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Determination of organophosphorus pesticides in peanut oil by dispersive solid phase extraction gas chromatography–mass spectrometry

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ABSTRACT

The organophosphorus pesticides including phorate, diazinon, tolclofos-methyl, fenitrothin, malathion, fenthion, isocarbophos, quinalphos and phenamiphos, in peanut oils were determined by liquid–liquid extraction coupled with dispersive solid phase extraction and gas chromatography–mass spectrometry (GC–MS). The mixture of multi-walled carbon nanotubes and alumina was used as adsorbent in dispersive solid phase extraction. The effects of some experimental conditions, such as types of multi-walled carbon nanotubes, amount of adsorbents and extraction time were examined. The limits of detection for the analytes were between 0.7 and 1.6 μg kg^{-1}. The obtained recoveries of the analytes in the samples were between 85.9 and 114.3% and relative standard deviations were lower than 8.48%.

1. Introduction

The increasing application of pesticides for agricultural purposes has caused a noticeable pollution of the environment, and is a threat to health. Some regulations are worked out for pesticide usage, especially as regards residual levels in commercial foods–peanut oils. Some organization, such as the Codex Alimentarius Commission of the Food and Agriculture Organization (FAO), the World Health Organization (WHO) [1] and the European Union [2], have established maximum residue limits (MRLs) in food for a number of pesticides.

Peanut oil is an organic material oil derived from peanuts, and is considered as an essential foodstuff in oriental countries, especially in China. The production of peanut oil in China was about 2×10^{11} kg per year. In order to prevent and control the plant diseases and eliminate pests (grub, cotton bollworm, and leaf spot) in the growth stage of peanut, organophosphorus pesticides (OPPs) are widely used. Most of the pesticides are lipophilic and can be accumulated in vegetable fats.

The common determination method for OPPs in edible oils is gas chromatography (GC) [3–23] due to its high separation efficiency and variety of selective detection methods. Other methods, such as high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) [16,24], liquid chromatography–time-of-flight mass spectrometry (LC/TOF–MS) [25] and reversed phase liquid chromatography–gas chromatography [26] were also applied. Up to now, OPP residues in edible oils were determined by several methods based on GC separation coupled with either nitrogen–phosphorus [4–9], electron capture [4,5,8,11], flame photometric [6,13,14], and flame ionization detection [14] or mass spectrometric (MS) detection [7,16–18]. GC coupled with nitrogen–phosphorus detection has high selectivity for determination of OPPs in edible oils. GC coupled with mass spectrometry (MS/MS) is particularly useful for qualitative and quantitative purposes, being mandatory to obtain unambiguous identification [19–22]. Because the edible oils contain some non-volatile compounds, such as triglycerides, the previous extraction and purification step are generally required.

In the food control analysis, isolation of pesticides from matrices containing relatively high content fat, such as peanut oil, requires complicated sample treatment procedures. The preparation of these samples for determination of pesticides by chromatographic methods requires the complete removal of the high molecular weight fat before sample introduction into chromatographic column. The widely used methods involve one or combination of some for the following methods: liquid–liquid extraction (LLE) [4,5,9,14,16,25], low-temperature precipitation [11,13], gel-permeation chromatography (GPC) [20–23], solid-phase extraction (SPE) [4,5,9,11,14,27], matrix solid-phase dispersion (MSPD) [16,25] and dispersive solid phase extraction (dSPE) [7,17]. So far, liquid partitioning with two kinds of organic solvents followed by a clean-up with SPE, GPC or MSPD is the current sample preparation choice for pesticide extraction in edible oils. In addition, a headspace solid-phase microextraction (HS-SPME) was also carried

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out with a fiber coating polydimethylsiloxane to extract 7 kinds of OPPs and their metabolites in olive oil samples [10]. Supercritical fluid extraction [28] developed as an on-line cleanup method has also been proposed as extraction and/or cleanup step.

The 'Quick Easy Cheap Effective Rugged and Safe' (QuEChERS) sample preparation method for determining pesticides in foods was first introduced in 2003 [29]. Since then, many modifications and studies of the method have been published [30–37]. QuEChERS method has many advantages over other traditional methods, such as high recovery for most of the pesticides, high sample throughput, less expenditure of organic solvent, and use of no chlorinated solvents [30]. The method can also be applied for the extraction of pesticides from some kinds of foodstuffs, such as rice [30], vegetables [31,35–37], olives [32], milk [33], honey [34] and fruits [35–37]. However, to the best of our knowledge, there was no report on the application of the method in the extraction of pesticides from edible oils.

In this work, a modified QuEChERS method suitable to extract pesticide residues from peanut oil was developed.

2. Experimental

2.1. Chemicals and materials

Pesticide standards, including phorate, diazinon, tolclofos-methyl, fenitrothin, malathion, fenthion, isocarbophos, quinalphos and phenamiphos, were purchased from National Institute of Metrology (Beijing, China). All pesticide standards used have a purity of ≥98%. Individual stock solutions of standards were prepared in methanol at a concentration of 1000 μg mL^{-1} and stored at the temperature of −20 °C. Methanol used in this work was of chromatographic grade and provided by Fisher Scientific Company (UK) (Pittsburgh, PA, USA). Acetonitrile and hexane were of analytical-reagent grade and purchased from Beijing Chemical Factory (Beijing, China). Working standard solutions of the pesticides were prepared by diluting standard stock solutions with methanol.

Three types of multi-walled carbon nanotubes (MWCNTs) (purity > 95%) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science (Chengdu, China). The parameters of the three types of MWCNTs are listed as follows:

Type 1: The outside diameter (OD) of MWCNTs varied between 10 and 20 nm, the length (*L*) ranged from 10 to 30 μm and the special surface area (SSA) was 200 m^2 g^{-1}.
Type 2: The OD of MWCNTs varied between 20 and 30 nm, the length ranged from 10 to 30 μm and the special surface area was >110 m^2 g^{-1}.
Type 3: The OD of MWCNTs was >50 nm, the length ranged from 10 to 20 μm and the special surface area was >60 m^2 g^{-1}.

Anhydrous sodium sulfate (analytical grade) and neutral alumina were supplied by Beijing Chemical Factory (Beijing, China). Before being used, the neutral alumina was incandesced at 650 °C for 4 h, and then baked at 105 °C for 2 h. After being cooled, it was deactivated with 5% water until no lumps were present and left in a tightly closed container.

2.2. Oil samples

The peanut oil samples (sample 1–7) produced in different geographical areas of China were purchased from supermarkets. No residues of the target pesticides in the 7 oil samples were detectable by a standard method recommended by China [38]. All experiments were carried out with sample 1 except for the experiment mentioned in Section 3.2.2 in which samples 1–7 were used.

2.3. Preparation of spiked samples

To obtain spiked samples, a proper volume of standard working solution at a proper concentration was added into 5.0 g of peanut oil in a 50 mL centrifuge tubes. After being well mixed, the samples were equilibrated for 1 h in the dark at room temperature.

2.4. Extraction and clean-up

5.0 g of peanut oil was weighed and transferred into a 50 mL of centrifuge tube. 10 mL of acetonitrile was added in the tube and the cap was screwed on. The tube containing sample and solvent was placed on the vortex mixer and shaken for 10 min (extraction time). The oil–acetonitrile emulsion was formed at the extraction period. The tube was then stored in the freezer overnight at −20 °C so that the precipitate is formed. Then the supernatant was transferred into a 10 mL centrifuge tube. 0.50 g of Na_2SO_4 was added into the tube to remove residual water. 100 mg of MWCNTs and 1.00 g of neutral alumina were added into the centrifuge tube. The mixture was vigorously shaken for 3.5 min (clean-up time) with a vortex mixer. Subsequently, the mixture was centrifuged for 4 min at 15,000 rpm at −4 °C. Then 7.0 mL of the supernatant was immediately filtered with a 0.22 μm membrane and transfered into a pear-shaped flask. The resulting solution was evaporated to dryness at a low pressure at 35 °C in a Heidolph-Laborata 4000 rotary evaporator from Heizbad WB. Then, the residue was dissolved in 1.0 mL hexane and the flask was washed with 0.5 mL hexane. The hexane solutions were combined and evaporated to dryness with a gentle N_2 flow. The residue was dissolved in 200 μL of hexane and the resulting solution was referred to as the analytical solution.

2.5. GC–MS analysis

Sample analysis was performed on a Shimadzu (Kyoto, Japan) GC–MS QP 2010 plus instrumentation. Chromatographic separation was conducted with a DB-5MS capillary column (5% phenyl polysiloxane as nonpolar stationary phase, 30 m × 0.25 mm I.D., film thickness of 0.25 μm; J&W Scientific, Folsom, CA, USA). Chromatographic conditions were as follows: injection temperature was maintained at 280 °C and the injection volume of the analytical solution was 1.0 μL; the split ratio was 1:10; the temperature program was set initially at 70 °C (held for 1 min), increased at a rate of 25 °C min^{-1} up to 180 °C, and then elevated to 210 °C at 4 °C min^{-1} (held for 3 min), and finally elevated to 280 °C at 5 °C min^{-1} (held for 6 min). Ultra-high-purity helium (99.999%) was used as the carrier gas at a constant flow of 1.0 mL min^{-1}. A solvent delay of 9.4 min was employed in the optimized method. The ion source, interface temperature and electron impact ionization energy were set at 200 °C, 250 °C and 70 eV, respectively. The mass spectrometer was operated in a selected ion monitoring (SIM) mode for quantitative analysis. The characteristic mass fragments used for quantitative and qualitative analysis and the retention times used for the qualitative analysis are shown in Table 1. Full-scan MS data were acquired in the range of *m*/*z* 50–550 to obtain the fragmentation spectra of the target analytes.

3. Results and discussion

3.1. Optimization of the extraction and clean-up

In the work, LLE was coupled with dSPE to extract the pesticides from the peanut oils. dSPE, which is often referred to as the "QuEChERS" method, is an emerging sample preparation method that is becoming increasingly popular in the area of multi-residue pesticide analysis in food and agricultural products.

Table 1
Analytical performances of the proposed method for the nine target pesticides.

Pesticide	t_R[a] (min)	Main fragment ions (m/z)[b]	Linear range ($\mu g\,kg^{-1}$)	LOD ($\mu g\,kg^{-1}$)	LOQ ($\mu g\,kg^{-1}$)	r
Phorate	10.21	65, 75, 121, **260**	5–200	1.3	4.3	0.9965
Diazinon	11.46	93, 134, 179, **304**	5–200	1.3	4.2	0.9941
Tolclofos-methyl	13.36	125, **265**, 267	5–200	0.7	2.2	0.9939
Fenitrothin	14.24	109, 125, **277**	7–200	1.6	5.4	0.9963
Malathion	14.55	93, 125, 127, **173**	5–200	1.4	4.7	0.9957
Fenthion	15.10	109, 125, 169, **278**	5–200	1.5	5.0	0.9911
Isocarbophos	15.46	120, 136, **289**	7–200	1.6	5.3	0.9947
Quinalphos	17.32	118, 146, 157, **298**	5–200	1.4	4.7	0.9953
Phenamiphos	19.04	80, 154, 195, **303**	5–200	1.4	4.6	0.9982

[a] Retention time.
[b] Ions for quantitative analysis are presented in bold.

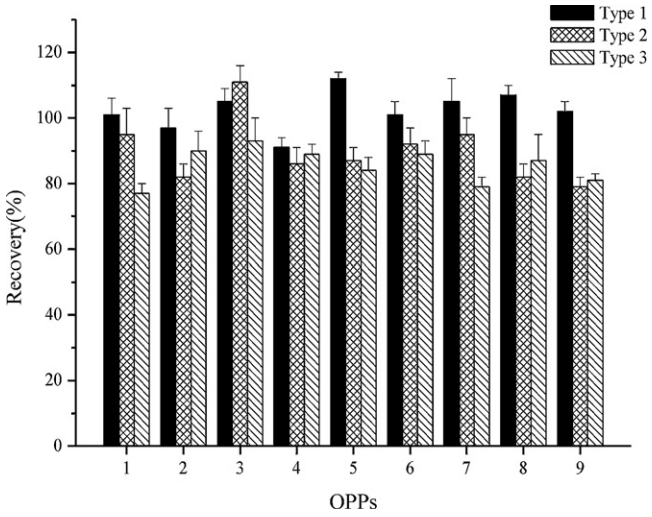

Fig. 1. Effect of types of MWCNTs in the extraction of organophosphorus pesticides in peanut oil: (1) phorate; (2) diazinon; (3) tolclofos-methyl; (4) fenitrothin; (5) malathion; (6) fenthion; (7) isocarbophos; (8) quinalphos; (9) phenamiphos.

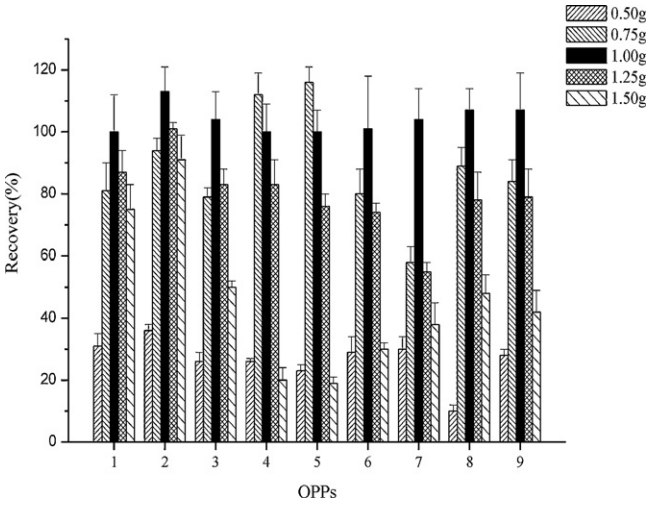

Fig. 3. Effect of amount of alumina neutral in the extraction of organophosphorus pesticides in peanut oil: (1) phorate; (2) diazinon; (3) tolclofos-methyl; (4) fenitrothin; (5) malathion; (6) fenthion; (7) isocarbophos; (8) quinalphos; (9) phenamiphos.

In order to achieve an adequate extraction performance, several parameters, including the type of MWCNTs, adsorbent amount and the clean-up time were optimized by analyzing spiked samples containing 20 $\mu g\,kg^{-1}$ of target analytes.

3.1.1. Type of MWCNTs

Three kinds of MWCNTs (70 mg Type 1, 70 mg Type 2, 70 mg Type 3) were used in dSPE studies in order to find out the adsorbent materials available for extracting the pesticide residues in the spiked samples. The concentration for each analyte was 20.0 $\mu g\,kg^{-1}$. The recoveries ($n = 3$) of the 9 pesticides determined

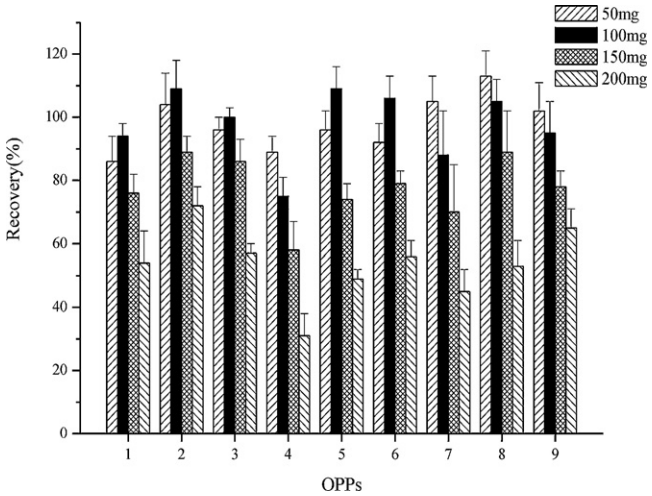

Fig. 2. Effect of amount of MWCNTs in the extraction of organophosphorus pesticides in peanut oil: (1) phorate; (2) diazinon; (3) tolclofos-methyl; (4) fenitrothin; (5) malathion; (6) fenthion; (7) isocarbophos; (8) quinalphos; (9) phenamiphos.

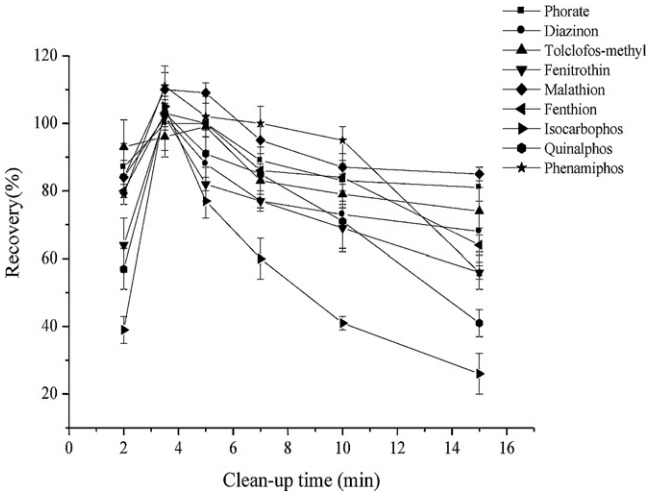

Fig. 4. Effect of clean-up time in the extraction of organophosphorus pesticides in peanut oil: (1) phorate; (2) diazinon; (3) tolclofos-methyl; (4) fenitrothin; (5) malathion; (6) fenthion; (7) isocarbophos; (8) quinalphos; (9) phenamiphos.

Table 2
Recoveries and precision for determination of the pesticides in spiked samples.

Sample	Added ($\mu g\,kg^{-1}$)	Phorate		Diazinon		Tolclofos-methyl		Fenitrothin		Malathion		Fenthion		Isocarbophos		Quinalphos		Phenamiphos	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	106.8	6.38	102.2	3.22	102.1	3.94	101.6	4.59	103.8	5.65	103.1	5.68	99.4	4.43	93.2	3.37	97.3	7.85
	130	94.7	4.47	96.5	7.32	85.9	5.86	100.5	5.69	85.9	7.66	106.5	3.65	89.3	4.23	98.2	5.74	104.7	8.17
2	10	103.4	3.13	101.7	2.73	106.2	7.02	93.2	4.62	98.9	6.39	107.0	2.93	98.2	8.48	93.2	6.57	111.7	3.22
	130	98.1	5.05	104.1	5.78	98.9	4.41	99.8	2.07	105.1	5.38	96.5	5.74	105.8	3.18	94.9	3.75	102.4	5.73
3	10	97.0	3.50	110.0	6.97	100.2	1.86	103.3	3.09	104.6	8.01	114.3	4.61	91.4	6.48	99.8	7.50	104.4	7.37
	130	101.9	6.90	90.9	3.87	93.0	5.19	96.9	5.71	102.9	3.60	95.4	4.98	105.0	3.96	102.8	6.40	98.4	6.17
4	10	92.6	4.47	96.2	6.90	96.1	7.06	103.8	5.69	105.9	5.87	98.6	5.63	104.3	2.81	98.2	6.07	101.3	5.85
	130	101.7	4.96	93.0	3.51	89.7	5.86	100.9	4.26	96.5	4.41	91.7	7.76	99.2	2.68	90.7	5.73	110.9	6.41
5	10	108.3	5.44	105.5	3.62	98.6	5.11	103.7	5.26	97.4	2.63	89.6	3.14	108.8	7.32	103.1	7.62	92.1	3.69
	130	97.1	5.86	109.3	2.74	108.9	3.87	107.8	8.25	93.3	4.32	92.8	4.16	106.0	6.15	96.7	2.47	105.5	1.88
6	10	104.1	4.35	99.9	2.04	97.0	7.47	96.2	7.94	88.7	4.81	106.3	4.46	109.2	2.68	95.4	6.12	104.9	3.62
	130	105.8	1.75	94.7	1.22	101.7	7.69	104.2	3.73	96.4	3.98	86.2	6.31	104.9	2.92	107.8	5.58	100.7	2.94
7	10	93.0	3.51	109.0	6.02	102.8	3.18	107.8	2.93	109.7	6.31	99.5	5.46	92.0	4.81	101.4	4.89	110.0	2.56
	130	97.5	4.23	94.9	3.56	105.2	6.32	89.4	4.01	105.7	3.00	94.6	5.69	100.6	6.02	96.9	3.19	105.0	3.97

Table 3
Comparison of methods for extracting pesticides from oils.

Extraction method	Sample	Sample treatment step	Determination method	Recovery (%)	LOD ($\mu g\,kg^{-1}$)	References
LLE-SPE	Olive oil	Olive oil $\xrightarrow[\text{dissolution}]{\text{hexane}}$ sample solution $\xrightarrow[\text{extraction}]{\text{acetonitrile}}$ extract $\xrightarrow[\text{clean-up}]{\text{ENVI-Carb SPE cartridge}}$ adsorbate $\xrightarrow[\text{elution}]{\text{acetonitrile, acetonitrile/toluene (95:5, v/v)}}$ eluate $\xrightarrow[\text{clean-up}]{\text{DIOL SPE cartridge}}$ adsorbate $\xrightarrow[\text{elution}]{\text{hexane, hexane/ethy1 acetate/methanol (98:2.5:2.5, v/v/v)}}$ analytical solution	GC–NPD	71.4–105.3	0.4–14.5	[4]
			GC–ECD	95.2–106.7	0.8–13.1	
LLE-MSPD	Olive oil	Olive oil $\xrightarrow[\text{extraction}]{\text{petroleum ether saturated with acetonitrile}}$ extract $\xrightarrow[\text{MSPD}]{\text{aminopropyl}}$ mixture $\xrightarrow[\text{clean-up and elution}]{\text{florisil, acetonrile}}$ analytical solution	GC–MS LC–MS/MS	73.2–129.7 83–104	3–60 0.2–3	[16]
LLE-GPC	Olive oil	Olive oil $\xrightarrow[\text{extraction}]{\text{acetonitrile saturated in hexane}}$ extract $\xrightarrow[\text{clean-up elution}]{\text{GPC, ethy1 acetate/ciclohexane (1:1, v/v)}}$ analytical solution	GC–MS/MS	89–105	0.5–20	[23]
LLE-dSPE	Soybean oil	Soybean oil $\xrightarrow[\text{extraction}]{\text{acetonitrile}}$ extract $\xrightarrow[\text{fat precipitation}]{\text{low temperature}}$ supernatant $\xrightarrow[\text{clean-up}]{\text{dSPE (PSA, C18)}}$ analytical solution	GC–MS	70–110	20–250	[7]
LLE-dSPE	Peanut oil	Peanut oil $\xrightarrow[\text{extraction}]{\text{acetonitrile}}$ extract $\xrightarrow[\text{fat precipitaion}]{\text{low temperature (−20°C)}}$ supernatant $\xrightarrow[\text{clean−up}]{\text{dSPE (MWCNTs, alumina netural)}}$ analytical solution	GC–MS	85.9–114.3	0.7–1.6	This method

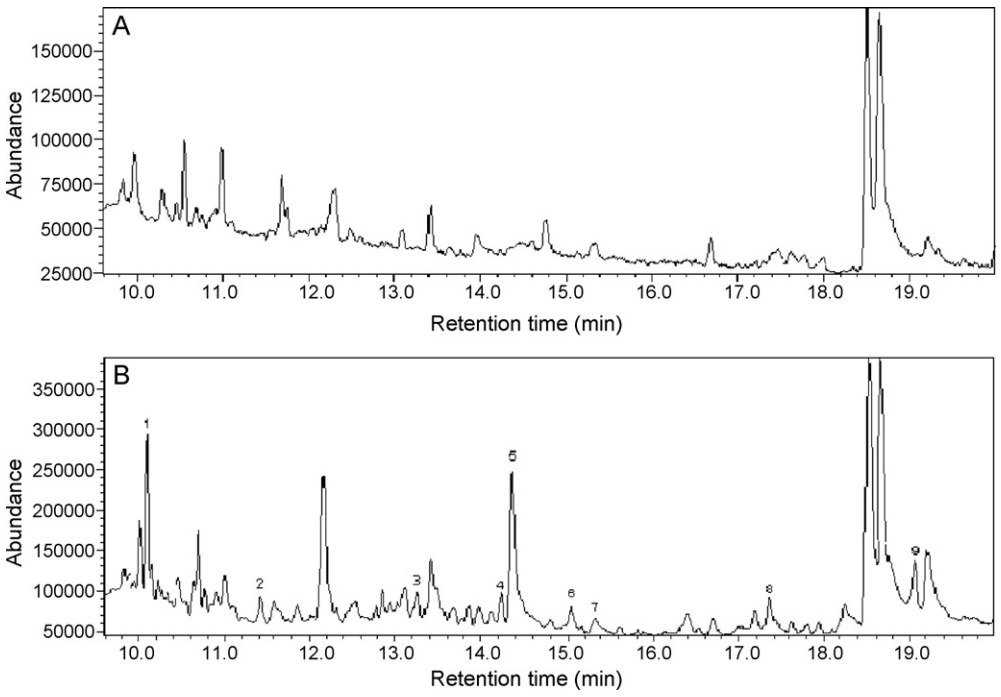

Fig. 5. Chromatograms (scan mode) of extracts of blank peanut oil sample (A) and spiked sample at analyte concentration of 50 μg kg^{-1} (B) obtained by the proposed method. (1) phorate; (2) diazinon; (3) tolclofos-methyl; (4) fenitrothin; (5) malathion; (6) fenthion; (7) isocarbophos; (8) quinalphos; (9) phenamiphos.

Table 4
Statistical analysis of recoveries of the analytes in edible oil samples obtained by different methods.

Analyte	Proposed method (mean ± SD, n = 3)	LLE-SPE (mean ± SD, n = 6)	t[a]	LLE-dSPE (mean ± SD, n = 6)	t[a]
Phorate	105.8 ± 5.5	–	–	58 ± 7.8	9.364
Diazinon	99.4 ± 5.1	97.1 ± 7.7	0.461	76 ± 7.8	4.638
Tolclofos-methyl	94.0 ± 4.5	–	–	–	–
Fenitrothin	101.0 ± 5.2	85.8 ± 5.3	4.077	82 ± 11.5	2.658
Malathion	94.8 ± 6.2	105.3 ± 8.6	1.859	88 ± 9.0	1.159
Fenthion	104.8 ± 4.9	100.8 ± 2.4	1.707	67 ± 7.5	7.793
Isocarbophos	94.4 ± 4.1	–	–	–	–
Quinalphos	95.7 ± 4.4	86.7 ± 8.0	1.778	93 ± 8.5	0.505
Phenamiphos	101 ± 8.1	–	–	–	–

[a] The critical value of $t(0.001, 7)$ is 5.405.

by GC–MS are shown in Fig. 1 and range from 91 to 112% for Type 1, 79 to 111% for Type 2, and 77 to 93% for Type 3. Type 1 MWCNT has the highest purifying ability due to its larger special surface area and higher value of length/outside diameter than those of other MWCNTs. When Type 1 was used the highest recoveries for all the target pesticides were obtained. Thus, Type 1 was selected as the adsorbent in dSPE.

3.1.2. Influence of the adsorbent amount

The influence of the amount of MWCNTs and neutral alumina on the recoveries was evaluated. Fig. 2 shows recoveries obtained with MWCNTs and Fig. 3 shows recoveries obtained with neutral alumina. As can be seen from Fig. 2, the recoveries for phorate, diazinon, tolclofos-methyl, malathion and fenthion are the highest when the amount of MWCNTs is 100 mg and those for fenitrothin, isocarbophos, quinalphos and phenamiphos, the recoveries are the highest when the amount of MWCNTs is 50 mg. Based on the experimental results, 100 mg was selected as the optimum amount of MWCNTs.

The effect of amount of neutral alumina on extraction recoveries was also important. It can be seen from Fig. 3 that 1.00 g neutral alumina offers the highest recoveries for most of the analytes. So 1.00 g was selected for further experiments.

3.1.3. Clean-up time

The effect of clean-up time was examined. As shown in Fig. 4, the highest recoveries are obtained in the time range from 3.5 to 5 min, and the recoveries are low when the extraction time is shorter than 2 min and longer than 7 min. On the one hand, the increase of clean-up time is beneficial to the clean-up of the sample. On the other hand, the increase of clean-up time results in the increase of adsorption of pesticides on adsorbents in clean-up step and the decrease of recoveries. Based the experimental results, the clean-up time was selected to be 3.5 min.

3.2. Method validation

3.2.1. Linearity, LOD and LOQ

In order to evaluate the performances of the proposed method for quantitative determination of 9 pesticides in peanut oils, a series of spiked samples were used for constructing standard curves and obtaining other analytical performances. As can be seen in Table 1,

the linear range is 5–200 $\mu g\,kg^{-1}$ with the correlation coefficients (r) between 0.9911 and 0.9982. The limits of detection (LODs) and quantification (LOQs) indicated in Table 1 were determined as the lowest concentrations yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively. The MRLs of the pesticides in peanuts under European Union regulation are 10–200 $\mu g\,kg^{-1}$ [2]. The LOQs are lower than the MRLs and should be appropriate to the goal of the proposed method.

3.2.2. Accuracy and selectivity

The pesticides were determined in triplicate at two levels (10 $\mu g\,kg^{-1}$ and 130 $\mu g\,kg^{-1}$) in seven spiked samples. The results obtained are given in Table 2. The recoveries ($\geq$85.9%), and the relative standard deviations ($\leq$8.48%) are acceptable.

The chromatograms of the extracts of blank peanut oil and spiked sample at analyte concentration of 50 $\mu g\,kg^{-1}$ are shown in Fig. 5. The results demonstrate that no interference peaks are observed at the retention times of the nine target analytes in the chromatogram of blank peanut oil, which indicates that the selectivity of the proposed method is satisfactory.

The proposed method was compared with SPE, MSPD, GPC and dSPE used for the extraction of pesticides from edible oil samples (Table 3). The recoveries of the analytes obtained by the different methods are different and the statistical test was performed. For the purpose, the Student's t-test was applied. As shown in Table 4, the statistical analysis indicates that there are no significant differences among recoveries obtained by the proposed method and LLE-SPE ($p < 0.001$) and there are no significant differences among recoveries of the analytes obtained by the proposed method and LLE-dSPE except for those of phorate and fenthion ($p < 0.001$). However, compared with the SPE, the proposed method has some advantages in the experimental cost, organic solvent consumption, and operation simplicity. Compared with other QuEChERS methods for the oil removal and pesticide detection, the proposed method has stronger purifying ability and higher sensitivity.

4. Conclusions

The MWCNTs were used as adsorbent of dSPE and successfully applied to the extraction of the 9 organophosphorus pesticides from peanut oil samples. The results indicated that the proposed method has some advantages in respect of extraction efficiency, sensitivity and expenditure of sample treatment time. The method could be extended to other analytes and other types of fatty food samples by varying the conditions of the sample treatment.

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