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Development of new solid-phase microextraction fibers by sol–gel technology for the determination of organophosphorus pesticide multiresidues in food

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Abstract

Allyloxy bisbenzo 16-crown-5 trimethoxysilane was first used as precursor to prepare the sol–gel-derived bisbenzo crown ether/hydroxyl-terminated silicone oil (OH-TSO) SPME coating. The coating procedure involving sol solution composition and conditioning process was presented. Compared with commercial SPME stationary phases, the new coatings showed higher extraction efficiency and therefore could provide higher sensitivity for organphosphorous pesticides (OPs). Limits of detection (LODs) were in the range of 0.003–1.0 ng/g for these OPs in food samples (honey, juice, orange and pakchoi). The optimal extraction conditions of the new coatings to OPs in these samples were investigated by adjusting extraction time, salt addition, extraction temperature, and dilution ratios of samples with distilled water by using SPME coupled with gas chromatography (GC)–flame photometric detection (FPD). The method was applied to determine the concentrations of OPs in real samples.

Keywords: Sol–gel technology; Solid-phase microextraction; Pesticides; Organophosphorus compounds; Bisbenzo crown ether

1. Introduction

The use of pesticides in food production has provided numerous benefits in terms of increasing production and quality. As a result, consumers are exposed to pesticides, usually in minute quantities, in several food groups including fruits, juices, honey and vegetables. Organphosphorous pesticides (OPs) are one of the most common classes involved in poisonous because of the inhibition of acetyl-cholinesterase [1]. Monitoring the trace levels of OPs in food is important for human health protection and environmental control.

The conventional methods for the analysis of OPs in food, such as liquid–liquid extraction [2–4], supercritical fluid extraction (SFE) [5] or solid-phase extraction (SPE) [6–8], are rather time-consuming, labor-intensive, and require relatively large volumes of solvents. Furthermore, the maximum residue limits (MRLs) for OPs established by governments and institutes of the world are near the level of determination, which make them difficult to analyze because of interfering compounds in food matrix. It is therefore desirable to enhance the sensitivity and limit the number of sample handling steps involved in analytical methods of OPs. Solid-phase microextraction (SPME), developed in 1989 at the University of Waterloo (Ontario, Canada) by Belardi and Pawliszyn [9], is an ideal alternative technique that eliminates the use of organic solvents, has the advantage of simplicity and integrates sampling, extraction, concentration and sample introduction into a single solvent-free step [10]. Thus, SPME has been applied to the determination of pesticide residue [11,12]. Magdic et al. [13] discussed the SPME of OPs using 100 μm thickness polydimethylsiloxane (PDMS) and 85 μm thickness polyacrylate (PA) fibers, and reported that extractions employing the latter were usually more effective. Sng et al. [14] extracted malathion and parathion using five fiber coatings (7 and 30 μm thickness PDMS, 85 μm thickness PA, 65 μm thickness Carbowax-divinylbenzene (CW-DVB) and PDMS-DVB), and found that the PDMS-DVB fiber was clearly the most effective. These results were similar to those reported by Goncalves et al. [15], who evaluated three different PDMS-DVB fibers for four pesticide groups.

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Musshoff et al. [16] described a simple and rapid procedure for the determinate of OPs in human blood using headspace (HS) SPME of 100 μm PDMS fiber and gas chromatography (GC)–mass spectrometry (MS). The detection limits are in the range between 0.01 and 0.3 μg/g. Most works concerning the determination of OPs are performed using commercial fiber. Jimenez et al. [17] noted that SPME of commercial fibers is useful for the analysis of pesticides in honey, however, the low reproducibility obtained suggests its use as a semiquantitive technique. The less efficiency, longer equilibrium times [18] of commercial fibers limited the application of SPME for determination of OPs.

To improve the performance of SPME for OPs, novel coating must be developed. Sol–gel technology has been widely used to prepare SPME fiber [19,20] because it can effectively create chemically bonded, porous, and highly crossed coating on the fused-silica fiber surface. Generally, methyltrimethoxysilane (MTMOS) [21] or tetraethoxysilane (TEOS) [22] is used as precursor, and compound containing functional group is added into sol–gel solution to prepare SPME fiber coatings for various needs. The content of this compound in fiber coating was usually low, which made the fiber lack enough selectively for analytes of interest. In this study, allyloxy bisbenzo 16-crown-5 trimethoxysilane synthesized by ourselves, was first used as precursor to prepare the sol–gel-derived bisbenzo crown ether/hydroxyl-terminated silicone oil (OH-TSO) SPME coating. The extraction efficiencies of the new coating for OPs were studied and optimized by adjusting the following parameters: extraction time, salt addition, extraction temperature, and dilution ratios of samples, by gas chromatography–flame photometric detection (FPD). Limits of detection (LODs), accuracy and precision studies have been made with this fiber. The apparent recoveries of spiked food samples (honey, juice, orange and pakchoi) are determined over 70%, LODs are in the range of 0.003–1.0 ng/g for OPs studied in these samples, and the coefficient variation is between 2.0 and 15.0%. The proposed methods have been applied to the analysis of OPs in real food samples.

2. Experimental

2.1. Equipment and reagents

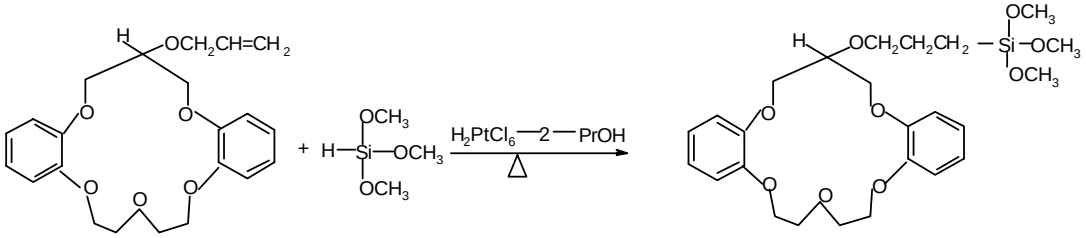
The SPME holder for manual use and fibers for comparison of PDMS (30 μm), CW-DVB (65 μm), PDMS-DVB (65 μm) and PA (85 μm) were obtained from Supelco (Bellefonte, PA, USA). SPME-GC experiments were carried out on an Agilent 6890 N GC system equipped with a capillary splitless injector system, a flame photometric detector (FPD). The HPCORE ChemStation (version A 09.01) software was used for instrument control and data analysis. A 30 m × 0.32 mm × 0.25 μm HP-5 coating fused-silica capillary column was used.

The operating conditions were as follows: the carrier gas was nitrogen at 2.6 ml/min; the FPD gases were hydrogen at 75 ml/min and air at 100 ml/min; the injector temperature was 270 °C and the FPD temperature was 250 °C; the oven temperature program had an initial temperature of 60 °C for 1 min, to 110 °C at 10 °C/min, to 160 °C at 8 °C/min, then to 260 °C at 5 °C/min for 2 min.

Pesticide-grade dichloromethane was obtained from Tedia Company Inc. (Fairfield, USA). Distilled water was used. OH-TSO, TEOS and trimethoxylsilane were obtained from the chemical plant of Wuhan University (Wuhan, China), the fused-silica fiber (140 μm o.d.) was purchased from Academy of post and telecommunication, Wuhan. Trifluoroacetic acid (TFA) was purchased from Aldrich (Allentown, PA, USA). Standard mix solution was prepared with dichloromethane to the concentration 10 μg/ml of each (except for dimethoate and methamidophos, which were 200 μg/ml) including trichlorfon, dichlorvos, acephate, azodrin, phorate, diazinon, methyl parathion, fenitrothion, malathion, fenthion, chlorpyrifos, ethion and triazophos. Tetrahydrofuran (THF) and 2-propanol (2-PrOH) were AR-grade, and they, before used, must be dehydrated. H_2PtCl_6 was AR-grade.

2.2. Synthesis of precursor

The reaction scheme for the synthesis of allyloxy bisbenzo 16-crown-5 trimethoxylsilane is shown below.



A mixture of 0.5 g (1.3 mmol) of allyloxy bisbenzo-16-crown-5, 400 μl of trimethoxysilane (4 mmol), 20 ml of anhydrous THF, and two or three drops of 0.1 M H_2PtCl_6-2-PrOH was stirred for 2 h at 50 °C in the presence of nitrogen, then heated for 20 h. The solvent was removed under vacuum and the residue was dissolved in anhydrous dichloromethane and filtered. After removal of the solvent, a light yellow waxy liquid, weighed 0.58 g (yield 93%) was obtained. The nuclear magnetic resonance (NMR) spectrum showed that peaks at δ 6.1(m, CH=) and δ 5.4(d, $=CH_2$) of

reactant were disappeared and peaks at δ 0.7–1.0 (t, $SiCH_2$) of target compound came out.

2.3. Preparation of SPME fiber

Seventy-five milligrams of allyloxy bisbenzo-16-crown-5 trimethoxysilane, 90 μl of OH-TSO, 50 μl of TEOS, 10 μl of PMHS were dissolved in 300 μl of methylene chloride. A 80 μl of TFA containing 5% (v/v) water was added to the resulting solution with ultrasonic agitation for 3 min. The mixture was centrifuged at 12 000 rpm/min for 5 min. The precipitate at the bottom of the tube was removed and the top clear sol solution was collected for the fiber coating. At the constant temperature of 20 °C, the pretreated fiber was dipped vertically into the sol solution and held inside the sol solution for about 10 min, then in the following 10 min the fiber was inserted vertically in the sol solution and drawn out several times (up-and-down), during which a sol–gel coating was formed on the bare surface of the fiber end. The up-and-down process was repeated every minute until the thickness of the coating required was obtained. The fiber was placed in a desiccator at room temperature for 24 h, this was followed by the condition process. The fiber was initially conditioned by placing it in a GC injector port kept at a temperature of 150 °C with a gentle N_2 flow (∼10 psi; 1 psi = 6894.76 Pa) for 2 h, and then conditioned again at 200–350 °C for 6 h, after removal from the injector, the fiber was cooled to room temperature and soaked in water and methylene chloride for 1 h, respectively. After dried, the fiber was conditioned at 330 °C under nitrogen for another 2 h, the final thickness of the fiber was 40 μm.

2.4. Sample preparation

Honey sample: The honey was diluted with distilled water in a proportion ratio (w/v). To study the influence of the ionic strength, different amount of NaCl was added into the same volume of honey–water solution and dissolved with the aid of an ultrasonic water bath. Aliquots of 23 ml of the honey–water solution containing NaCl were placed in 25 ml vial. Then, 23 μl of a solution in methylene chloride containing the OPs in a known concentration were added to the vial. The vial was covered with a cap wrapped with membrane after a magnetic spin bar (PTFE) was added and put into a water bath to obtain the adequate temperature, during stirring, the fiber was introduced in the vial.

SPME for orange and juice samples: Sample of juice or its solution diluted by water, NaCl were placed in 25 ml vial, then spiked at proper concentration of OPs. Orange samples were comminuted and homogenized, homogenate was further diluted by distilled water, and NaCl was added into this solution. Then 23 ml of the solution was used for SPME process.

SPME for vegetable: Ten grams of pakchoi was cut and homogenized with 100 ml of water, and the mixture of 23 ml of homogenate was used for SPME extraction.

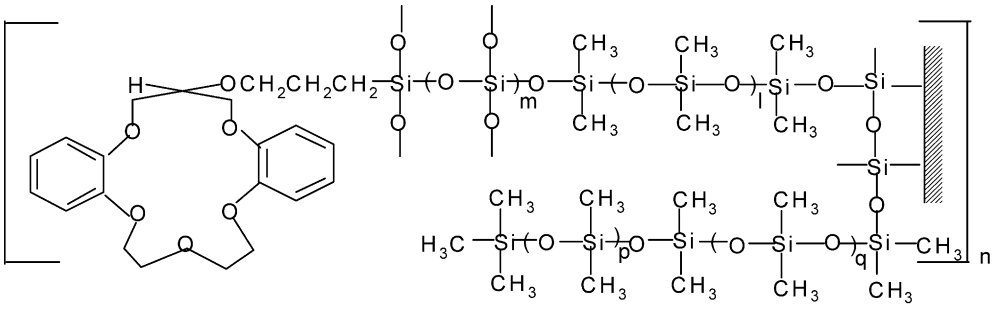
Before SPME extraction, all solutions of samples were stated for 2 h in order to make them reach equilibrium.

3. Results and discussion

3.1. Optimization and possible mechanism of the sol–gel process

Optimization of the sol–gel process was effected by varying the type of the silane precursors or by adding a compound with special function agent into the coating. Unlike the common sol–gel process, in which only one of tetraalkoxysilanes was used as the sol–gel precursor to produce silica fiber, here, the use of crown ether derivation of trimethoxysilane as precursor can provide important advantages.

There are five major reaction processes that occur during the sol–gel formation of the method studied. (1) Hydrolysis of crown ether derivation of trimethoxysilane catalyzed by TFA took place. To overcome cracking and shrinkage during the drying step of sol–gel reaction, TEOS as co-precursors was used in our process, which was also hydrolyzed in this condition. (2) The hydrated silica tetrahedral can easily interact in a condensation reaction to form ≡Si–O–Si≡ bonds. The product can condensate with hydrated product of crown ether derivation of trimethoxysilane as following. (3) The condensation products can further undergo polycondensation reactions to produce a three-dimensional sol–gel network. (4) In the sol–gel solution, hydroxyl-terminated silicone oil, used as a coating ingredient, can grow the silica network by chemical binding with above polymer and can help to spread the stationary phase on the fiber surface uniformly. (5) The silanol groups exposed on the fiber surface can also chemically bind with the polymeric network to create a surface-bonded polymeric coating. A dried gel still contains a very large concentration of chemisorbed hydroxyl on the surface of the pores, which may influence the reproducibility of the fiber. Poly(methylhydrosiloxane) (PMHS), a well-known surface deactivation reagents was added to the coating sol solution, after sol–gel coating, the newly created surface layer with containing physically bound molecules of PMHS that will perform the deactivation reaction during the fiber conditioning step. The details of the sol–gel process are similar as Zeng et al. has discussed [22]. But, here, the ratio of the mass of benzo-crown ether in this coating, which is about 33%, is much larger than that in sol–gel SPME fiber prepared by common sol–gel method, which is just about 3% [22]. The structure of fiber coating is as the following.



3.2. The lifetime of the coating

A coating's lifetime is important for practical application. The coating is damaged mainly by high temperature of the injection port of gas chromatography and/or solvent in the sample matrix. Being strong chemical bonding provided by sol–gel technology, the fiber coating can work at 350 °C. Such high thermal stability can expand the SPME application range toward higher boiling-point compounds. On the other hand, the chemical stability of the coating is very well because the response of chromatography of OPs by SPME had no obvious decrease after the fiber was dipped in different polar solvent, *n*-hexane, methylene chloride, acetone, distilled water for 1 h, respectively, which is due to strong adhesive of the coating to the fiber surface and wrapped by the three-dimensional network. The sol–gel crown coating swells hardly in solvents and can not slip off the fused-silica substrate. The novel SPME fiber is characterized by its high thermal and solvent stability. Thus, the lifetime of this fiber is longer than that of commercial fibers. The fiber can be used over 200 times while all commercial fibers can only be used about 40–100 times.

3.3. Extraction characteristics for OPs

As can be seen from Fig. 1, in overall, the new crown ether fiber presented higher response to OPs than the commercial fibers when they were used in extracting OPs from the aqueous solution at the same concentration and the same extraction conditions.

OPs are relatively high water-soluble analytes, which was an important factor in determining the overall partition ratio for a given analyte between the SPME fiber coating and water. The integrated peak areas(Fig. 2), and hence the partition ratios, for ethion, phorate, methyl parathion, diazinon, malathion, appeared to be inversely related to their solubilities in water, which are 2, 50, 55, 60, 145 μg/ml, respectively. The solubilities of trichlorfon, methamidophos, acephate, azodrin in water are too high, and determination of them by SPME method had not any advantage. So, in the subsequent experiments these pesticides were not studied.

3.4. Optimization of SPME method

Except for fiber type, there are several other variables must be studied and optimized in the determination of OPs by SPME method, including extraction time, ionic strength of the solution, extraction temperature. In general, sample temperature has a double influence. Higher temperature can increase the diffusion coefficient of analytes in water and shorten the extraction time. Also, elevated temperatures decrease the partition coefficient between the coating and analytes because adsorption is generally an exothermic process. Chromatographic response increased slightly at temperature 25–55 °C for most of the compounds, while at higher temperature (50–70 °C), the response decreased in some sort (Fig. 3 for honey, and Fig. 4 for orange juice). For distilled water and pakchoi, the optimal extraction temperatures were 32 and 20 °C, respectively (Figs. 5 and 6). In fact, opti-

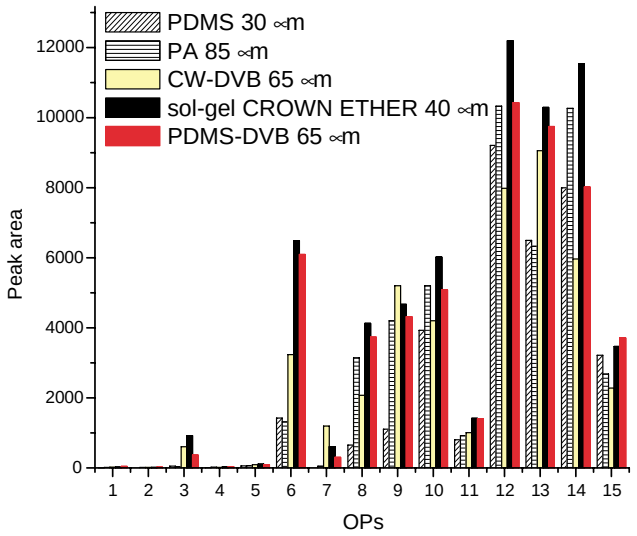


Fig. 1. Comparison of extraction efficiency of the sol–gel crown ether coating and four commercial fibers by direct SPME method. Peaks: (1) trichlorfon, (2) methamidophos, (3) dichlorvos, (4) acephate, (5) azodrin, (6) phorate, (7) dimethoate, (8) diazinon, (9) methyl parathion, (10) fenitrothion, (11) malathion, (12) fenthion, (13) chlorpyrifos, (14) ethion, (15) triazophos extraction time, 60 min; extraction temperature: 32 °C; desorption time, 5 min; desorption temperature 270 °C, saturated solution with NaCl; constant stirring. Concentration of OPs: 20 ng/ml of each (except for dimethoate and methamidophos, which were 200 ng/ml).

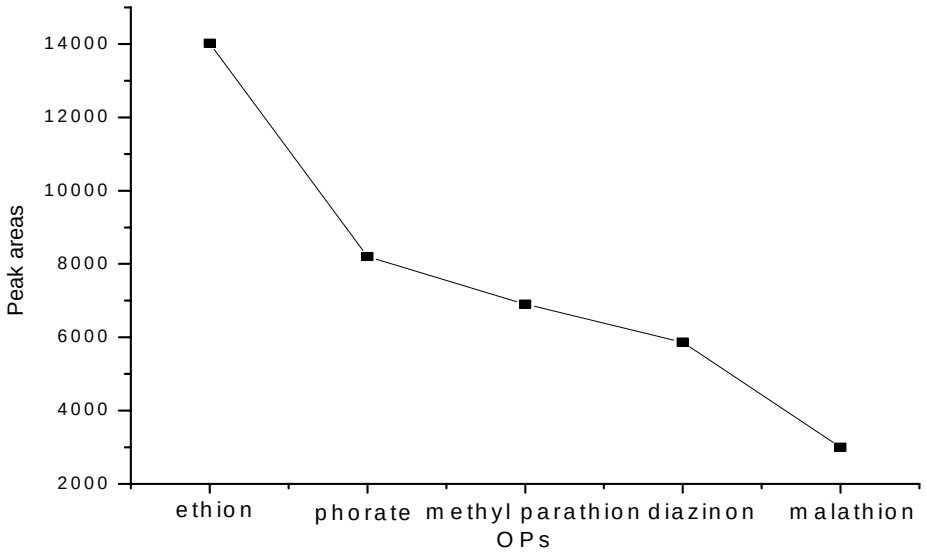


Fig. 2. The relationship between the extaction efficiency and water solubilies of OPs Extraction time, 120 min; extraction temperature: 32 °C; desorption time, 5 min; desorption temperature 270 °C, saturated solution with NaCl; constant stirring. Concentration of OPs: 20 ng/ml of each above OPs.

mization of extraction temperature is generally less important when working by direct immersion of the fiber in the aqueous sample than when dealing with headspace SPME [23].

The influence of the extraction time was similar to that of the previous fibers. The chromatographic signal increased gradually with the extraction time and stabilized at about 120 min for most of the compounds in distilled water at the extraction temperature of 32 °C, this indicated that a state of equilibrium had been reached in the partition process. The similar study had been done for OPs in honey, juice, pakchoi samples by the direct SPME of the novel fiber. The equilibrium times were about 120, 160, 200 and 240 min for most of OPs studied in water, honey, juice, and pakchoi, at temperatures of the optimization, respectively, which were much shorter than extracting by commercial fibers [18].

It can be observed that the presence of NaCl helps the extraction from water, peak areas increased from 10 to 300% depending on the pesticide (Fig. 7). Similar positive effect of the addition NaCl to the honey and juice samples over extraction efficiency of most compounds can also be obtained. However, the addition NaCl to pakchoi sample decreased the response of OPs (Fig. 8), which is because the suspended

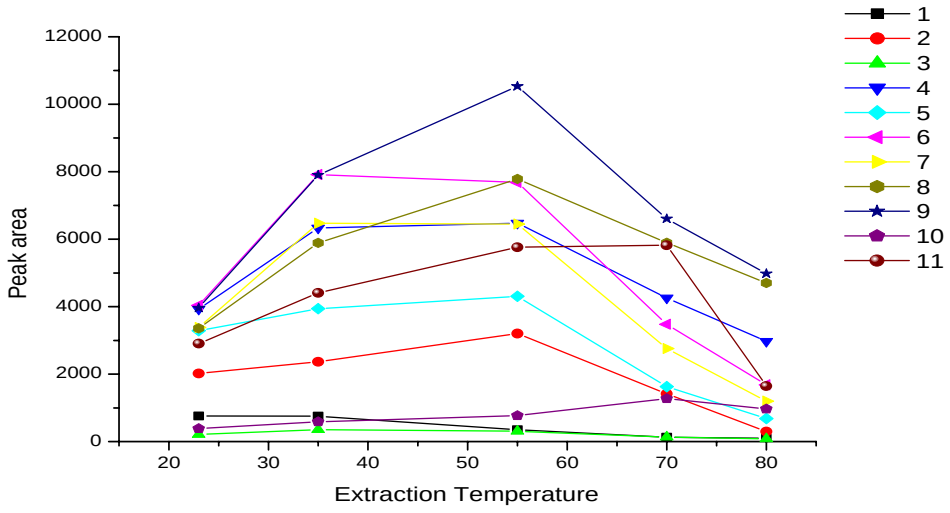


Fig. 3. Effect of the extraction temperature on the response of 20 ng/ml OPs (for honey 1:5). Peaks: (1) Dichlorvos, (2) phorate, (3) dimethoate, (4) diazinon, (5) methyl parathion, (6) fenitrothion, (7) malathion, (8) fenthion, (9) chlorpyrifos, (10) ethion, (11) triazophos. Other conditions are the same as in Fig. 1 except for the extraction temperature.

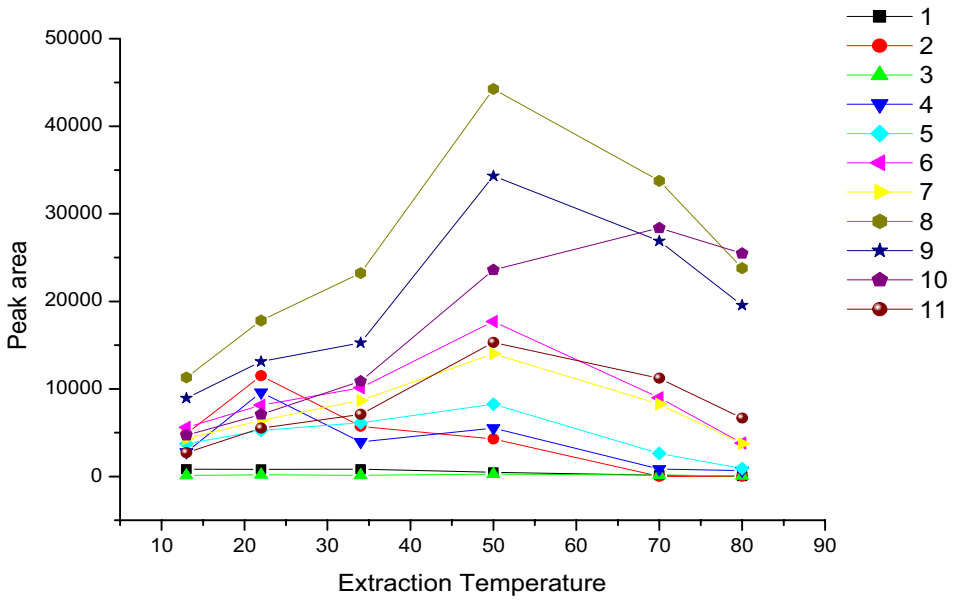


Fig. 4. Effect of the extraction temperature on the response of 20 ng/ml OPs (for orange juice 1:50). Other conditions are the same as in Fig. 1 except for the extraction temperature. See Fig. 3 for peak identification.

pieces of pakchoi in heterogeneous system may easily adsorb the OPs although salt can decrease the solubilities of OPs in water solution.

3.5. Effect of sample matrix

It can be seen from Fig. 9 that the sample matrix can affect the extraction efficiency of OPs. For example, the extraction amount of ethion (peak 10) from diluted honey with water (1:5 w/w, Fig. 9b) was much smaller than from diluted juice with water (1:50 w/w, Fig. 9c) at the same concentration of OPs in solution.

Homogenates of honey, orange, juice and pakchoi, and their solutions by different ratios with water were spiked with the target analytes to produce a concentration of 20 μg/l of each OPs. The integration peak areas of these OPs obtained by above SPME method were illustrated in Fig. 10. The peak area obtained by SPME-GC-FPD

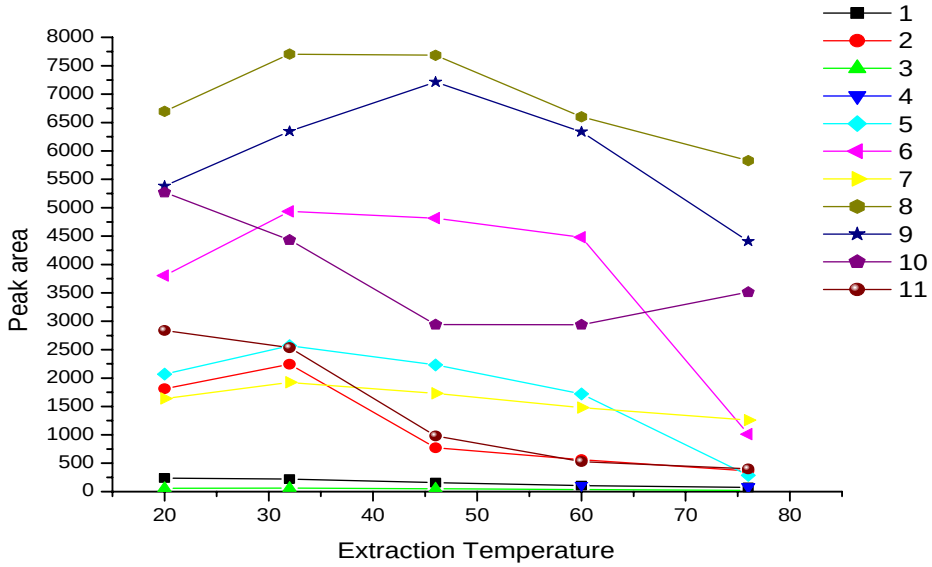


Fig. 5. Effect of the extraction temperature on the response of 20 ng/ml OPs (for water). Other conditions are the same as in Fig. 3 except for the extraction temperature.

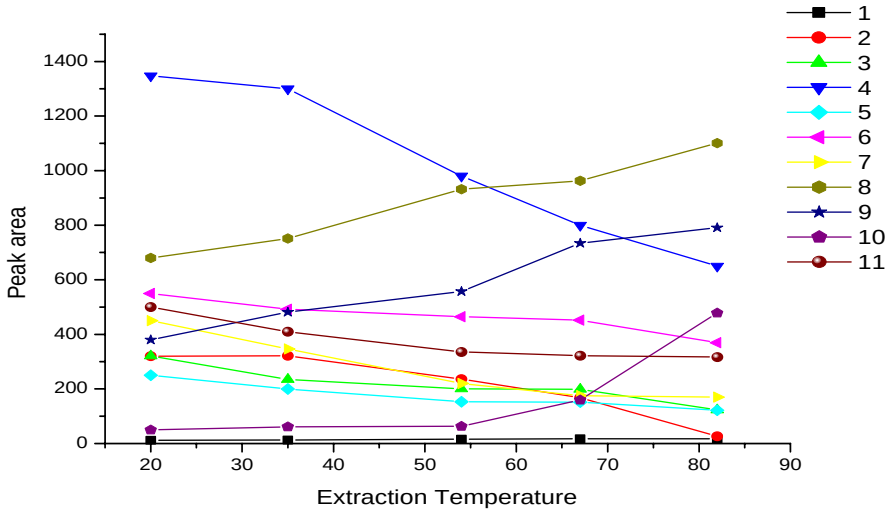


Fig. 6. Effect of the extraction temperature on the response of 20 ng/ml OPs (for pakchoi 1:10). Other conditions are the same as in Fig. 3 except for the extraction temperature.

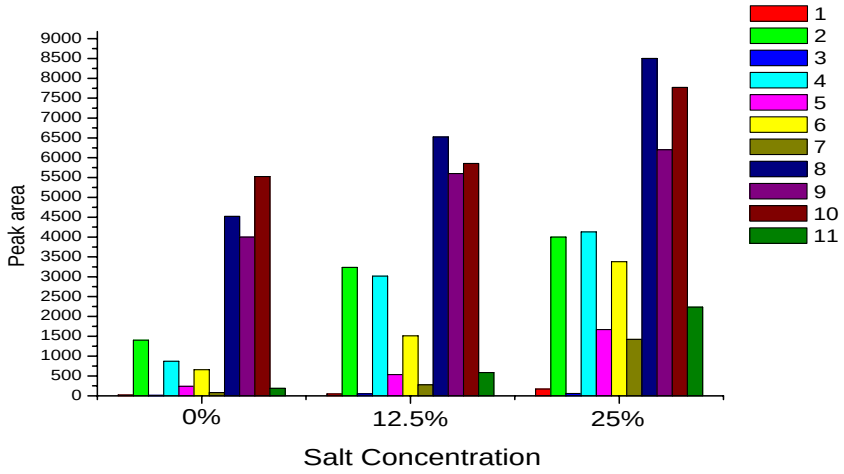


Fig. 7. Salt effect curves of the new fiber for 20 ng/ml of each above OP in water. Other conditions as in Fig. 3.

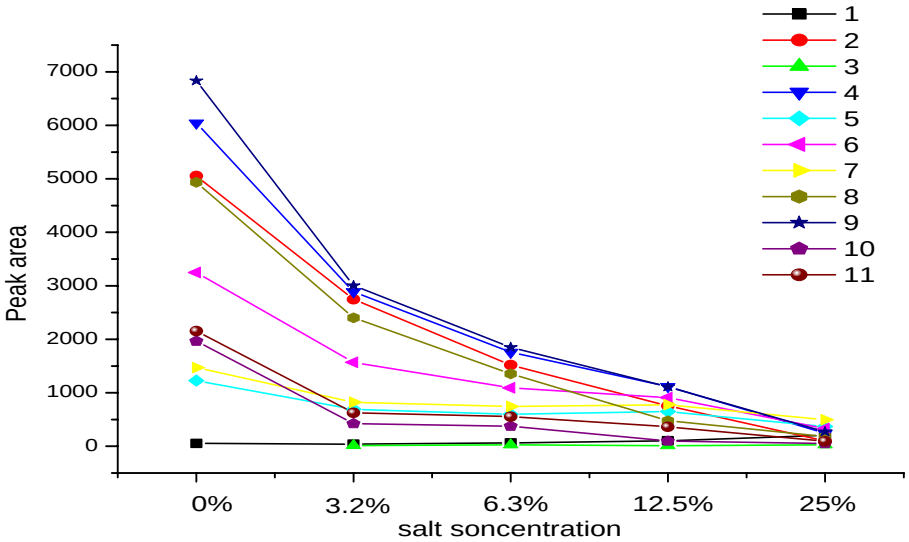


Fig. 8. Salt effect curves of the new fiber for OPs in pakchoi solution. Other conditions as in Fig. 3.

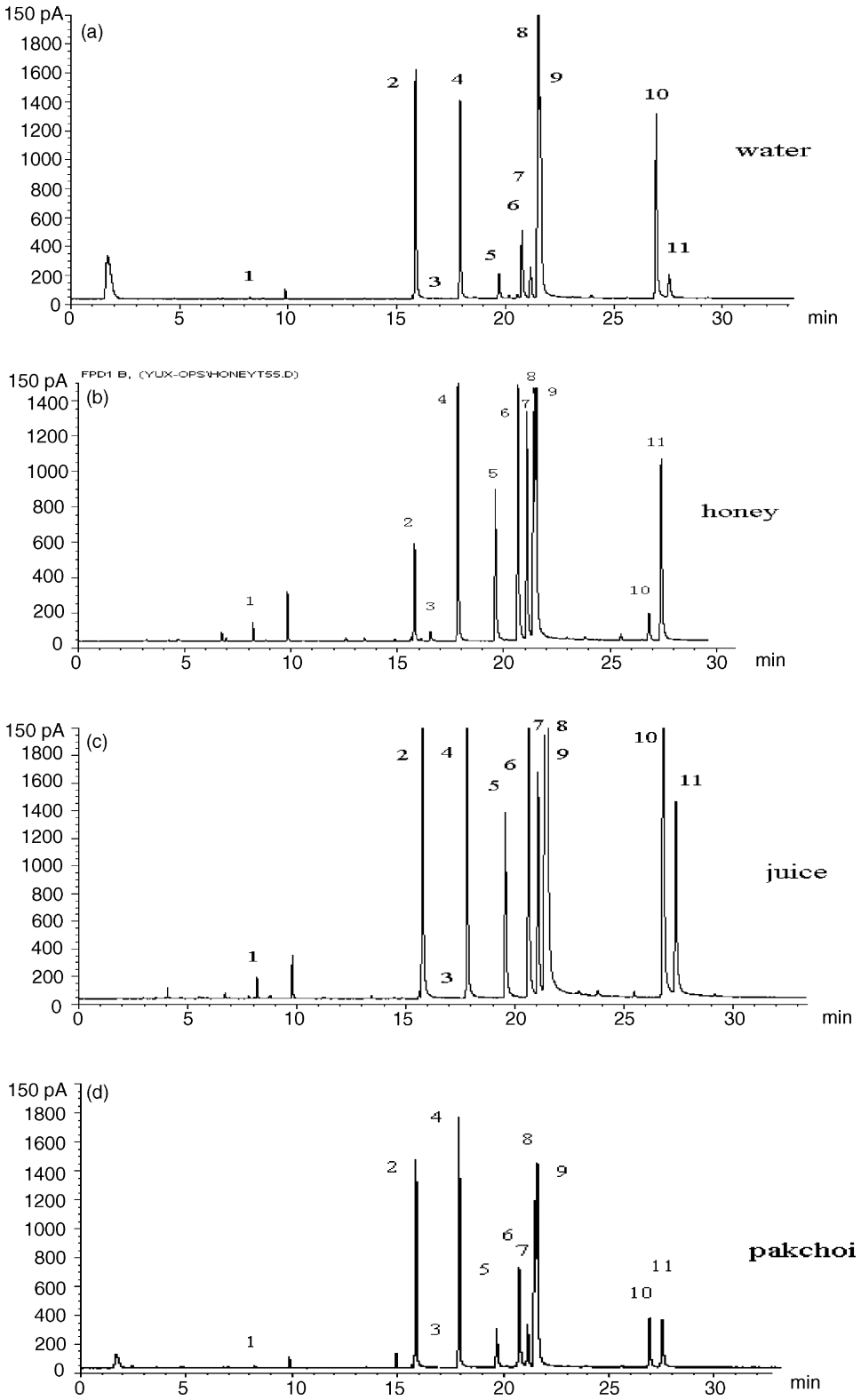


Fig. 9. Chromatogram obtained by using the procedure proposed for the new fiber on the spiked samples of 20 ng/g of each OP: (a) water; (b) honey; (c) juice, and (d) pakchoi. See Fig. 3 for peak identification.

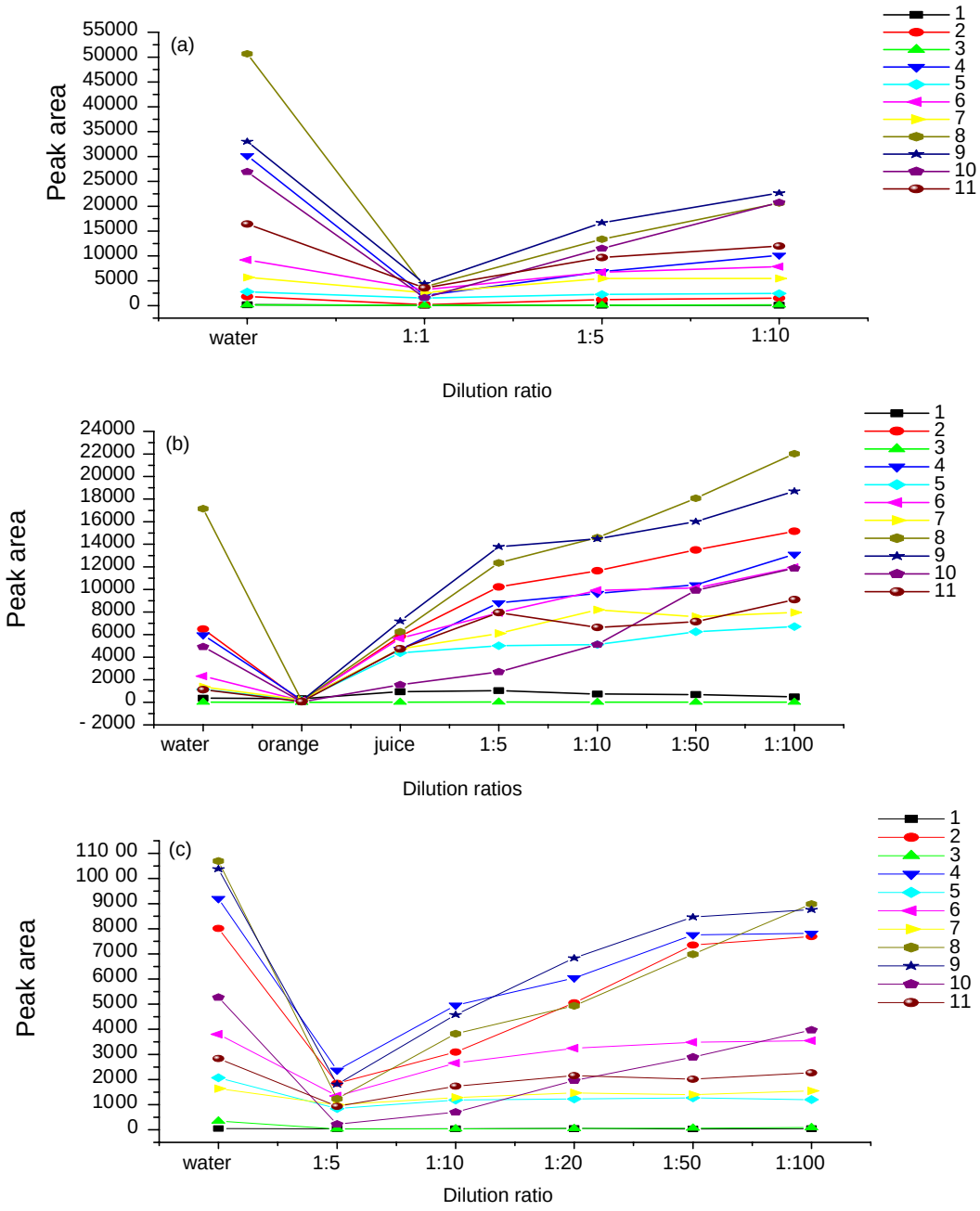


Fig. 10. Effect of dilution of samples with distilled water by different dilution ratios (w/w): (a) for honey; (b) for orange and juice; (c) for pakchoi. Other conditions are as in Fig. 1. See Fig. 3 for peak identification.

from homogenates of samples (A_{sample}) were less than that from aqueous solution ($A_{aqueous}$) spiked at the same concentration. Ratios, defined as $A_{sample}/A_{aqueous}$, were 10–30% when honey sample diluted by 1:1 (w/w) with water, while the value increased to 50–80% as the dilution ratio was 1:10. For orange homogenate, the ratios were very poor, but when it was filtrated and diluted with water, ratios were improved just as the honey sample. Furthermore, it is more effective to extract OPs from these systems at dilution ratio 1:50, 1:100 than from water.

3.6. Limit of detection, precision and accuracy

Based on the method development described above, the following conditions were chosen for the analytical method of OPs in water: extraction temperature, 32 °C, saturated solution with NaCl; in honey: 23 ml of diluted honey (1–5 dilution), saturated with NaCl, extraction temperature, 55 °C; in juice: 23 ml of diluted juice (1–50 dilution) saturated with NaCl, extraction temperature, 50 °C; in pakchoi: 23 ml of diluted homogenate(1–20 dilution), extraction temperature, 20 °C; extraction time was 60 min for all these samples.

Table 1
The LOD, R.S.D., relative recoveries and correlation coefficient (r^2) of the method for the determination of OPs

OPs	Honey				Juice				Pakchoi			
	LOD (ng/g)	R.S.D. (%)	Rc[a] (%)	r^2[b]	LOD (ng/g)	R.S.D. (%)	Rc[a] (%)	r^2[b]	LOD (ng/g)	R.S.D.[a] (%)	Rc[a] (%)	r^2[b]
Dichlorvos	0.10	12.1	78.2	0.9936	0.093	8.9	82.3	0.9969	0.80	9.1	80.2	0.9930
Phorate	0.029	3.8	95.0	0.9958	0.008	5.2	89.5	0.9982	0.10	2.3	86.2	0.9956
Dimethoate	0.70	15.0	74.4	0.9923	0.20	9.2	80.1	0.9966	1.0	8.5	76.8	0.9925
Diazinon	0.040	4.1	92.5	0.9991	0.009	2.6	93.6	0.9992	0.21	2.6	89.6	0.9921
Methyl parathion	0.028	5.5	89.6	0.9988	0.011	5.0	95.6	0.9987	0.33	6.0	93.5	0.9910
Fenitrothion	0.018	4.3	99.2	0.9987	0.009	6.3	94.2	0.9993	0.20	5.2	92.8	0.9936
Malathion	0.020	3.6	94.7	0.9935	0.010	2.0	90.1	0.9991	0.17	4.5	88.2	0.9992
Fenthion	0.004	7.6	95.0	0.9993	0.003	6.7	88.2	0.9986	0.063	5.6	89.0	0.9942
Chlorpyrifos	0.005	6.8	105.2	0.9990	0.004	6.0	96.3	0.9956	0.080	6.0	101.2	0.9981
Ethion	0.042	2.1	93.8	0.9935	0.006	3.1	87.6	0.9921	0.20	3.5	87.2	0.9991
Triazophos	0.010	3.0	92.9	0.9980	0.010	3.2	93.5	0.9935	0.20	4.2	96.8	0.9955

[a] Rc: relative recovery.
[b] r^2: correlation coefficient.

To evaluate the precision of the measurements, analyses of samples spiked at 10 μg/l of each pesticide were performed in six times. The analyses led to the relative standard deviations (R.S.D.s) of the peak areas from 2.1 to 15.0%, 2.0 to 9.2%, 2.3 to 9.1% for honey, juice, pakchoi sample, respectively. The limits of detection were estimated to be the concentrations of the OPs that produce signals three times of the background noise. It can be seen that LODs were 0.004–0.7 ng/g for honey sample, 0.003–0.2 ng/g for juice sample, 0.063–1.0 ng/g for pakchoi sample for the OPs studied which are much lower concentrations, sufficient to meet the demands of environmental monitors, food supervision, and so on. The calibration curves were found to have good linearity by correlation coefficients (r^2) of more than 0.99 in the range 0.5–200 ng/g, 1.0–500 ng/g, and 1.0–200 ng/g for honey, juice, and pakchoi, respectively. The relative recovery, defined as C_{test}/C_{spike} (the percent of determination results to the spiked concentration) study was carried out by spiking at 20 μg/l of each OPs in non-contaminated samples. The calculated average relative recoveries and LODs, R.S.D.s results were listed in Table 1.

Finally, real contaminated honey, orange, and pakchoi samples were analyzed by above method with standard addition quantitation procedure. There are 10.2 ng/g fenitrothion, 2.1 ng/g triazophos in orange, 5.6 ng/g phorate in honey, 6.8 ng/g methyl parathion in pakchoi (Fig. 11).

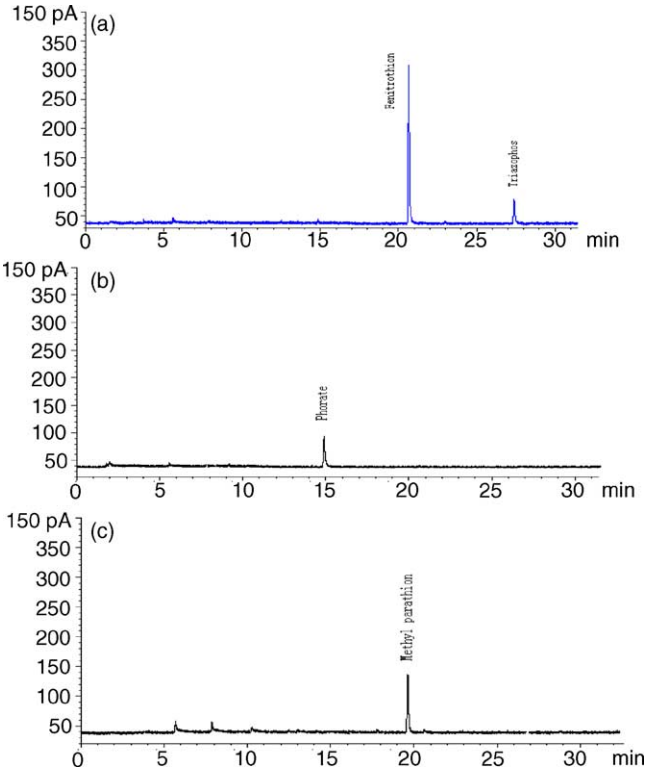


Fig. 11. The chromatograms of the contaminated orange sample (a), honey (b) and pakchoi (c) by SPME-GC-FPD with the novel fiber.

4. Conclusion

We have demonstrated a simple method for the preparation of a new sol–gel crown ether fiber. It shows excellent extraction characteristics for OPs. A method for a large number of OPs to get rapid information about amount in food samples was established and applicable for routine inspections.

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