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Single-walled carbon nanotubes coated fibers for solid-phase microextraction and gas chromatography–mass spectrometric determination of pesticides in Tea samples

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ABSTRACT

Using a single-walled carbon nanotubes (SWCNTs) as stationary phase of solid-phase microextraction (SPME) fibers, a simple, low cost and environmentally friendly method for extraction of 13 pesticides in Tea samples has been developed following gas chromatography–mass spectrometric determination. Potential factors affecting the extraction efficiency were investigated and optimized, including extraction and desorption time, extraction temperature, stirring rate, solution pH and ionic strength. Under optimized conditions, the linearity of the developed method was in the range of 0.125–25 ng/mL with correlation coefficients greater than 0.9928 and the limits of detections (LODs) were 0.027–0.23 ng/mL ($S/N = 3$). Meanwhile, the relative standard deviations (RSDs) for five successive measurements with single fiber, fiber-to-fiber, day-to-day were 2.3–13.0, 8.2–14.6 and 4.1–12.5%, respectively, indicating good reproducibility of the proposed method. The fiber had high extraction efficiency for studied pesticides in comparison with commercial poly(dimethylsiloxane) (PDMS) and polyacrylate (PA) fibers and could be used for more than 70 times without decrease of efficiency. The developed method was successfully applied for the analysis of real samples including green Tea, oolong Tea, white Tea, and flower Tea, and the recoveries of the pesticides spiked in these samples ranged from 75.1 to 118.4%. Chlorfenapyr and λ-cyhalothrin were found in the Tea samples bought randomly from local market. The results demonstrated that the developed SWCNTs-SPME method was a simple, efficient pretreatment and enrichment procedure for pesticides in complex matrices.

1. Introduction

Since solid-phase microextraction (SPME) was introduced by Arthur and Pawliszyn [1], this technique has attracted increasing attention due to its advantages of simplicity of operation, solventless nature, high extraction efficiency and feature of preconcentration. This technique is based on the distribution of the analytes to a fused-silica fiber coated with a stationary phase, and the analytes can be desorbed from the fiber to a suitable separation and detection system such as gas chromatography (GC) and high-performance liquid chromatography (HPLC). The sorbent coated on the fiber, used to adsorb the analytes from samples, is a key part for the extraction ability of SPME. Up until now, the number of widely used commercial SPME fiber is limited and the extracting phases used are mainly focused on polymers. Non-polar phase poly(dimethylsiloxane) (PDMS) is good at extracting non-polar analytes, such as BTEX (benzene, toluene, ethylbenzene and *o*-xylene) and polycyclic aromatic hydrocarbons (PAHs) [2–5]. While polyacrylate (PA) fiber is a polar phase and it has great affinity for polar compounds [6–8]. And mixed-phase coating such as poly(dimethylsiloane)–divinylbenzene (PDMS–DVB) [8,9], poly(ethylene glycol)–divinylbenzene (PEG–DVB) [10], carboxen–poly(dimethylsiloxne) (CAR–PDMS) [11], carbows–divinylbenzene (CW–DVB) [12,13], polyacrylonitrile (PAN) [13], and divinylbenzene–carboxen–polydimethylsiloxane (PDMS–CAR–PDMS) [14] have been successfully applied for many organic compounds in biological samples. However, these commercial fibers are relatively expensive and still show some drawbacks such as lower thermal and chemical stability, short lifetime and poor reproducibility.

To overcome this problem, some home-made SPME fibers have been explored to replenish with commercial SPME fiber such as polymer materials [12], calix open-chain crown ether [15], HPLC chemically bonded silica stationary phase [16], solid sorbents [17]. Also various approaches including vapor deposition [18], sol–gel technology [19,20], electrochemical procedures [17,21], physi-

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cal deposition [22] and direct use of uncoated fiber [23] have been proposed for the production of SPME fibers. However, these laboratory-made SPME fibers reported in literatures could only partially overcome the limitations of commercial SPME fibers. Therefore, it is interesting to develop a low cost and novel SPME coating which can be also easily prepared.

As new carbon-based nano-materials, the potential of carbon nanotubes (CNTs) as sorbents of solid-phase extraction (SPE) to remove many kinds of pollutants from air [24] and water [25–27] have been investigated in recent years. CNTs have high surface area, mechanical strength and chemical stability. According to the carbon atom layers in the wall of the nanotubes, CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). In recent years, MWCNTs have been proven to possess great potential to be used as SPE sorbent [28–30] and SPME fiber coating [22] for analysis of pesticides and organic pollutants in water. As far as we know, only few studies have been carried out to use SPME for Tea sample since the complex matrices may cause interference in the extraction procedure. Even so, there are still no previous references to the use of SWCNTs-SPME coating for the determination of pesticides in this type of sample.

In this work, we report a novel, simple and rapid method to prepare a SWCNTs SPME fiber for Tea samples. The performance of the prepared fiber was studied by extracting 13 pesticides (ethoprophos, thiometon, terbufos, tefluthrin, iprobenfos, vinclozolin, octachlorodipropyl ether, isofenphos, phenthoate, chlorfenapyr, propiconazol, EPN, and λ-cyhalothrin) in Tea samples using gas chromatography–mass spectrometry (GC–MS). The SWCNTs coated fiber was characterized by scanning electron microscopy (SEM), and analytical merits were evaluated. The SWCNTs coated fiber offered good extraction efficiency for SPME of pesticides. To explore the potential of the SWCNTs coated fiber in agricultural commodities, this developed method was applied to the analysis of Tea samples in local market.

2. Experimental

2.1. Chemicals and materials

Pesticide standards octachlorodipropyl ether and λ-cyhalothrin were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Ethoprophos, thiometon, terbufos, tefluthrin, iprobenfos, vinclozolin, isofenphos, phenthoate, chlorfenapyr, propiconazol, EPN were purchased from Sigma (St. Louis, MO, USA). HCl (36.5%), NaOH, NaCl, acetone were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals used were of analytical grade and purified water by Milli-Q system was used throughout the experiments. The stock solutions of each pesticide of 1000 mg/L were prepared with acetone. All the stock solutions were stored at −20 °C in darkness until used. A mixture of these pesticides was prepared by diluting the stock solutions with acetone, and working standard solutions were prepared by diluting the standard solutions with purified water daily.

SWCNTs (main range of diameter <2 μm, 5–15 μm length, >90% purity) was purchased from Shenzhen Nanotech Port Co. (Shenzhen, China) and dried for 3 h at 130 °C to remove the absorbed water and then kept in desiccator for storage. The specific surface area of the SWCNTs is more than 300 m^2/g.

The commercial SPME fiber used in this experiment included 100 μm PDMS and 85 μm PA from Supelco (Bellefonte, CA, USA).

2.2. Instrumentation

An Agilent Technology (AT, Palo Alto, CA) 6890 gas chromatograph equipped with an HP5973 mass selective detector was employed. The analysis was carried out on a HP-5MS fused-silica capillary column (30 m × 0.25 mm × 0.25 μm film thickness) with the following oven temperature programme: the initial oven temperature was 50 °C (held for 1 min), and then increased to 240 °C at a rate of 15 °C/min, finally increased to 300 °C at a rate of 5 °C/min and held for 10 min. Helium (purity ≥ 99.999%) was used as a carrier gas at a flow rate of 1.2 mL/min. The injection temperature was set at 180 °C for sample injection.

The mass spectrometer was operated with an EI source in the scan mode. The electron energy was 70 eV, and the interface temperature was maintained at 300 °C with ion source at 230 °C. The selective scan range was from *m*/*z* 50–550 and solvent delay was set to 7 min. Mass spectrometric confirmation was carried out in the SIM mode using the characteristic fragment ions for each pesticide. Three fragment ions were monitored for each compound, in order to maximize the detector signal, the most abundant and characteristic ion in the spectrum was selected for quantification, and the other for confirmation purpose (Table 1).

2.3. Procedures

2.3.1. Preparation of SWCNTs coated fiber for SPME

The end of the fused-silica fiber (2 cm) was dipped into acetone for 5 min to remove the protective polyimide layer, then cleaned with water and dried in the air at room temperature. The bare fiber was painted with a layer of silicone rubber glue firstly. Then the fiber with a layer of glue should move through a hole with diameter about 150 μm, to control the thickness of the glue. After this, the fiber was inserted into the SWCNTs powder immediately for one minute. Finally, the fiber was pulled out and shaken to remove the excessive SWCNTs powder, then dried overnight at room tem-

Table 1
Monitoring ions and quantitative ion of 13 pesticides.

Peak no.	Retention time (min)	Pesticides selected	Monitoring ions	Quantitative ion
1	10.70	Ethoprophos	158, 97, 126	158
2	11.33	Thiometon	88, 125, 60	88
3	11.78	Terbufos	231, 57, 153	231
4	12.07	Tefluthrin	177, 197, 141	177
5	12.24	Iprobenfos	91, 204, 123	91
6	12.59	Vinclozolin	212, 79, 91	212
7	12.82	Octachlorodipropyl ether	132, 79, 130	132
8	13.78	Isofenphos	213, 58, 121	213
9	13.84	Phenthoate	274, 125, 93	274
10	14.91	Chlorfenapyr	59, 137, 308	59
11	15.73/15.85	Propiconazol	259, 173, 261	259
12	16.79	EPN	157, 169, 141	157
13	17.96	λ-Cyhalothrin[a]	181, 197, 208	181

[a] λ-Cyhalothrin showed an addition very small peak at 17.71 min related to isomerization event but the peak was not used for the quantification of λ-Cyhalothrin in our experiment.

perature. The fiber coated with SWCNTs was aged at 210 °C under nitrogen for 30 min in GC inlet before SPME experiments.

A modified micro-syringe assembly was used as a SPME device [1]. The fiber coated with SWCNTs was inserted into the needle of a 5-μL syringe to replace the plunger for SPME experiments.

2.3.2. Sample preparation

Tea sample was grinded and sieved through prescription sieve (0.425 mm aperture size). Then, 1.0 g of homogenized sample powder was added to a 20-mL centrifugal tube and extracted with 10 mL acetone by ultrasonic for 30 min. The mixture solution was then centrifuged at 4000 rpm for 10 min, and the supernatant was collected in a precleaned test tube. A volume of 1.00 mL of supernatant was pipetted and diluted to 20 mL with sodium chloride solution (15% NaCl, w/v, pH 5.5), waiting for the following SPME procedure.

2.3.3. Solid-phase microextraction procedure

A 25-mL glass vial with a magnetic stir bar in was used as sample container. 20 mL of sample solution or aqueous standard solution was placed in the vial. The vial was immediately closed airtight with a Teflon-lined cap and immersed in a thermostatic water bath at 50 °C with a constant magnetic stirring rate of 600 rpm. The needle of syringe penetrated the septum of the vial and the coated fiber was pushed to immerse it into the standard or sample solution for 40 min at 50 °C. After extraction, the fiber was withdrawn, removed from the sample vial and immediately inserted into the GC injection port for thermal desorption at 180 °C for 3 min. Between two extractions, the fiber was conditioned at 230 °C for 30 min under nitrogen flow.

3. Results and discussion

3.1. Surface structure of the fiber

The surface characteristic of the SWCNT-coated fiber was investigated by SEM and Fig. 1 shows the image of the coated fiber. It can be seen from Fig. 1a, the SWCNTs coating possessed a rough and porous surface, which should significantly increase the surface areas of the coating and lead to higher extraction capacity in comparison with conventional polymeric phases. The thickness of the coating was about 50 μm (Fig. 1b). The present MWCNTs coating was a little thinner in comparison with commercial SPME fibers used.

3.2. Optimization of SPME process

Prior to the application of SPME for the determination of pesticides in Tea samples, several experimental parameters, including extraction temperature, extraction time, stirring rate, sample pH, ionic strength, desorption temperature and time were systematically studied before validating the SWCNT-coated fiber and analytical method. All experiments were performed in triplicate and the means of the results were used for optimization.

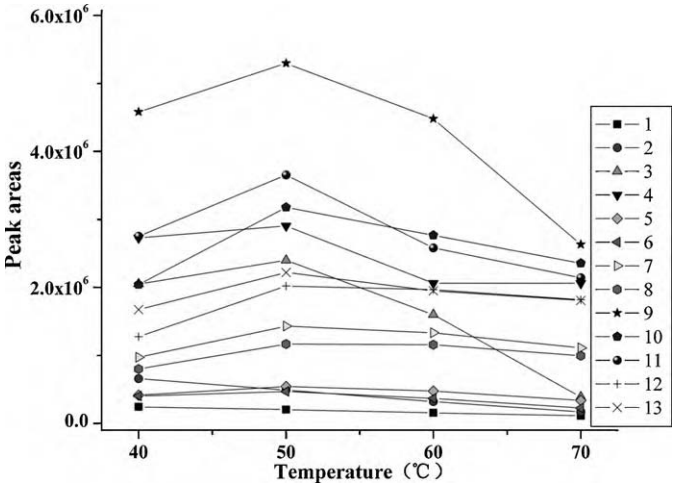

Fig. 2. Effect of extraction temperature on extraction efficiency. Extraction time: 30 min; stirring speed: 500 rpm; desorption time: 5 min; desorption temperature: 200 °C. Compounds – 1: ethoprophos, 2: thiometon, 3: terbufos, 4: tefluthrin, 5: iprobenfos, 6: vinclozolin, 7: octachlorodipropyl ether, 8: isofenphos, 9: phenthoate, 10: chlorfenapyr, 11: propiconazol, 12: EPN, 13: λ-cyhalothrin. The concentration of analytes: 5.0 ng/mL.

The extraction temperature had two opposite effects on the extraction efficiency. High extraction temperature normally improves extracting rate, but simultaneously reduces the distribution coefficient and extraction sensitivity. The influence of temperature in the extraction was studied in the range of 40–70 °C. As shown in Fig. 2, the extraction efficiency reached maximum at 50 °C. Thus, 50 °C was used for subsequent experiments.

Extraction time is another important parameter for the extraction performance of analytes because SPME is an equilibrium-based technique. Generally, extraction efficiency improves with the increase of extraction time before equilibrium. In our experiment, the extraction time was changed from 10 to 50 min to test its influence. It can be seen from Fig. 3 that extraction efficiency enhanced with the time up to 40 min. However, as the extraction time ranging from 40 to 50 min, the extraction performance of thiometon, propiconazol and λ-cyhalothrin decreased slowly, while, the extraction efficiency of other analytes kept almost unchanged. Therefore, 40 min was selected in consideration of sensitivity and time efficiency.

Magnetic stirring can accelerate mass transfer of the analytes between the aqueous sample and the SPME fiber. But at the

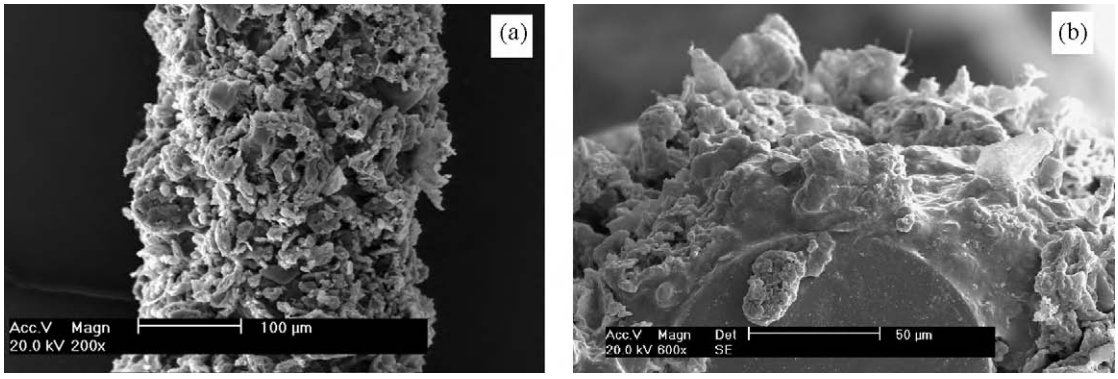

Fig. 1. SEM images of the SWCNTs coated fiber: (a) the image of the fiber's surface and (b) the image of the fiber's cross-sectional.

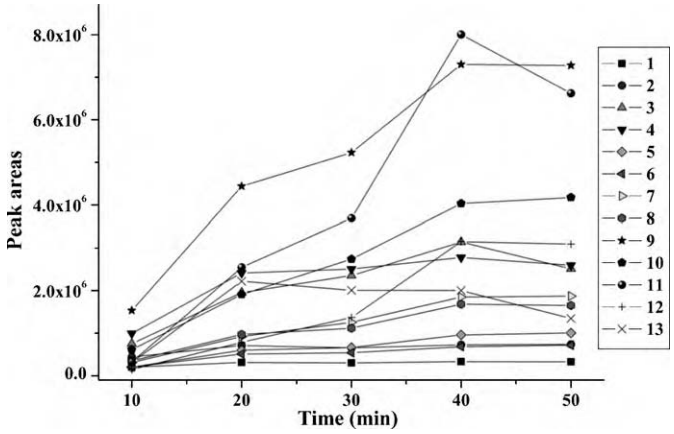

Fig. 3. Effect of extraction time on extraction efficiency of SWCNTs-SPME. Extraction temperature: 50 °C; other conditions as in Fig. 2. See Fig. 2 for compounds identification.

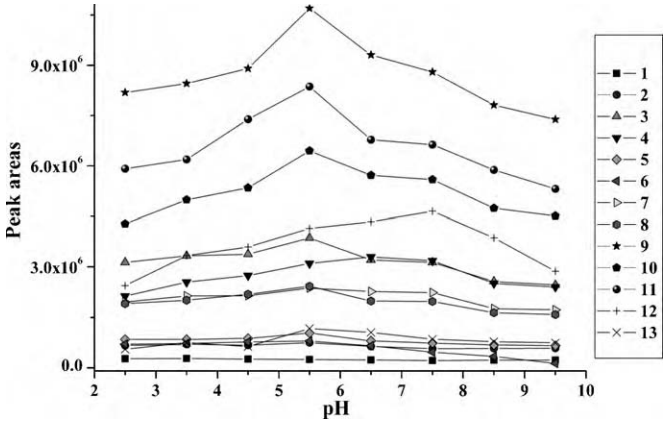

Fig. 4. Effect of solution pH. Extraction time: 40 min; extraction temperature: 50 °C; stirring speed: 600 rpm; other conditions as in Fig. 2. See Fig. 2 for compounds identification.

same time, it would speed up the volatile substances into the headspace which is unfavorable to the direct SPME mode used in this experiment. The effect of stirring rate was investigated in the 300–700 rpm range. The results showed a positive effect on the peak area of chlorfenapyr, propiconazol and EPN but no significant differences on that of other analytes when stirring rate was less than 600 rpm. Further increase of stirring rate led to a slight increase in that of chlorfenapyr, propiconazol and EPN but with less repeatability. For further experiments, a stirring rate of 600 rpm was selected.

In general, the efficiency of analytes adsorption onto fiber can be affected by sample composition. For absorptive-type of fiber coating, analytes in neutral form are much easier to be extracted than those in ion form. For this reason, pH between 2.5 and 9.5 were optimized. Maximum sensitivity was attained at pH 5.5 (Fig. 4) for most analytes, and this value was selected. Furthermore, effect of ionic strength on extraction efficiency by adding NaCl was investigated with various concentrations of NaCl (0, 5, 10, 15, and 25%, w/v). Salting-out effect was not obvious for most analytes except for phenthoate and propiconazol. The highest efficiency was observed for phenthoate and propiconazol at 15% concentration, and the value was chosen for subsequent investigation.

Complete desorption of the absorbed analytes would allow for re-use of the fiber and probably improve the sensitivity. Both desorption temperature and desorption time were optimized in this work. Five temperatures, i.e. 160, 180, 200, 220, and 240 °C, were examined to evaluate the effect of desorption temperature. The results showed that a temperature of 180 °C was sufficient for complete desorption of all 13 pesticides in 3 min.

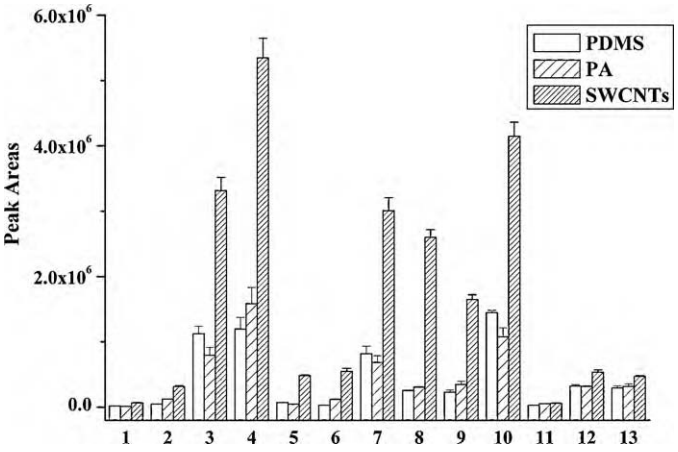

Fig. 5. Comparison of extraction efficiency for the pesticides obtained by the laboratory-made SPME fiber to commercial PDMS (100 μm) and PA (85 μm) SPME fibers. Extraction time: 20 min; stirring speed: 1400 rpm; desorption time: 7 min; desorption temperature: 230 °C. See Fig. 2 for compounds identification. Error bars show the standard deviation of the mean ($n = 3$).

3.3. Comparison of the SWCNTs coated fiber with commercial fibers

The SWCNTs coated fiber was compared with two commercial SPME fibers (100 μm PDMS and 85 μm PA) which are the most commonly used commercial SPME fiber for the extraction of pesticides. The results (shown in Fig. 5) indicated that the extraction efficiency

Table 2
Analytical performance of the established SPME method for 13 pesticides.

Analyte	Linear range (ng/mL)	Correlation coefficient (R^2)	LODs (ng/mL)	RSD (%) ($n = 5$)		
				One fiber	Fiber-to-fiber	Day-to-day
Ethoprophos	0.125–25	0.9959	0.097	5.0	9.1	11.0
Thiometon	0.5–25	0.9974	0.20	8.2	12.1	8.4
Terbufos	0.25–10	0.9985	0.091	9.2	8.2	4.1
Tefluthrin	0.5–25	0.9948	0.027	9.8	14.6	10.4
Iprobenfos	0.25–25	0.9955	0.20	3.8	10.4	12.5
Vinclozolin	0.25–25	0.9928	0.091	2.3	9.8	7.5
Octachlorodipropyl ether	0.5–25	0.9933	0.10	11.1	12.5	12.5
Isofenphos	0.25–10	0.9947	0.23	6.1	9.4	11.4
Phenthoate	0.125–7.5	0.9967	0.043	4.6	10.4	7.4
Chlorfenapyr	0.125–10	0.9966	0.085	8.0	9.8	11.6
Propiconazol	0.125–25	0.9978	0.029	8.4	10.6	12.1
EPN	0.125–10	0.9962	0.071	9.1	13.6	11.7
λ-Cyhalothrin	0.125–10	0.9952	0.029	13.0	10.8	9.6

Table 3
Average recoveries of spiked pesticides at three level concentrations from four different Tea samples.

Compounds	Green Tea recoveries (%)			Oolong Tea recoveries (%)			White Tea recoveries (%)			Flower Tea recoveries (%)		
	Spiked level (mg/kg)			Spiked level (mg/kg)			Spiked level (mg/kg)			Spiked level (mg/kg)		
	0.15	0.50	2.0	0.15	0.50	2.0	0.15	0.50	2.0	0.15	0.50	2.0
Ethoprophos	112.2	96.9	97.5	111.2	114.8	92.5	107.0	96.1	105.3	112.2	81.7	97.1
Thiometon	75.1	100.3	90.5	117.6	95.7	82.7	97.2	89.9	114.2	103.3	86.1	87.6
Terbufos	88.5	95.7	98.6	81.3	81.4	92.2	108.6	110.1	104.5	97.0	113.7	95.0
Tefluthrin	95.8	92.1	92.8	80.2	86.3	102.3	108.2	102.5	85.2	117.4	106.0	110.8
Iprobenfos	113.2	95.7	97.0	91.7	85.0	80.0	97.1	102.3	109.2	79.4	82.9	93.0
Vinclozolin	91.4	112.0	92.6	82.1	92.1	83.3	101.7	85.4	111.2	88.2	108.4	91.2
Octachlorodipropyl ether	94.3	111.4	101.3	118.3	99.9	102.6	81.0	80.9	93.3	79.1	79.2	97.6
Isofenphos	90.3	101.0	81.5	85.2	90.6	110.3	106.0	109.5	101.5	96.8	108.0	81.5
Phenthoate	94.7	104.4	96.1	81.0	80.2	99.5	112.9	98.7	100.8	91.9	78.5	82.8
Chlorfenapyr	82.4	98.5	80.1	80.5	112.5	93.7	104.0	102.3	89.5	93.2	96.6	98.4
Propiconazol	106.4	106.2	97.4	89.4	116.7	113.2	86.5	89.9	101.6	99.6	103.4	94.2
EPN	102.8	108.1	90.5	108.1	75.2	113.7	87.0	89.9	102.2	116.5	88.8	95.7
λ-Cyhalothrin	111.1	118.4	95.2	105.8	91.2	84.9	85.4	116.8	90.1	79.6	107.4	97.4

of pesticides by the SWCNTs fiber with less cost was superior to those of the commercial ones.

3.4. Method validation and application to real samples

To evaluate potential of analytical applicability of the developed SPME method for GC–MS determination of pesticides in Tea samples, the analytical figures of merit following the analytical procedures described in Section 2 are summarized in Table 2. Under the optimal conditions, the calibration plots were linear over the range of 0.125–25 ng/mL with correlation coefficients (R^2) between 0.9928 and 0.9985. The limits of detections (LODs) of 13 pesticides were in the range of 0.027–0.23 ng/mL. The relative standard deviations (RSDs) for five replicate extractions of the pesticides at 2.5 ng/mL using one SPME fiber were 2.3–13.0%. The fiber-to-fiber reproducibility for five parallel prepared fibers for SPME of the pesticides at 2.5 ng/mL was 8.2–14.6% (RSDs). The day-to-day reproducibility for five days analysis of pesticides using one SPME fiber was 4.1–12.5% (RSDs). The durability experiment for one fiber showed no apparent loss in performance of SWCNTs coating over 70 times of extraction due to the high chemical stability of SWCNTs. These results showed that the developed SWCNTs fiber was stable and reproducible for SPME.

In addition, accuracy of the method was checked by recovery studies for four different Tea samples spiked at three concentration levels. That was, 0.015–0.2 mL working solution containing pesticides at 10 mg/L was added into 1.0 g of homogenized sample powder and mixed. After being kept at room temperature for 1 h, the spiked samples were then extracted with acetone. Three replicates were analyzed in each case and the analytical results are shown in Table 3. Recoveries for 13 analytes were 75.1–118.4% in green Tea, 75.2–118.3% in oolong Tea, 80.9–116.8% in white Tea and 78.5–117.4% in flower Tea, respectively. Therefore, the proposed method could be used for trace level analysis of pesticide

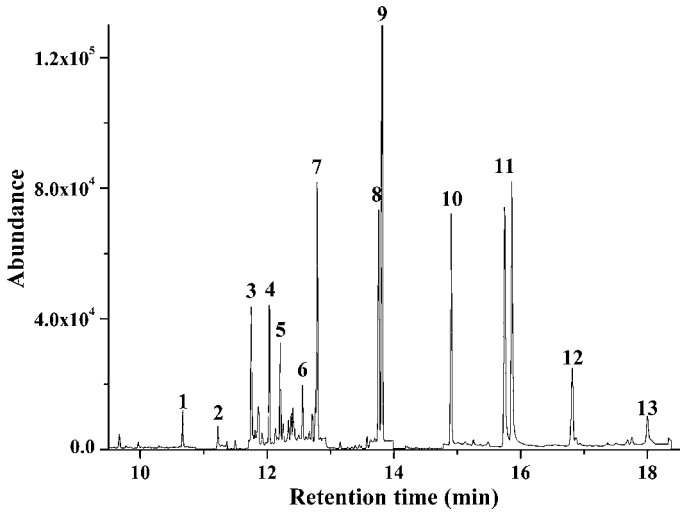

Fig. 6. SPME–GC–MS chromatogram obtained from a blank Tea spiked with 13 pesticides at 0.5 mg/kg under optimum conditions. See Fig. 2 for compounds identification.

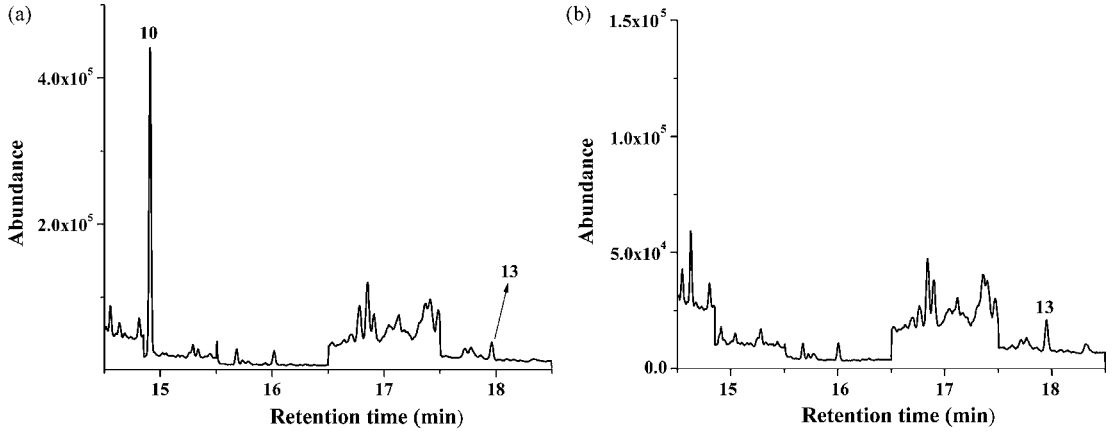

Fig. 7. Chromatograms of the developed method for analyzing real samples under optimum conditions. (a) Green Tea sample and (b) jasmine Tea sample. See Fig. 2 for compounds identification.

multi-residues in Tea. Fig. 6 showed a typical SPME–GC–MS chromatogram obtained from a spiked Tea sample under the optimized experimental conditions.

The developed method was further applied to determine the content of the pesticides in jasmine Tea and green Tea randomly bought from local market. The chromatograms of both obtained by the developed SPME–GC–MS technique are shown in Fig. 7. No more pesticides were found in Tea samples, except for chlorfenapyr (with the content of 1.59 mg/kg in green Tea) and λ-cyhalothrin (with the content of 0.054 mg/kg in green Tea, and 0.017 mg/kg in jasmine Tea, respectively). The residues in Tea were lower than the MRLs of Japan (50 mg/kg for chlorfenapyr, and 15 mg/kg for λ-cyhalothrin), and those of EU (0.1 mg/kg for chlorfenapyr, and 1 mg/kg for λ-cyhalothrin). Therefore, the residues in Tea were acceptable.

4. Conclusions

In this study, a novel SWCNTs coated SPME fiber with excellent performance was developed. The performance of the SWCNTs fiber for SPME was evaluated through determination of the pesticides in Tea samples and the results showed that the SWCNTs fiber exhibited higher extraction efficiency and equivalent service life (more than 70 times) in comparison with commercial SPME fibers, e.g., PDMS and PA, as well as good linearity range, LODs, precision and accuracy. In addition, there were other advantages including low cost, easy of preparation, low solvent-consumption, and less time in sample preparation. Based on these features, this work provided a rapid and facile method for routine trace analysis of pesticides in Tea samples, and moreover, was expected to have a potential use in other complex matrix samples.

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