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Application of polyphenylmethylsiloxane coated fiber for solid-phase microextraction combined with microwave-assisted extraction for the determination of organochlorine pesticides in Chinese teas

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Abstract

Polyphenylmethylsiloxane (PPMS) as a novel coating for solid-phase microextraction (SPME) combined with microwave-assisted extraction (MAE) has been applied to determine the concentrations of organochlorine pesticides (OCPs) in Chinese teas. The characteristics of PPMS fiber, the extraction modes of SPME, the extraction time, temperature, and salt effects were investigated. Microwave irradiation time and power were also studied. Compared with commercial polydimethylsiloxane (PDMS) fiber and homemade sol–gel polymethylsiloxane (PMS) fiber, the novel porous sol–gel PPMS fiber exhibited high sensitivity and selectivity for OCPs compounds, higher thermal stability (to 350 °C) and long service life (more than 150 times). The recoveries of MAE is compared with that of ultrasonic extraction (USE), MAE–SPME–gas chromatography (GC)/electron-capture detection (ECD) methods showed better results for Chinese teas. Linear ranges of OCPs in the blank green tea was 0.1–10^3 ng/l. Detection limits of this method are below 0.081 ng/l. Recoveries of this method are between 39.05 and 94.35%. The repeatability of the technique was less than 16% relative standard deviation (R.S.D.). The tested pesticides in three Chinese teas were at the ng/g level.

Keywords: Solid-phase microextraction; Microwave-assisted extraction; Polyphenylmethylsiloxane; Pesticides; Organochlorine compounds

1. Introduction

Pesticides have played an important role in increasing agricultural productivity. Because of their high toxicity and widespread uses in agricultural areas, the residues could be left in our environment [1]. Organochlorine pesticides (OCPs) have very low solubilities in water and are resistant to metabolism. Some OCPs were banned in the 1970s due to their toxicity, and persistence [2]. Therefore the determination of pesticides in water, plants, soils, foodstuff, etc. is of major importance for human health protection and environmental control. Most determinations of OCPs were based on chromatographic methods with various detections, such as flame ionization detection (FID) [3], mass spectrometric (MS) detection [4–7], and electron-capture detection (ECD) [3,4,6–8].

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Solid-phase microextraction (SPME), developed by pawliszyn and co-workers [9]. SPME can be coupled easily to gas chromatography (GC), high-performance liquid chromatography (HPLC) [10], capillary electrophoresis (CE) [11], inductivity coupled plasma mass spectrometry (ICP-MS) [12] and Raman spectrometry (RS) [13]. A wide range of analytes from volatile to non-volatile compounds has been determined by SPME. These included environmental pollutants such as pesticides [4,14,15], phenols [16,17], polychlorinated biphenyls (PCBs) [18,19], polycyclic aromatic compounds (PAHs) [20] and inorganic compounds [21].

Sol–gel chemistry offers a simple material systems and for applying them as surface coatings [22]. Sol–gel chemistry also provides an efficient way of incorporating organic components into inorganic polymeric structures in solutions under mild thermal conditions [23]. There are many advantages of sol–gel technology, such as it can provide strong adhesion of the coating to the substrate due to chemical bonding, high thermal stability, porous structure and large surface area. Malik and co-workers firstly applied sol–gel coating for a SPME fiber (10 μm polydimethylsiloxane (PDMS)) [24]. Caruso and co-workers [25] developed sol–gel technique for SPME-HPLC determination of organometals. We have applied sol–gel technique to prepare sol–gel polyethylene glycol (PEG) [26] and hydroxyfullerene [27] fibers for the determination of both polar and non-polar compounds.

Microwave-assisted extraction (MAE) is a rather new technique which has been applied to the extraction of organic compounds from different types of matrices (soil, seeds, food, . . .) including the extraction of pollutants from environmental samples [28]. The MAE followed by SPME is a useful combination which combines extraction speed with concentration. SPME coupled with MAE for the determination of veltol and veltol-plus in solid food sample [29], off-flavor compounds in catfish tissue [30], chlorophenols in water [31] and organochlorine pesticides in medicinal plants [32] have been studied.

Our interest is aimed on the determination of organochlorine pesticides in Chinese teas. Because tea is now one of the most popular drinks in the world, and its consumption nearly ranks with that of coffee. According to the degree of fermentation, tea is classified into green tea (unfermented), oo-long tea (semi-fermented), and black tea (fully fermented). Tea is consumed as a popular beverage worldwide because of its characteristic aroma, flavor and health benefits [33]. Same as other crops, possible contamination of tea would include atmospheric deposition, applications of chemical and organic fertilizers, fungicides, and pesticides, soil factors, production produces, irrigation with polluted water, etc. Only a few studies were published in this area of pesticide research [32,34]. The complexity of the matrix made the identification and quantification of organochlorine pesticides in Chinese teas difficult. Water was chosen as an extracting solvent of MAE process in this work. People usually boil or infuse Chinese teas in water for certain time and drink it. Acting as an extracting solvent, water molecules with a high dielectric constant were characterized by a high ability to absorb microwave energy [35]. Water had been successfully used as the extracting solvent of MAE process for triazine from soil [36].

In this paper, polyphenylmethylsiloxane (PPMS) and polymethylsiloxane (PMS) coated fibers were prepared on the surface of the fused-silica fiber using sol–gel technique. Compared with commercial PDMS fiber, the sol–gel fibers showed better selectivity toward non-polar compounds (such as OCPs), higher thermal stability (to 350 °C) and longer service lifetime (more than 150 times).

The fibers are evaluated through the determination of OCPs residue in Chinese teas including two green teas and one oo-long tea using MAE–SPME–GC/ECD.

2. Experimental

2.1. Instrumentation and reagents

The SPME devices for manual sampling and a 100 μm commercial PDMS fiber for comparison were obtained from Supelco (Bellefonte, PA, USA). SPME–GC experiments were carried out on a Hewlett-Packard 6890 GC system equipped with a capillary splitless injector system, and μ-electron-capture detection (μ-ECD) system. A 30 m × 0.25 mm i.d., 0.25 μm HP-5 coating fused-silica capillary column (Hewlett-Packard) was used. Separation conditions were as follows: Initial column temperature 100 °C

(2 min), increased to 190 °C at 10 °C min^{-1} (hold 2 min), and finally increased to 280 °C at 20 °C/min (hold 5 min). The temperature of injector and detector were, respectively, 280 and 300 °C. Nitrogen (99.999%, purity) was used as the carrier gas and make-up gas. The GC split valve was set to open after 4 min of insertion.

In order to confirm the existence of OCPs in the sample, a GC–MS measurement was performed. A combination of an HP 6890 plus GC series and HP 5973N mass spectrometer detector was used. The capillary column was a fused-silica HP-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The carrier gas was helium. The injector was in splitless mode and the temperature program was the same as described for the GC/ECD measurements. The transfer line and mass spectrometer (MS) were, respectively, held at 280 and 230 °C. The MS worked in selected-ion-monitoring (SIM) mode. A Hitachi Model CT6D Centifuge (Hitachi, Japan) was used to separate the sol solution from the precipitate. To mix various solution ingredients thoroughly and ultrasonic extraction (USE), an ultrasonator model SY-1200 (Shengyuan, Shanghai, China) was used. Ultra pure water from a Milli-Q system (Millipore, Bedford, MA, USA) with conductivity 18 MΩ was used in all cases. The fused-silica fiber (140 μm o.d.) with protective polyimide coating was obtained from Academy of Post and Telecommunication, Wuhan, China.

Polyphenylmethyvinylsiloxane and polymethylvinylsiloxane were purchased from Brockville, Ontario. Hydroxyterminated silicone oil (OH-TSO), vinyltriethoxylsilane (VTEOS), tetraethoxysilane (TEOS), poly(methylhydrosiloxane) (PMHS) were obtained from the Chemical Plant of Wuhan University. Trifluoroacetic acid (TFA) was obtained from Aldrich (Allentown PA, USA). 2,2′-Azobis(2-methylpropionitrile) (AIBN) was obtained from Shanghai Chemical Factory, Shanghai. All solvents used were analytical or research grade. A standard mixture, containing α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlorepoxide, endosultan I, *p,p′*-DDE, dieldrin, endrin, endosulfan II, *p,p′*-DDD, endrin aldehyde, endosulfansulfate, *p,p′*-DDT chlorinated compounds (2000 μg/ml in toluene:hexane, 50:50) was provided by Institute of Hydrobiology, the Chinese Academy of Science, Wuhan.

The standard stock mixtures were then diluted to the required concentration using methanol to produce standard solutions (100 μg/l) and maintained at 4 °C in a refrigerator.

Two green teas and oo-long tea were bought in local supermarket. One green tea A was produced from Hangzhou and another B from Hubei province. Oo-long tea was originated from Fujian. The blank green tea used has been monitored for the studied pesticides and was provided by Hubei Entry-Exit Inspection and Quarantine Bureau Technique Center, China.

Glassware silanization was performed prior to use by soaking the glassware overnight in a toluene solution at a concentration of 10% dichlorodimethylsilane. The glassware was rinsed with toluene and methanol, then thoroughly dried at 150 °C for 3 h.

2.2. Fiber preparation

Prior to sol–gel coating, the protective polyimide layer was removed from the fiber by immersed it in acetone for 3 h. Then the fiber was dipping in 1 M NaOH solution for 1 h, to expose the maximum number of silanol groups on the silica surface of the fiber. After this it was placed in 0.1 mol/l HCl solution for 30 min to neutralize the excess NaOH, cleaned again and air dried at room temperature.

The sol–gel solution was prepared by mixing 40 mg PPMS, 100 μl OH-TSO, 100 μl TEOS, 50 μl VTEOS, 10 μl PMHS and 10 mg AIBN dissolved in 800 μl dichloromethane, then mixed thoroughly for 20 min with ultrasonic agitation in a plastic tube, 120 μl TFA (containing 5% ultra pure water) was sequentially added to the resulting solution with ultrasonic agitation for another 3 min. Then the mixture was centrifuged at 12,000 rpm for 5 min. There were some white precipitate at the bottom of the plastic tube. The top clear sol solution was transferred to another tube for fiber coating. After ∼20 min, the treated fiber was dipped vertically into the sol–gel solution, and a sol–gel coating was formed on the bare outer surface of the fiber end. For each fiber this coating process was repeated several times in the same sol solution until the desired thickness of the coating was obtained. After that, the fiber was illuminated through ultraviolet light (125 W, 366 nm) for 60 min. The coated fiber was placed in a desiccator at room temperature for 24 h and conditioned, respectively, at

100, 200, 300 and 350 °C for 1 h under nitrogen in the GC injector. After removed from the injector, the fiber was cooled to room temperature, and it was ready for SPME and SPME–GC experiments. The final thickness of the fiber was 70 μm. A polymethylsiloxane fiber was also coated by the sol–gel technique with similar preparation. The thickness of PMS fiber was 75 μm.

2.3. SPME procedure

Three kinds of SPME fiber were used in this work including 70 μm PPMS, 75 μm PMS and commercial 100 μm PDMS. They were all conditioned before used. PPMS and PMS fibers were, respectively, conditioned at 350 and 320 °C for 2 h. Commercial PDMS fiber was conditioned at 250 °C for 1 h.

All analyses were performed with 25 ml vials containing 15 ml solution, equipped with a stirring bar. Fifteen microliters stock standard solution was diluted with 15 ml ultra pure water to give aqueous solution of 100 ng/l in concentration. To prevent the analytes evaporation, the vial was sealed with an aluminum cap with a PTFE-faced septum.

In the HS–SPME extraction, the fiber was exposed to the headspace above the samples for 40 min at 90 °C, and 5 g NaCl was added. In the direct-immersed SPME extraction, the analytes were extracted by immersing the coated fiber to aqueous samples for 40 min at 60 °C.

The last step, the same of both processes, was the thermal desorption of the analytes in the injection port of the gas chromatograph at 280 °C for 4 min.

2.4. Microwave-assisted extraction procedure

Galanz microwave oven WP750SL23 (China) was used for all MAE experiments. A 0.5 g portion of the grounded Chinese tea was accurately weighed into the Teflon-lined extraction vessel. Then, 15 ml ultra pure water was added. After ensuring that a new rupture membrane was in place, the extraction vessel was closed. Extractions were performed for 10 min at 80% power. After extraction, the vessels were allowed to cool to room temperature before they were opened. The extract was transferred to 25 ml vial and adjusted with ultra pure water to 15 ml for SPME extraction.

2.5. Ultrasonic extraction procedure

Ultrasonic extraction using a water-bath was performed with 0.5 g grounded Chinese tea and 15 ml ultra pure water in 25 ml vial, the vial was sealed with an aluminum cap with a PTFE-faced septum. The suspensions were sonicated with continuous power for 1 h. Then it was performed for SPME extraction.

3. Results and discussion

3.1. Characteristics of the new coatings

The choice of the most suitable coating is very important for achieving good selectivity of the target analytes. The principle of “like dissolves like” can be applied to fiber selection. The organochlorines under investigation fall into a non-polar class with relatively high octanol–water coefficients (log Pow) [37], and very low solubility in water. Hence, these analytes would be expected to partition more readily into a non-polar fiber coating rather than a polar one. PPMS and PMS coatings are belonged to non-polar coatings which exhibit a high affinity for non-polar compounds (such as OCPs). Commercial PDMS fiber belongs to non-polar coating which is selected for comparing with homemade sol–gel fiber. The comparison of extraction quantities of commercial PDMS and two novel sol–gel fibers for 100 ng/l OCPs under their own optimal SPME conditions is represented in Fig. 1. The result reveals that PPMS and PMS fibers have a better efficiency for OCPs than commercial PDMS, which is because the surface area of sol–gel fibers are larger due to their porous and three-dimensional net structure. However, PPMS coating responds to the OCPs more sensitively than that of PMS coating does, due to the phenyl groups incorporated into PPMS coating, which should extract some compounds through the π–π interactions.

The thermal stability and life span are the crucial characters of coating in practical application. An important operation in SPME fiber technology is the creation of a stable stationary phase coating. Generally, for commercial PDMS fiber, the thermal stability of such coating is less than 280 °C [38] which limits the

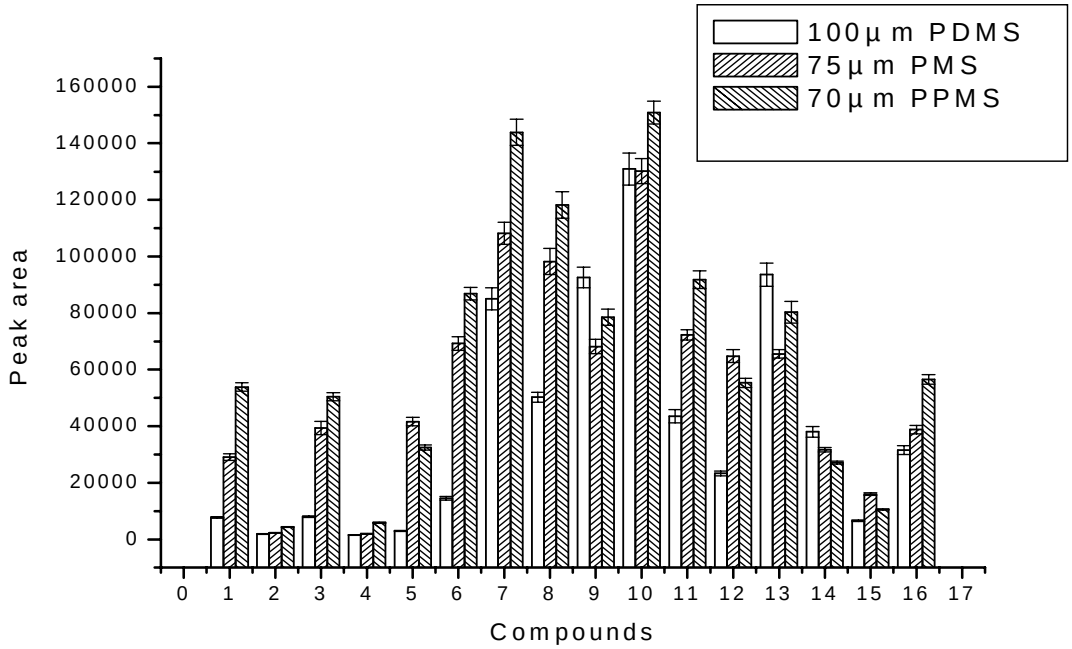

Fig. 1. The comparison of extraction quantities using three different fibers for 100 ng/l OCPs. (1) α-HCH, (2) β-HCH, (3) γ-HCH, (4) δ-HCH, (5) heptachlor, (6) aldrin, (7) heptachlor epoxide, (8) endosulfan I, (9) *p,p′*-DDE, (10) dieldrin, (11) endrin, (12), endosulfan II, (13) *p,p′*-DDD, (14) endrin aldehyde, (15) endosulfan sulfate, (16) *p,p′*-DDT. Optimal conditions: (1) Extraction time 40 min; extraction temperature: 90 °C; desorption temperature: 280 °C; desorption time: 4 min; 5 g NaCl; constant stirring; headspace (70 μm PPMS and 75 μm PMS fibers). (2) Extraction time 180 min; extraction temperature: 100 °C; desorption temperature 270 °C; desorption time: 6 min; 5 g NaCl; constant stirring; headspace (100 μm PDMS fibers).

molecular mass range of analyte that can be handled by SPME–GC and the life time of commercial fibers is shorter in the range of 50–100 times. The thermal stability of PPMS and PMS fibers were studied. The extraction quantities of PPMS fiber are not significantly affected after the fiber was conditioned for 1 h at 250, 280, 300, 310, 320, 330, 340 and 350 °C, respectively. This shows the high thermal stability of PPMS fiber, even over 350 °C. For PMS fiber, its highest operating temperature is 320 °C. PMS fiber is also conditioned for 1 h at 250, 280, 290, 300, 310 and 320 °C, respectively. It showed no sign of bleeding at 320 °C. Such a high operation temperature of the sol–gel fiber is due to strong adhesion of the coating to the substrate through chemical bonding. Compared with commercial PDMS fiber, it often start bleeding at 200 °C [24]. The operating temperature generally remain with the range of 200–270 °C [38]. On the other hand, because of phenyl group in PPMS polymer, thermal stability of it is better than that of PMS fiber. The change of extraction efficiencies of PPMS fiber in extracting some OCPs from the aqueous solution after being used for 50, 100 and 150 times is studied. The results indicate that its extraction efficiencies of OCPs have no obvious decline after used for 150 times. Based on above all facts, PPMS fiber is selected for subsequent experiments.

3.2. Optimization of SPME conditions

Except for fiber type, there are several other variables must be studied and optimized in the determination of OCPs by SPME method, including extraction mode, extraction time, extraction temperature and salt effects.

The conditions of direct immersed (DI) and headspace SPME for the determination of OCPs in samples are optimized and make a comparison

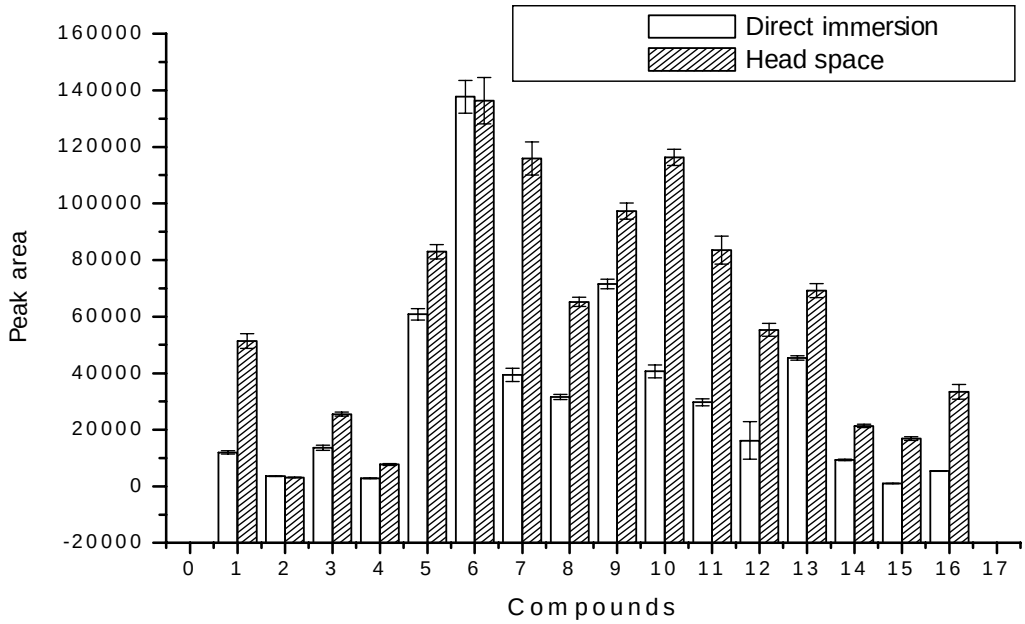

Fig. 2. Effect of the types of direct immersed and headspace extraction on extraction efficiencies (100 ng/l OCPs).Compounds notions as in Fig. 1. Direct immersed extraction: extraction time 40 min; extraction temperature 60 °C; no NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min. Headspace extraction: extraction time 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min.

Table 1
Limits of detection (LODs), linear range, correlation coefficients and precision for the analysis of OCPs in blank green tea with MAE–SPME–GC/ECD using the PPMS fiber

Compound	LOD[a] (ng/l)	Linear range (ng/l)	R.S.D. (%, $n = 6$) 100 ng/l	Correlation coefficient (R)
α-HCH	0.031	0.1–10^3	10	0.9998
β-HCH	0.072	0.1–10^3	2	0.9997
γ-HCH	0.039	1–10^3	7	0.9994
δ-HCH	0.081	1–10^3	10	0.9996
Heptachlor	0.024	0.1–10^3	3	0.9998
Aldrin	0.035	0.1–10^3	4	0.9996
Heptachlor epoxide	0.019	0.1–10^3	8	1
Endosulfan I	0.051	0.1–10^3	5	0.9997
p,p′-DDE	0.061	0.1–10^3	6	0.9996
Dieldrin	0.077	0.1–10^3	5	0.9999
Endrin	0.063	0.1–10^3	6	0.9995
Endosulfan II	0.060	1–10^3	2	0.9968
p,p′-DDD	0.017	0.1–10^3	9	0.9976
Endrin aldehyde	0.021	1–10^3	5	0.9966
Endosulfan sulfate	0.053	1–10^3	5	0.9925
p,p′-DDT	0.015	0.1–10^3	11	0.9968

[a] Signal-to-noise = 3.

between the two modes, the results obtained are summarized in Fig. 2. It shows that almost of all OCPs except β-HCH and aldrin have higher extraction efficiencies for headspace mode. Headspace extraction is selected for subsequent experiments.

The equilibration time is determined by exposed the fiber to the headspace above the samples from 20 to 100 min. It is 20 min for HCHs and 80 min for other OCPs. Under similar conditions, the commercial PDMS fiber need several hours to reach equilibration [3]. Because the porous structure of sol–gel fiber helps faster mass transfer during extraction, so the equilibration time is shorter, but it is a rather lengthy extraction time. According to the theory of non-equilibrium [39], the amount of analyte absorbed onto the fiber is proportional to the initial concentration in sample matrix under the non-equilibrium conditions, therefore the sampling time is fixed at 40 min. However, in such case, the extraction time and stirred speed must be controlled very well to ensure good reproducible data.

The extraction temperature has two opposing effects, so there is an optimal extraction temperature at which one can obtain ideal adsorbed quantities and rapid equilibrium time. The amount of absorbed OCPs reaches a maximum at 90 °C. So we choose to extract and enrich at 90 °C.

The effect of ionic strength on the extraction efficiency is determined by analyzing solutions containing different amounts of NaCl (0, 1, 3, 5 g). Generally it is observed that 1 and 3 g NaCl increase the extraction efficiencies of all OCPs extracted by the fiber, in comparison with no salt addition. It exhibits the higher amounts extraction for eleven of all OCPs when 5 g NaCl is added. Therefore, for the analysis of all OCPs, the conditions selected for the method is 5 g NaCl addition.

The OCPs are little effected by pH because they are non-ionizable compounds in aqueous solution. So extraction for OCPs with SPME is carried out using the neutral solution. The optimum desorption conditions are also studied. Based on the

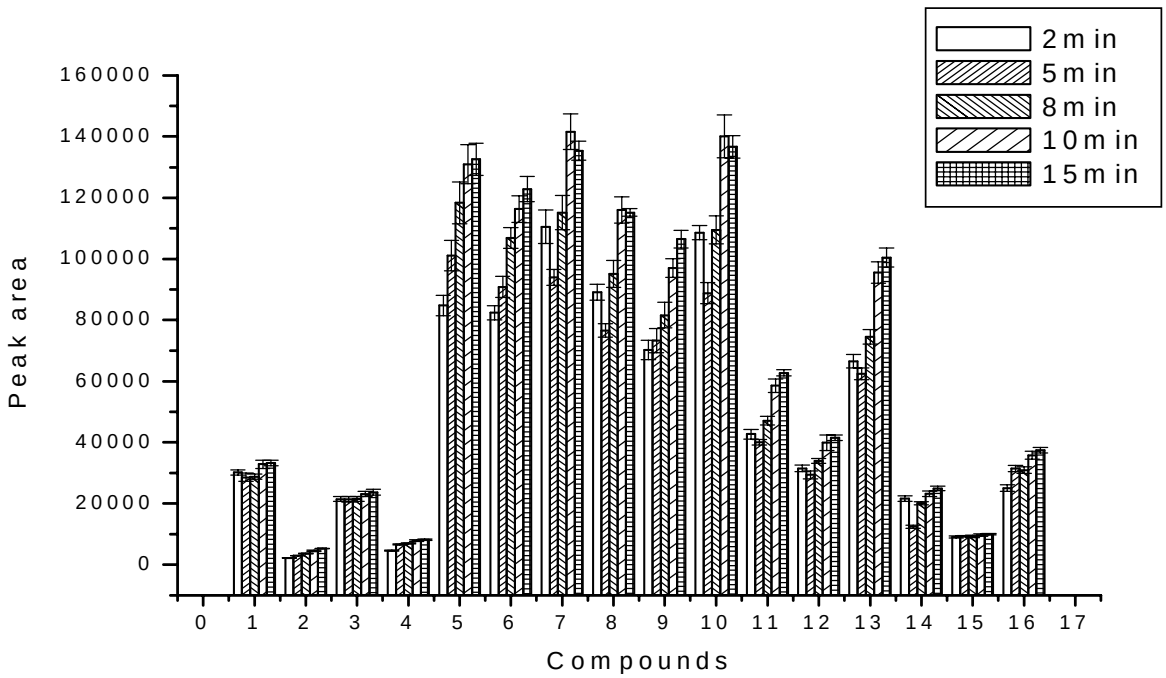

Fig. 3. Effect of microwave heating time on the extraction efficiency (100 ng/l OCPs). Compounds notions as in Fig. 1. Microwave heating power: 60%; extraction time: 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min.

results, the fiber desorbs at 280 °C for 4 min in all experiments.

3.3. Optimization of MAE conditions

MAE has a good potential to extract compounds from solid matrices. Therefore, MAE is a complimentary method to combine with HS–SPME for Chinese tea samples. Green tea was used as the representative sample to optimize the MAE extraction condition. 0.5 g ground green tea spiked 100 ng/l standard OCPs solution in 15 ml ultra pure water was extracted by MAE. Conditions affecting heating, including microwave irradiation time and irradiation power were investigated.

The purpose of microwave heating is to extract OCPs from solid tea to water. The extract is analyzed by optimized SPME–GC procedure. Fig. 3 shows that 10 min is the optimum irradiation time when irradiation power is fixed to 60%. Under the same irradiation time (10 min) and SPME–GC procedure, the extraction efficiency of OCPs in water are increased with a higher irradiation power (Fig. 4). The optimum MAE extraction condition for OCPs from tea is 80% of irradiation power and 10 min of irradiation time.

3.4. Analytical data

The blank green tea spiked standard OCPs in a convenient range (0.1, 1, 5, 10, 50, 100, 1000 ng/l) are used for calibration of the overall treatment (MAE–SPME–GC/ECD) procedures. Fig. 5 shows a typical chromatogram of OCPs standard (100 ng/l) obtained by MAE–SPME–GC/ECD. Linear calibration curves can be obtained for concentrations ranging from 0.1 to 1000 ng/l of OCPs except for γ-HCH, δ-HCH, endosulfan II, endrin aldehyde, endosulfan sulfate from 1 to 1000 ng/l and correlation coefficients are above 0.9925 (Table 1). The limits of detection (LODs) calculated via three times the background noise level are below 0.081 ng/l. The precision of the method is evaluated by six replicated determinations of spiked 100 ng/l OCPs with the blank green tea after MAE–SPME–GC/ECD, expressed as the relative standard deviation (R.S.D.), is less than 11%.

The accuracy of the determination of OCPs in Chinese tea is quantified by the apparent recovery of the spiking method (Table 2). For the two concentrations (50 and 100 ng/l) are spiked to 0.5 g grounded green tea A and 15 ml ultra pure water in vial. The apparent recovery is defined as C_{net}/C_{spike} (net concentration (C_{net}) = tested concentration (C_{test}) − native concentration (C_{native}), spiked concentration (C_{spike})).

Table 2
Comparison of the recoveries of MAE–SPME–GC/ECD and USE–SPME–GC/ECD methods of OCPs in spiked green tea A

Compounds	MAE spiked (50 ng/l) (R.S.D. %, $n = 6$)	MAE spiked (100 ng/l) (R.S.D. %, $n = 6$)	USE spiked (50 ng/l) (R.S.D. %, $n = 6$)	USE spiked (100 ng/l) (R.S.D. %, $n = 6$)
α-HCH	67.01 (9)	61.68 (8)	4.79 (11)	6.63 (10)
β-HCH	90.13 (8)	93.33 (7)	12.74 (9)	29.08 (11)
γ-HCH	57.63 (6)	66.44 (5)	12.98 (8)	11.99 (9)
δ-HCH	77.44 (5)	94.35 (5)	4.21 (6)	4.97 (6)
Heptachlor	85.76 (13)	91.39 (11)	6.25 (14)	4.61 (12)
Aldrin	87.07 (12)	101.17 (10)	5.57 (13)	7.79 (11)
Heptachlor epoxide	64.25 (11)	70.21 (10)	2.23 (12)	5.53 (11)
Endosulfan I	52.37 (12)	66.24 (13)	8.52 (12)	9.0 (12)
p,p′-DDE	65.89 (11)	79.82 (11)	4.6 (13)	5.1 (13)
Dieldrin	56.69 (10)	63.24 (9)	27.66 (12)	36.29 (11)
Endrin	45.91 (11)	54.01 (12)	1.75 (14)	2.98 (14)
Endosulfan II	47.03 (13)	50.71 (12)	2.54 (16)	6.69 (15)
p,p′-DDD	44.25 (14)	45.39 (13)	1.51 (15)	3.15 (14)
Endrin aldehyde	39.05 (11)	43.47 (9)	11.60 (13)	15.92 (12)
Endosulfan sulfate	41.33 (10)	44.26 (9)	3.1 (12)	2.5 (11)
p,p′-DDT	40.54 (16)	46.78 (15)	4.42 (19)	16.47 (17)

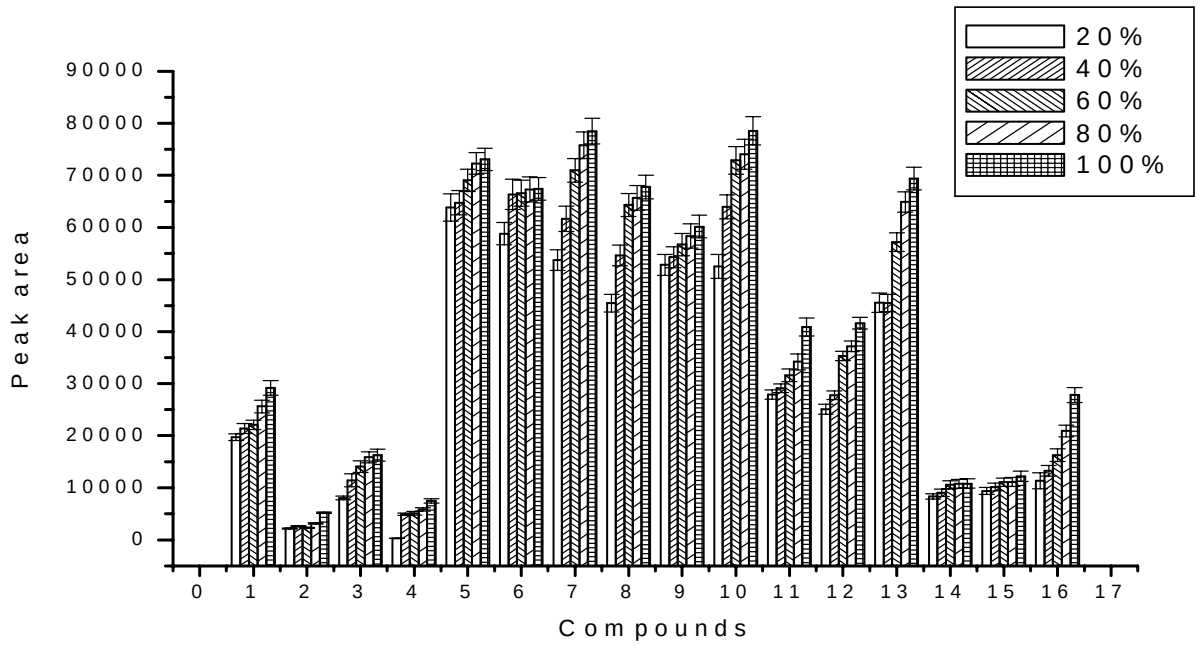

Fig. 4. Effects of microwave heating power on the extraction efficiency (100 ng/l OCPs). Compounds notions as in Fig. 1. Microwave heating time: 10 min; extraction time: 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min.

The recoveries of OCPs by MAE–SPME–GC/ECD are 39.05–90.13% for spiked 50 ng/l standard OCPs (R.S.D. $<$ 16%, $n = 6$) and 43.47–101.17% for spiked 100 ng/l standard OCPs (R.S.D. $<$ 15%, $n = 6$). MAE efficiency was also compared with that of ultrasonic extraction technique. The recoveries of OCPs by USE–SPME–GC/ECD method are from 1.51 to 27.66% (R.S.D. $<$ 19%, $n = 6$) for spiked 50 ng/l

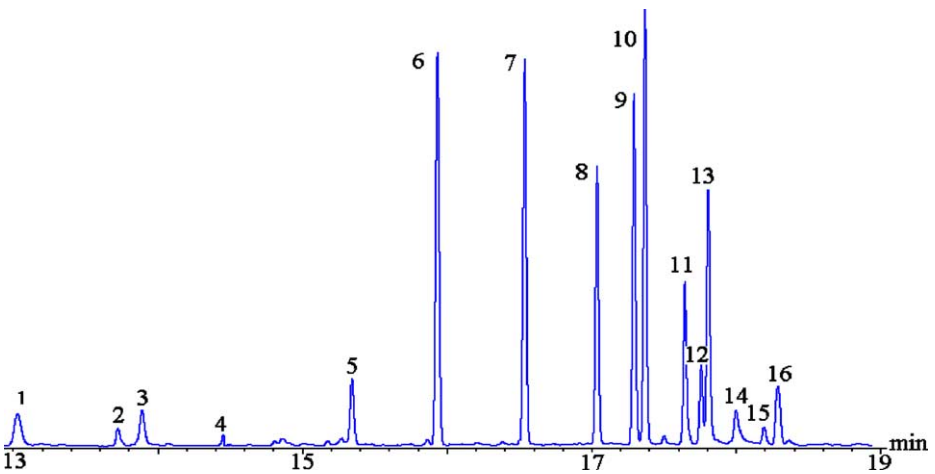

Fig. 5. The chromatogram of MAE–SPME–GC/ECD analysis of OCPs (100 ng/l) using PPMS fiber. Compounds notions as in Fig. 1. Microwave heating power: 80%; microwave time: 10 min; extraction time: 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min.

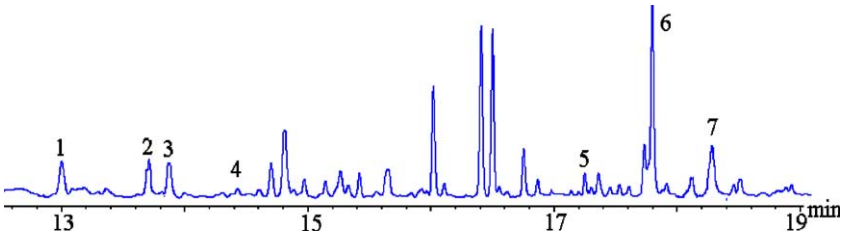

Fig. 6. Chromatogram of MAE–SPME–GC/ECD analysis of green tea B using PPMS fiber. (1) α-HCH, (2) β-HCH, (3) γ-HCH, (4) δ-HCH, (5) *p,p′*-DDE, (6) *p,p′*-DDD, (7) *p,p′*-DDT. Microwave heating power: 80%; microwave time: 10 min; extraction time: 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature: 280 °C; desorption time: 4 min.

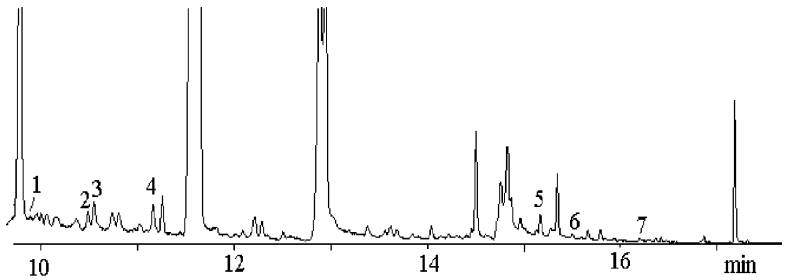

Fig. 7. Chromatogram of MAE–SPME–GC/MS analysis of green tea B using PPMS fiber. (1) α-HCH, (2) β-HCH, (3) γ-HCH, (4) δ-HCH, (5) *p,p′*-DDE, (6) *p,p′*-DDD, (7) *p,p′*-DDT. Microwave heating power: 80%; microwave time: 10 min; extraction time: 40 min; extraction temperature 90 °C; 5 g NaCl; constant stirring; desorption temperature 280 °C; desorption time: 4 min.

standard OCPs and from 2.5 to 36.29% (R.S.D. < 17%, $n = 6$) for spiked 100 ng/l standard OCPs. The results show that MAE provides more efficient analyte recoveries along with small extraction time than USE does.

Figs. 6 and 7, respectively, show the chromatogram of extraction of green tea B using PPMS fiber by MAE–SPME–GC/ECD and MAE–SPME–GC/MS. Since there are many volatile/semi-volatile components existing in tea infusions, the high selectivity characteristic of mass spectrometer is used as the detector of GC for affirming the existence of OCPs in Chinese teas. The MAE–SPME–GC/MS with selected-ion-monitoring process is treated of three Chinese teas separately. From their *m/z* value and retention time, the existence of α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT in green tea B are identified. However, there is no δ-HCH in green tea A and in oo-long tea. The concentrations of OCPs determined in samples are summarized in Table 3. The results show that there are mainly HCHs and DDT of OCPs residues in three

Table 3
The concentration of OCPs determined in three Chinese teas

Compounds	*m/z*	Green tea A (ng/g) (R.S.D. %, $n = 6$)	Green tea B (ng/g) (R.S.D. %, $n = 6$)	Oo-long tea (ng/g) (R.S.D. %, $n = 6$)
α-HCH	181, 183	1.07 (5)	1.81 (6)	1.96 (5)
β-HCH	183, 109	4.46 (7)	11.2 (5)	5.88 (4)
γ-HCH	181, 183	1.56 (7)	2.26 (5)	3.09 (7)
δ-HCH	183, 109	ND	1.88 (6)	ND
p,p′-DDE	246, 318	2.40 (5)	2.74 (8)	1.60 (7)
p,p′-DDD	235, 237	1.82 (8)	4.09 (8)	0.11 (8)
p,p′-DDT	235, 237	3.92 (6)	5.25 (8)	4.69 (5)

ND: not detected.

Chinese teas. The levels of HCHs and DDT in three Chinese teas are within the safety limit of 0.2 mg/kg.

4. Conclusion

Comparison with commercial 100 μm PDMS fiber, the novel porous sol–gel PPMS fiber exhibits higher sensitivity and selectivity for OCPs compounds, higher thermal stability (to 350 °C) and longer service life (more than 150 times).

This study demonstrated that MAE–SPME–GC/ECD is a simple, rapid and precise, reproducible method for analyzing multi-residue OCPs in Chinese teas. This method verifies over a wide range of linearity ($0.1–10^3$ ng/l) in the blank green tea samples for all OCPs except for γ-HCH, δ-HCH, endosulfan II, endrin aldehyde, endosulfan sulfate ($1–10^3$ ng/l). Furthermore, the detection limits below 0.081 ng/l for all OCPs studied. The repeatability (R.S.D. $< 16\%$, $n = 6$) is sufficient for precise determination at the trace level. This method is also applied to determine OCPs in actual Chinese teas from a local market. Since there are many volatile/semi-volatile components existing in tea infusions, MS detector is used for affirming the existence of OCPs in Chinese teas. The tested pesticides in the samples are at the ng/g level.

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