.06.056

uncommonly published in literatures [19–21]. Taken in account its superiority and potential, sol–gel imprinting technology for preparing SPME fiber coatings has not yet been fully demonstrated and need to be further explored.

As a common and broad-spectrum organophosphorus pesticide (OPP), diazinon has been considered as one of the most frequently detected OPPs residues in vegetables [22]. Taking into account the complexity of matrix and the low maximum residue limits

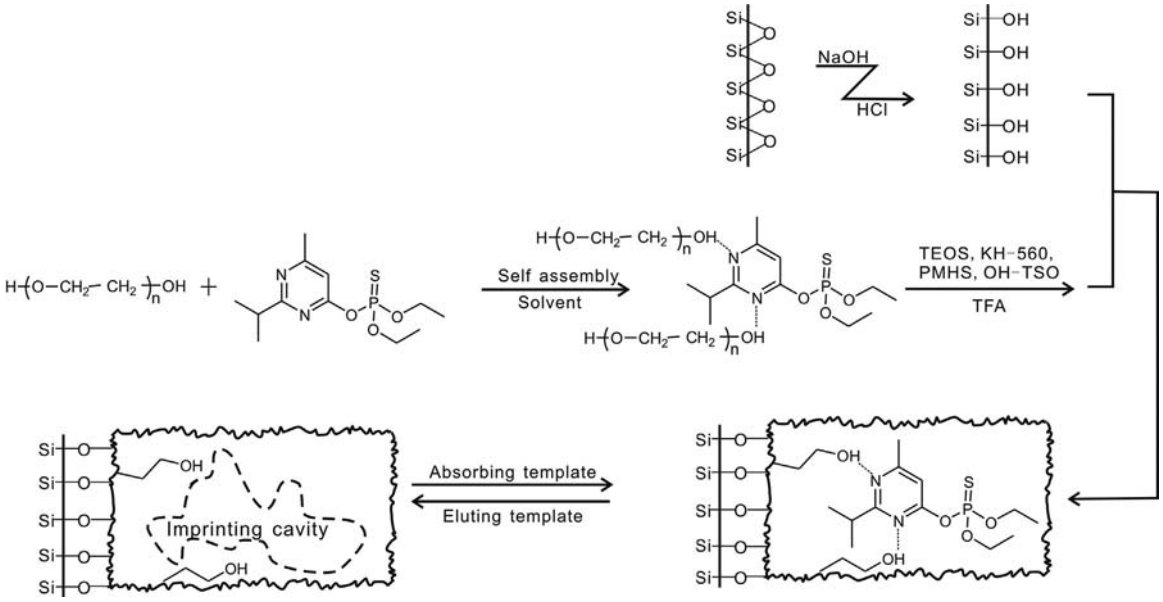

Fig. 1. Schematic representation of diazinon imprinted SPME fiber preparation.

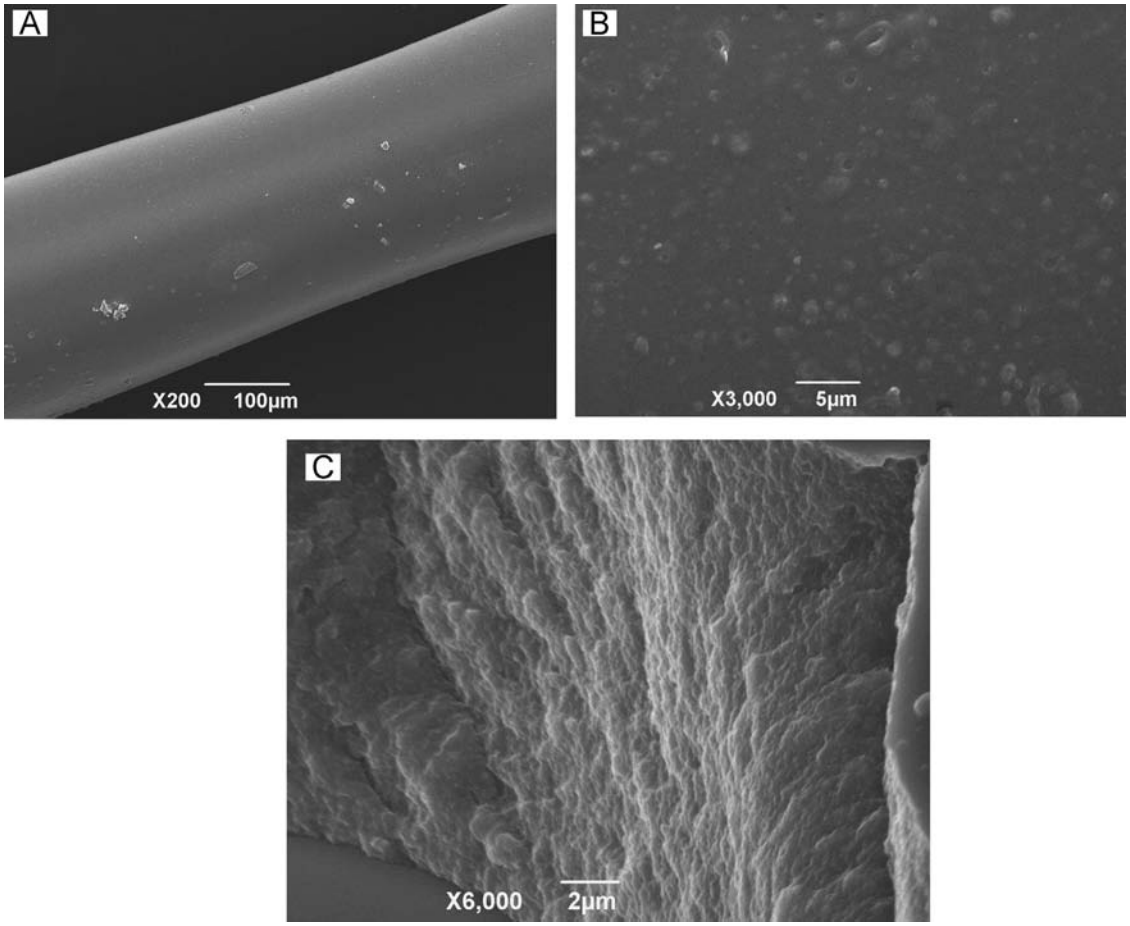

Fig. 2. Scanning electron micrographs of the prepared sol–gel coated fiber at (A) 200-fold magnification (surface image), (B) 3000-fold magnification (surface image) and (C) 6000-fold magnification (cross-sectional image).

established for vegetables, sensitive and selective analytical methods for OPPs are considerably indispensable. In this paper, a novel MIP-SPME fiber with diazinon as template was prepared by sol–gel technique. Polyethylene glycol (PEG) was chosen as functional monomer. Characteristics of the fiber were evaluated. The selectivity and extraction capability of the MIP-coated fiber were investigated in comparison with commercial fibers and the NIP-coated fiber. After optimization of extraction parameters, a method for selective analysis of diazinon and its analogs by MIP-SPME coupled with gas chromatography-nitrogenphosphorus detector (GC-NPD) was developed and applied to determine trace OPPs in vegetable samples.

2. Experimental

2.1. Chemicals, standard solutions and samples

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. PEG-20M (average molar mass ranging from 14,000 to 16,000 g mol^{-1}), sodium chloride (NaCl) and other reagents were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Water was doubly distilled.

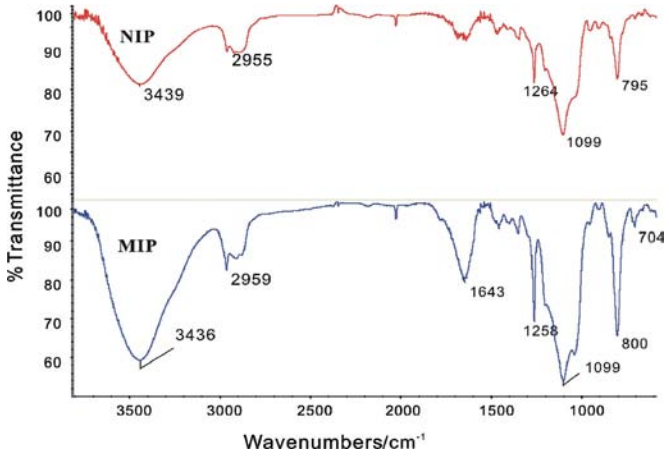

Fig. 3. Infrared spectra (KBr pellet) of MIP and NIP SPME coatings.

Ethyl nonanoate (97%) was purchased from Alfa Aesar (Lancs, England). Diazinon (98.0%), isocarbophos (99.0%), and stock standard solutions of pirimiphos-methyl, pirimiphos-ethyl and parathion-methyl at a concentration of 100 μg mL^{-1} in methanol were purchased from Helishun Technology Co., Ltd. (Beijing, China). The stock solutions of diazinon, isocarbophos and ethyl nonanoate were prepared in methanol at a concentration of 1 mg mL^{-1} and stored at 4 °C in a refrigerator. The responses of different pesticides differ from each other in the NPD. Therefore, a mixed stock solution of five OPPs was prepared in methanol with each concentration in the range of 0.01–0.2 mg mL^{-1}. Working standard solutions of insecticides were prepared by diluting the stock solution with methanol.

Five kinds of fresh vegetables (cucumber, green pepper, Chinese cabbage, eggplant and lettuce) were randomly purchased from a local market (Wuhan, China). 150 g of each vegetable was homogenized along with 150 mL of 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. Apparatus and chromatographic conditions

The chromatographic analysis was carried out on an 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. A personal computer equipped with a chromatopac model N2000 (Hangzhou Mingtong Technology Co., Ltd., Hangzhou,

Table 1
Influence of solvents on the extraction ability of the MIP-coated fiber.

Compound	r[a]					
	Untreated	10% Acetic acid in methanol	Water	N-pentane	Acetone	Benzene
Diazinon	1.00	1.06	0.94	1.02	1.14	1.32
Parathion-methyl	1.00	1.41	1.51	1.36	1.62	1.41
Pirimiphos-methyl	1.00	1.14	1.13	1.11	1.13	1.24
Isocarbophos	1.00	1.36	1.46	1.44	1.28	1.39
Pirimiphos-ethyl	1.00	1.13	1.11	1.25	0.98	1.08

[a] The ratio (r) was obtained by comparison of the peak areas after and before solvent treatment. HS-SPME conditions: spiked water sample, 4 mL; extraction temperature, 70 °C; extraction time, 30 min. The concentration was 250 μg L^{-1} for isocarbophos and 25 μg L^{-1} for the others.

Table 2
Influence of temperatures on the extraction ability of the MIP-coated fiber.

Compound	Peak areas (n=3, %)[a]					Analysis of variance[b]
	260 °C	280 °C	300 °C	320 °C	340 °C	
Diazinon	155,891 (7.7)	163,209 (5.8)	160,118 (6.8)	162,791 (6.1)	163,640 (3.3)	F=0.18, P=0.94
Parathion-methyl	81,506 (10.1)	82,852 (2.6)	74,680 (4.3)	81,300 (12.3)	82,011 (5.7)	F=0.48, P=0.75
Pirimiphos-methyl	122,567 (6.4)	113,514 (8.3)	119,528 (5.0)	125,455 (5.3)	126,908 (4.1)	F=0.44, P=0.78
Isocarbophos	27,323 (8.6)	27,501 (9.7)	25,959 (8.5)	26,672 (3.1)	26,557 (3.3)	F=0.13, P=0.96
Pirimiphos-ethyl	169,530 (1.9)	165,597 (12.6)	168,199 (5.1)	176,382 (6.0)	169,233 (3.6)	F=0.15, P=0.96

[a] SPME conditions were the same as that in Table 1.
[b] Significant at P≤0.05.

China) was used to process chromatographic data. Compounds were separated on an SE-54 capillary column (30 m × 0.32 mm × 0.33 μm, Lanzhou ATECH technologies Co., Ltd., Lanzhou, China). The applied oven temperature programming was as follows: initial temperature, 60 °C (3 min); increased to 180 °C at 15 °C min^{-1}, held for 5 min; then raised at 5 °C min^{-1} to 220 °C, held for 2 min. The temperatures of the injector and the detector were set at 250 °C and 270 °C, respectively. Nitrogen (99.999%) was used as carrier gas and kept at a linear velocity of 12–15 cm s^{-1} for all the analyses.

A magnetic stirrer DF-101S (Zhengzhou Greatwall Scientfic Industrial and Trading Co., Ltd., Zhengzhou, China) with a stirring speed of 600 rpm was employed for stirring the sample during extraction. The commercially available polydimethylsiloxane/divinybenzene (PDMS/DVB, 65 μm) and divinybenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm) coated fibers for comparison were purchased from Supelco (Bellefonte, PA, USA). The surface characteristic study of the fibers was evaluated by using a JSM-6390LV scanning electron microscope (JEOL, Tokyo, Japan). Infrared analyses of the MIP- and NIP-coated fibers between 400 and 4000 cm^{-1} were completed with a Nicolet Nexus 470 FT-IR spectrometer (Thermo Nicolet, USA) where KBr was used to prepare the sample tablets. A Perkin-Elmer TGA-2 thermogravimetric analyzer (Netzsch, Selb, Germany), over the temperature range of 50–600 °C at a rate of 10 °C min^{-1}, was used to investigate the thermal stability of the coating.

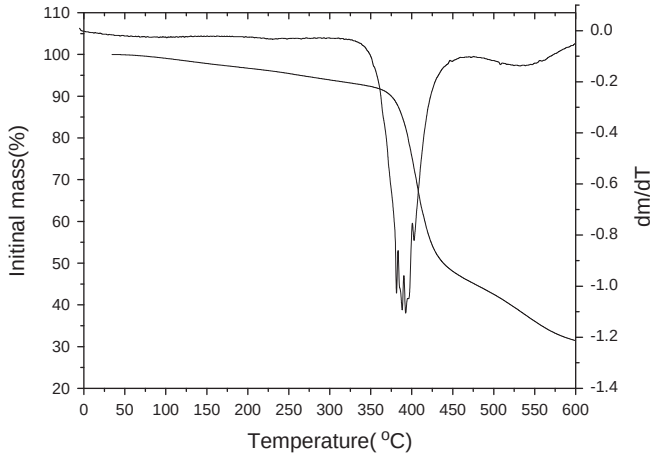

Fig. 4. Thermogravimetric analysis curves of the coating.

2.3. Preparation of MIP- and NIP-coated fibers

MIPs were developed by sol–gel technology. Briefly, 100 mg of PEG and 86 mg of diazinon were added into 700 μL of toluene 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, 50 μL of KH-560 and 100 μL of TEOS were added and mixed thoroughly by ultrasonic agitation for 5 min. And then, 80 μL of TFA containing 5% water was added to the resulting solution and the mixture was sonicated for another 5 min. Sequentially, the mixture was centrifuged at 12,000 rpm for 8 min and the top clear sol solution was moved to another tube for fiber coating. After the treated fiber [23] was dipped vertically into the sol–gel solution for 20 min, a sol–gel coating was formed on the bare outer surface of the fiber end (about 1 cm). For each fiber, this coating process was repeated several times until the desired thickness of the coating was obtained. The fibers were placed in a desiccator at room temperature for 48 h, and then conditioned at 150, 220 and 250 °C under nitrogen for 1 h in the GC injection port. The NIP-coated fibers were also prepared according to the above procedure in the absence of diazinon.

2.4. SPME procedure

Two grams of homogenized and spiked sample were added into a 10 mL glass vial containing a magnetic stirring bar and 1.2 g of NaCl. After dilution with 2 mL of distilled water, the sample was extracted via headspace SPME (HS-SPME) at 70 °C for 30 min by stirring at 600 rpm. After absorption of the analytes, the fiber was retracted back into the needle, removed from the sample vial, and immediately thermally desorbed at 250 °C for 8 min and analyzed by GC. All the determinations were performed in triplicate except extra explanations. The average values and their standard deviations were reported.

It should be noted that, extraction ability, chemical and thermal stability of the MIP-coated fibers were performed in spiked water samples. The selectivity was investigated in both spiked water and cucumber samples. For the linearity and recovery studies, homogenized samples were spiked and kept at 4 °C for three days and then extracted by HS-SPME as described above. Prior to extraction, all of the fibers were conditioned in the GC injector.

2.5. Recoveries and quantification

Recoveries were obtained by the standard addition method with three spiking levels of known quantities of OPPs in each kind

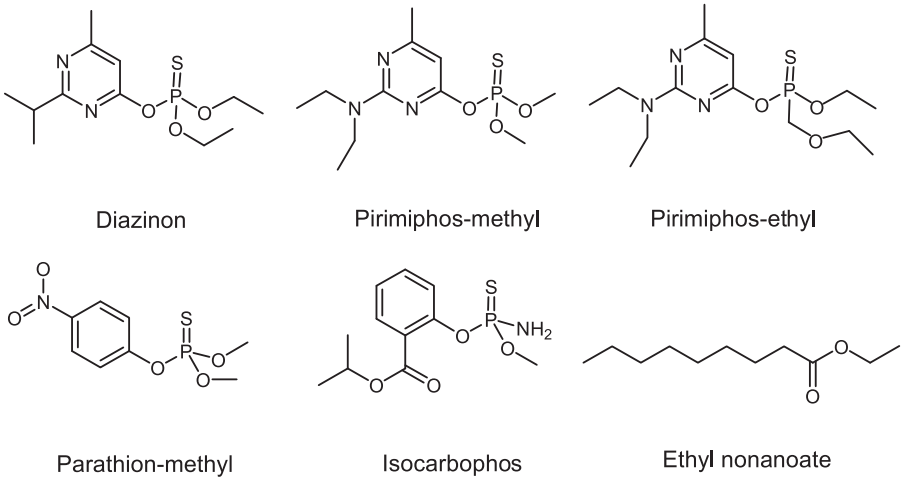

Fig. 5. Chemical structures of the test analytes.

of vegetable. 2 g of the spiked sample was analyzed by the proposed method in triplicate. A plot of the responses versus the concentrations of analyte addition was then developed, and the unknown concentration initially present in the sample was calculated by extrapolation, which was the *x*-intercept in the plot.

2.6. Statistics

Analysis of variance (ANOVA) was performed to evaluate significant differences by using SAS system Version 8.0 (SAS Institute Inc., Cary, NC). The difference was considered to be statistically significant with values of $P \leq 0.05$.

3. Results and discussion

3.1. Preparation of MIP-coated fibers

The properties of MIP-coated fiber depend mainly on the composition of polymer and the ratio of template to functional monomer. The selection of functional monomer is crucial in molecular imprinting because it dominates the interaction between the fiber and analytes. According to the similarity principle, a polar fiber is required for the extraction of polar diazinon from aqueous media. Our previous work [24,25] demonstrated that the sol–gel PEG/OH-TSO fiber was suitable for the extraction of polar compounds. Considering this, PEG was used as the monomer in this paper. The polymerization solvent is also a critical issue in the preparation of coating materials owing to its great effect on the sol–gel formation and the morphological structure of fibers. When acetone and dichloromethane were used, the fibers were non-homogeneous and difficult to coat. In contrast, homogeneous and dense coating could be easily prepared using toluene as a solvent. Given different interactions established between functional monomers and templates before polymerization, an appropriate ratio of template molecule to functional monomer is needed to ensure the predicted imprinted result. Beltran et al. [26] reviewed the ratio normally used in the non-covalent approach, and confirmed that it was in a range from 1:4 to 1:8, which was thereby tested in our study. The results obtained were similar when the ratios of 1:4 and 1:8 compared. A ratio of 1:8, consequently, was chosen (the molecular weight of PEG was calculated as $–CH_2CH_2O–$) in consideration of the high price of the template. The simplified preparation scheme of diazinon imprinted SPME fiber is shown in Fig. 1.

More than a dozen fibers could be coated with one sol solution. This method overcomes the need for fresh sol solution for each coating, results in economy of materials, and reduces cost. Five fibers with an approximate thickness of 50 μm were randomly selected to investigate the fiber-to-fiber reproducibility for the analysis of OPPs. And the relative standard deviations (RSDs) were 3.7–8.3%.

3.2. Characterization of MIP-coated fibers

The morphological structure of the prepared fiber was investigated with scanning electron microscope. Fig. 2A illustrated that the MIPs were homogeneously and densely coated on the fused silica fiber. Fig. 2B showed there were a large number of globules and holes on the surface, which significantly increased the surface area. As shown in Fig. 2C, highly cross-linked and folded structure was observed on the cross-section of the fiber coating, which would be able to provide enhanced stationary-phase loading as well as fast mass transfer.

The infrared spectra of MIP (before removing the template) and NIP coatings were performed. As shown in Fig. 3, a stronger absorption peak at 1643 cm^{-1} of MIP coating owing to the stretching vibration of C=N could not be found in the NIP coating. That corresponds to the pyrimidine ring of the template molecule. Other absorption peaks matched both MIP and NIP coatings. In this sense, the composition of the MIP-coated fiber was in accordance with that of the NIP-coated fiber.

The chemical stability was evaluated by the soaking test, in which the MIP-coated fiber was immersed into 10% (v/v) acetic acid in methanol, water, n-pentane, acetone and benzene for 0.5 h under a stirring speed of 600 rpm. Afterwards, it was applied to extract spiked water samples and compared with the initial extraction ability before exposed to the cited medium. The results, as shown in Table 1, indicated that the MIP-coated fiber not only remained good surface quality without any desquamation and swelling, but also conducted equivalent or even better extraction performance in comparison with the untreated one.

Table 2 illustrated the thermal stability of the MIP-coated fiber. No statistically significant difference ($P \leq 0.05$) in extraction efficiency was observed when the fiber was conditioned for 30 min at 260, 280, 300, 320 and 340 °C. The thermogravimetric analysis, as shown in Fig. 4, was also performed to investigate the thermal stability of the MIP coating. An obvious mass loss occurred at around 350 °C. There were two fast mass loss peaks judging from the derivative thermogravimetric curve. The first was about 375 °C and the second was around

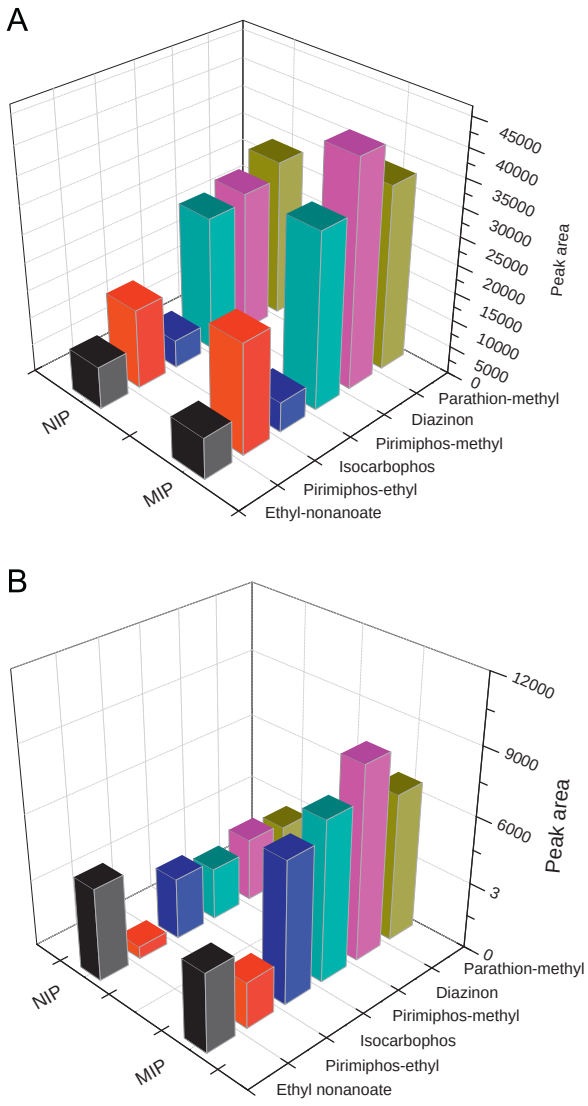

Fig. 6. Selectivity investigation of the MIP-coated fiber. SPME was performed in spiked water (A) and cucumber sample (B) under the optimal conditions. The concentration was 200 μg kg^{-1} for isocarbophos and 20 μg kg^{-1} for the others.

450 °C. Both of the results showed that the sol–gel-MIP-SPME fiber was thermally stable over 350 °C, better than the monolithic MIP fiber by situ polymerization [15,27] and MIP-coated fibers by multiple co-polymerization method [10,12,13].

The MIP-coated fibers have a lifetime of more than 100 uses for headspace SPME of OPPs without a substantial change in the properties of the coating.

3.3. Selectivity

Six compounds were tested for the selectivity of the prepared sol–gel MIP-coated fiber, and the NIP-coated fiber was used as comparison. Their molecular structures are illustrated in Fig. 5. Pirimiphos-methyl, pirimiphos-ethyl, parathion-methyl and isocarbophos, thereinto, were structural analogs of diazinon and ethyl nonanoate was a reference compound.

According to the results shown in Fig. 6A, an imprinting factor of 1.59, 1.31, 1.38, 1.12, 1.07 and 0.98 in spiked water was achieved for diazinon, pirimiphos-methyl, pirimiphos-ethyl, parathion-methyl, isocarbophos and ethyl nonanoate, respectively. When the fiber was applied to spiked cucumber sample (Fig. 6B), the imprinting factor changed to 3.06, 3.08, 3.70, 2.54, 2.51 and 0.85, respectively. The results, in contrast with no selectivity found to reference compound, firstly indicated that the MIP-coated fiber possessed selectivity to diazinon and its structural analogs. Secondly, the selectivity was related to the complementarities of size, shape, and functional groups between analytes and the recognition cavity of MIPs. Diazinon, pirimiphos-methyl and pirimiphos-ethyl share the highest structural similarity, and parathion-methyl and isocarbophos possess rather less similarity in shape and size with diazinon, while no similarity is found for ethyl nonanoate at all. Thirdly, the recognition of targets by MIP-coated fiber was favored with cucumber sample, indicating its potential in complicated samples. It seemed that the selectivity of the sol–gel fiber was lower than those reported in some literatures by polymerization method [10,12], as a probable result of our selectivity achieved in real aqueous sample instead of hydrophobic organic solvent.

3.4. Extraction ability

A series of spiked diazinon standard aqueous samples were used to investigate the extraction capacity of MIP and NIP-coated fibers. Fig. 7 shows the curves of the chromatographic responses versus the concentrations of diazinon. It indicated that the extraction amount rose continuously along with the increase of concentration for both fibers. Nonetheless, the MIP-coated fiber possessed larger extraction yield than NIP-coated fiber. Such different capacity originated from different extraction mechanism. For the MIP-coated fiber, the predetermined recognition sites after removing the template were able to selectively rebind diazinon, while it was mainly non-specific adsorption and weaker interaction for the NIP-coated fiber.

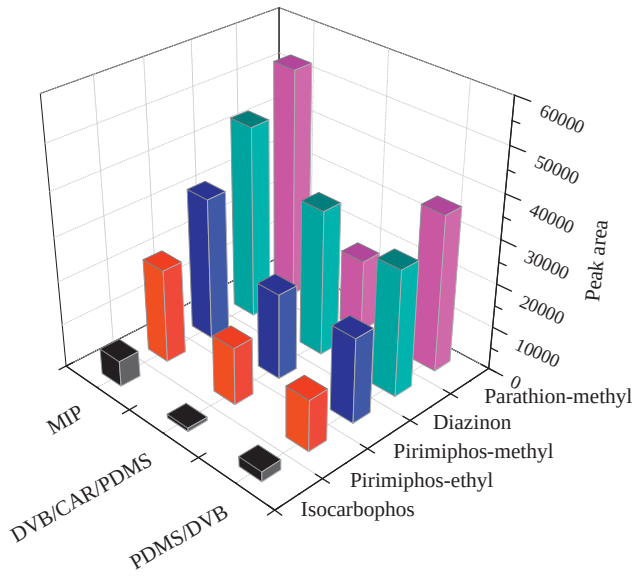

Fig. 8. Comparison of extraction capability using MIP-coated fiber and commercial fibers in spiked water samples. The concentration was 250 μg L^{-1} for isocarbophos and 25 μg L^{-1} for the others.

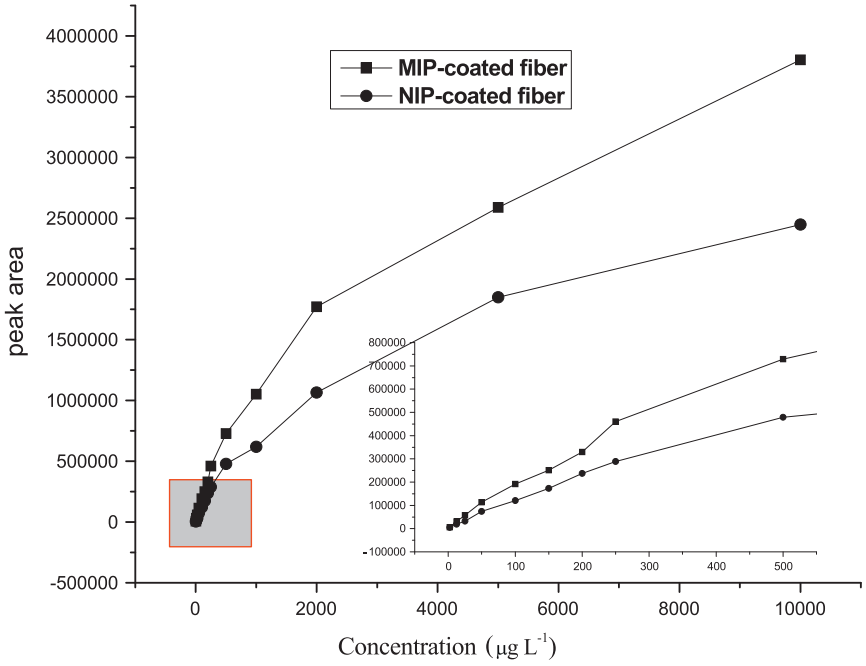

Fig. 7. Extracted amount curves of diazinon on the MIP- and NIP-coated fibers in spiked water samples.

To further verify the extraction ability of the MIP-coated fiber, the extraction efficiency was compared with those of the commercial PDMS/DVB and DVB/CAR/PDMS fibers for the analysis of OPPs. As shown in Fig. 8, the MIP-coated fiber provided rather higher responses to the five OPPs than the tested commercial ones. The higher extraction ability was mainly due to the interaction between fibers and analytes. Additionally, the porous and rough structure should also contribute to the enhanced extraction efficiency.

3.5. Optimization of the HS-SPME conditions

Several parameters associated with SPME efficiency including extraction temperature, extraction time and salt concentration were optimized in this study.

The extraction temperature and extraction time for MIP-SPME of OPPs were investigated in the ranges of 40–80 °C and 20–60 min, respectively. Experimental results indicated that the extraction efficiency was best at 70 °C for 30 min.

Different amounts of NaCl (0, 0.4, 0.8, 1.2 and 1.6 g) were added into 4 g of samples. An increase in extraction efficiency was observed from 0 to 1.2 g of NaCl except for pirimiphos-ethyl. When NaCl was over 1.2 g, a decreased chromatographic signal was obtained for most OPPs. Considering that, 1.2 g of NaCl was selected for the following experiments.

3.6. Linearity, detection limit and precision

There are differences between the behavior of the native analytes and spiked ones when samples spiked directly, and it needs to age for some time to simulate real samples. Therefore, it is necessary to investigate the incubating time to estimate the similarity in vegetables. A representative result was achieved in cucumber sample by preliminary study considering the chromatographic response and time (data not shown). Fig. 9 shows the equilibrium was reached at the fourth day. Accordingly, the homogenized and spiked samples were kept at 4 °C for three days before analysis.

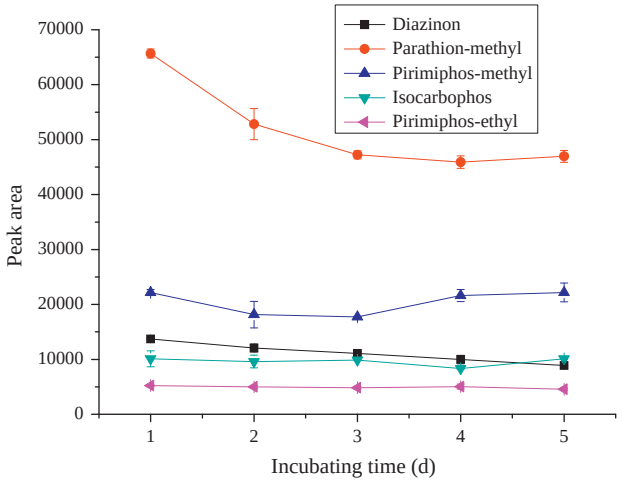

Fig. 9. Influence of incubating time in spiked cucumber sample.

Cucumber sample was chosen for validation of the method. The results can be seen in Table 3. The linear ranges were achieved in the μg kg^{-1} levels and the linear correlation coefficients for all analytes were greater than 0.995. The precision, expressed as RSD, gave satisfactory outcomes, ranging from 2.66% to 11.65%. The limits of detection (LODs), calculated based on the peak area at a signal-to-noise ratio of 3, were between 0.017 and 0.77 μg kg^{-1}. Without an expensive instrumentation or a labeling procedure, the LODs for diazinon obtained by the present method were much lower than those by the reported methods.

3.7. Analysis of real samples

Cucumber, green pepper, Chinese cabbage, eggplant and lettuce were collected and processed to confirm the potential application of the proposed MIP-SPME-GC-NPD method for the analysis of pesticide residues. The experimental results showed that the selected vegetable samples were free of OPPs contamination.

Table 4
Spiking levels and recoveries in vegetables.

Pesticides	Spiking levels (μg kg^{-1})	Recovery (%)				
		Cucumber	Eggplant	Chinese cabbage	Lettuce	Green pepper
Diazinon	20	99.9	99.7	99.8	99.0	99.7
	8	101.2	103.4	101.6	112.0	102.3
	4	98.4	95.9	98.0	85.1	97.3
Parathion-methyl	10	99.8	100.7	100.4	99.0	100.5
	6	101.8	93.7	95.9	112.6	98.1
	2	97.7	110.9	106.5	81.2	105.9
Pirimiphos-methyl	20	100.5	100.5	100.5	99.8	99.8
	8	97.0	95.8	95.6	102.1	101.5
	4	102.8	105.3	105.9	97.3	98.3
Isocarbophos	200	98.9	99.7	100.3	99.5	99.1
	80	113.5	103.4	96.8	106.2	109.9
	40	82.7	94.5	105.4	88.1	88.9
Pirimiphos-ethyl	30	99.0	100.3	99.4	99.3	99.4
	12	111.3	97.2	106.8	107.9	106.8
	6	86.0	104.5	89.7	88.1	91.5

Table 3
The linear ranges, correlation coefficients (R^2), precision (RSD) and limits of detection (LODs).

Compound	Linear range (μg kg^{-1})	R^2	RSD[a] (%, n=5)	LODs (μg kg^{-1})			
				MIP-SPME GC-NPD[b]	SPE GC-IT/MS	QuEChERS LC-MS/MS	MAE GC–MS
Diazinon	4–160	0.9985	5.40	0.048	30	5	0.4
Parathion-methyl	2–80	0.9976	4.75	0.017	50	–	–
Pirimiphos-methyl	4–160	0.9950	8.45	0.019	–	3	–
Isocarbophos	40–1600	0.9950	2.66	0.77	–	–	–
Pirimiphos-ethyl	6–240	0.9978	11.65	0.19	–	–	–
Ref.				This work	[28]	[29]	[30]

[a] Spiking level: diazinon and pirimiphos-methyl, 12 μg kg^{-1}; parathion-methyl, 6 μg kg^{-1}; pirimiphos-ethyl, 18 μg kg^{-1}; isocarbophos, 120 μg kg^{-1}.
[b] LODs were estimated on the basis of 3:1 signal-to-noise ratio.

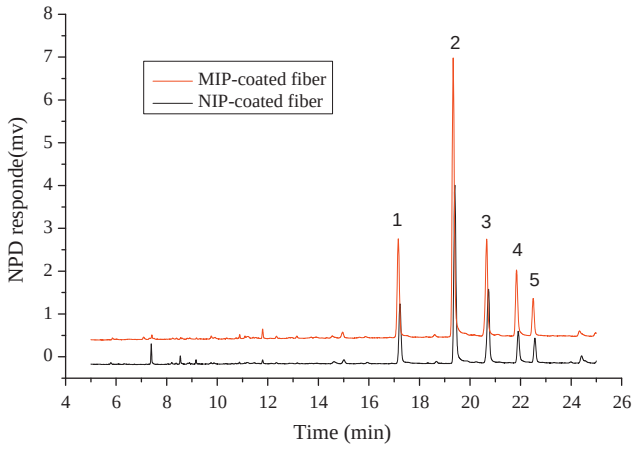

Fig. 10. Chromatograms of spiked green pepper samples with MIP- and NIP-coated fibers using SPME-GC method. The concentration was 200 μg kg^{-1} for isocarbophos and 20 μg kg^{-1} for the others. Peak: 1, diazinon; 2, parathion-methyl; 3, pirimiphos-methyl; 4, isocarbophos; 5, pirimiphos-ethyl.

And then, recovery tests were performed in order to study accuracy. These tests were based on the addition of known amounts of pesticides to different matrix. As shown in Table 4, the recoveries for five OPPs in the spiked cucumber, eggplant, Chinese cabbage, lettuce and green pepper were 82.7–113.5%, 93.7–110.9%, 89.7–106.8%, 81.2–112.6%, and 88.9–109.9%, respectively. Typical chromatograms of the spiked green pepper by MIP and NIP-coated fibers are shown in Fig. 10. It revealed that the extraction amount of five OPPs could be apparently improved by the MIP-coated fiber while the interferences from sample matrix were partially eliminated in comparison with the NIP-coated fiber.

4. Conclusions

A simple method was introduced to prepare water-compatible MIP-SPME fibers based on sol–gel technique using PEG as functional monomer and diazinon as template molecule. The fiber showed very high extraction capacity as well as excellent solvent and thermal stability. Most importantly, the fiber demonstrated relatively high selectivity in real aqueous sample instead of hydrophobic organic solvent. As a result, the extraction amounts of diazinon and its structural analogs were improved significantly while the interferences from sample matrix were partially eliminated in comparison with the NIP-coated fiber. Low detection limits and satisfactory recoveries were achieved, showing the potential of the sol–gel MIP-coated fiber for selective enrichment in complicated matrix.

Acknowledgments

This work was kindly supported by the National Natural Science Foundation of China (Grant no. 30901007), the Youth Chenguang Project of Science and Technology of Wuhan City of China (Grant no. 201150431115) and the Fundamental Research Funds for the Central Universities (Program no. 2011PY010).

References

[1] K. Balamurugan, K. Gokulakrishnan, T. Prakasam, Saudi Pharm. J. 20 (2012) 53–61.
[2] I. Bakas, N.B. Oujji, E. Moczko, G. Istamboulie, S. Pilesky, E. Piletska, E. Ait-Addi, I. Ait-Ichou, T. Noguer, R. Rouillon, J. Chromatogr. A 1274 (2013) 13–18.
[3] Y. Hiratsuka, N. Funaya, H. Matsunaga, J. Haginaka, J. Pharm. Biomed. Anal. 75 (2013) 180–185.
[4] D.L. Xiao, P. Dramou, N.Q. Xiong, H. He, D.H. Yuan, H. Dai, J. Chromatogr. A 1274 (2013) 44–53.
[5] Y.P. Duan, C.M. Dai, Y.L. Zhang, L. Chen, Anal. Chim. Acta 758 (2013) 93–100.
[6] W.P. Zhang, Z.L. Chen, Talanta 103 (2013) 103–109.
[7] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[8] E.H.M. Koster, C. Crescenzi, W.D. Hoedt, K. Ensing, G.J. de Jong, Anal. Chem. 73 (2001) 3140–3145.
[9] E. Turiel, J.L. Tadeo, A. Martin-Esteban, Anal. Chem. 79 (2007) 3099–3104.
[10] X.G. Hu, Y.L. Hu, G.K. Li, J. Chromatogr. A 1147 (2007) 1–9.
[11] Y.L. Hu, Y.Y. Wang, X.G. Chen, Y.F. Hu, G.K. Li, Talanta 80 (2010) 2099–2105.
[12] X.G. Hu, Q.L. Cai, Y.N. Fan, T.T. Ye, Y.J. Cao, C.J. Guo, J. Chromatogr. A 1219 (2012) 39–46.
[13] X.G. Hu, J.L. Pan, Y.L. Hu, Y. Huo, G.K. Li, J. Chromatogr. A 1188 (2008) 97–107.
[14] X.G. Hu, J.L. Pan, Y.L. Hu, G.K. Li, J. Chromatogr. A 1216 (2009) 190–197.
[15] Y. Hu, J. Pan, K. Zhang, H. Lian, G. Li, Trends Anal. Chem. 43 (2013) 37–52.
[16] A.R. Khorrami, E. Narouenezhad, Talanta 86 (2011) 58–63.
[17] R. Gupta, A. Kumar, Biotechnol. Adv. 26 (2008) 533–547.
[18] E. Turiel, A. Martín-Esteban, Anal. Chim. Acta 668 (2010) 87–99.
[19] B.B. Prasad, K. Tiwari, M. Singh, P.S. Sharma, A.K. Patel, S. Srivastava, J. Chromatogr. A 1198 (2008) 59–66.
[20] M.K.Y. Li, N.Y. Lei, C.B. Gong, Y.J. Yu, K.H. Lam, M.H.W. Lam, H.X. Yu, P.K.S. Lam, Anal. Chim. Acta 633 (2009) 197–203.
[21] A.R. Khorramia, A. Rashidpur, Anal. Chim. Acta 727 (2012) 20–25.
[22] D. Sharma, A. Nagpal, Y.B. Pakade, J.K. Katnoria, Talanta 82 (2010) 1077–1089.
[23] X.J. Li, Z.R. Zeng, S.Z. Gao, H.B. Li, J. Chromatogr. A 1023 (2004) 15–25.
[24] C.W. Ye, X.N. Zhang, Y.L. Gao, Y.L. Wang, S.Y. Pan, X.J. Li, Anal. Chim. Acta 710 (2012) 75–80.
[25] C.W. Ye, X.N. Zhang, J.Y. Huang, S.S. Li, S.Y. Pan, Y.L. Wang, X.J. Li, J. Chromatogr. A 1218 (2011) 5063–5070.
[26] A. Beltran, F. Borrull, P.A.G. Cormack, R.M. Marcé, Trends Anal. Chem. 29 (2010) 1363–1375.
[27] D. Djozan, T. Baheri, J. Chromatogr. A 1166 (2007) 16–23.
[28] C.J. Tao, J.Y. Hu, J.Z. Li, S.S. Zheng, W. Liu, C.J. Li, Bull. Environ. Contam. Toxicol. 82 (2009) 111–115.
[29] O. Esturk, Y. Yakar, Z. Ayhan, J. Food Sci. Tech. 48 (2011) 1–9.
[30] X. Zhao, X. Xu, R. Su, H.Q. Zhang, Z.M. Wang, J. Chromatogr. A 1229 (2012) 6–12.