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Optimization of a single-drop microextraction procedure for the determination of organophosphorus pesticides in water and fruit juice with gas chromatography-flame photometric detection

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Abstract

A single-drop microextraction (SDME) procedure was developed for the analysis of organophosphorus pesticides (OPPs) in water and fruit juice by gas chromatography (GC) with flame photometric detection (GC-FPD). The significant parameters affecting the SDME performance such as selection of microextraction solvent, solvent volume, extraction time, stirring rate, sample pH and temperature, and ionic strength were studied and optimized. Two types of SDME mode, static and cycle-flow SDME, were evaluated. The static SDME procedure provided more sensitive analysis of the target analytes. Therefore, static SDME with tributyl phosphate (TBP) as internal standard was selected for the real sample analysis. The limits of detection (LODs) in water for the six studied compounds were between 0.21 and 0.56 ng/mL with the relative standard deviations ranging from 1.7 to 10.0%. Linear response data was obtained in the concentration range of 0.5–50 ng/mL (except for dichlorvos 1.0–50 ng/mL) with correlation coefficients from 0.9995 to 0.9999. Environmental water sample collected from East Lake and fruit juice samples were successfully analyzed using the proposed method, but none of the analytes in both lake water and fruit juice were detected. The recoveries for the spiked water and juice samples were from 77.7 to 113.6%. Compared with the conventional methods, the proposed method enabled a rapid and simple determination of organophosphorus pesticides in water and fruit juice with minimal solvent consumption and a higher concentration capability.

Keywords: Single-drop microextraction; Organophosphorus pesticides; GC-FPD; Water; Fruit juice

1. Introduction

Organophosphorus pesticides (OPPs) are still widely used in many countries for agriculture and disease control. These compounds represent risks to the environment in respect of human health and the well-being of non-target species. Public concern over OPPs contamination of the environment has risen over recent decades to the extent that it has now become a significant food safety issue.

The recognized mechanism of action of OPPs is presumed to be the inhibition of acetylcholinesterase (AChE), the enzyme which control the levels of neurotransmitter acetylcholine (ACh) [1]. AChE occurs throughout the central and peripheral nervous system of vertebrates, and its normal physiological action is to hydrolyze the neurotransmitter acetylcholine so that activation of cholinergic receptors is transient. Inhibition of AChE results in accumulation of ACh and signs of cholinergic toxicity. There is evidence that AChE inhibition correlated with the emergence and severity of clinical signs of poisoning by AChE-inhibiting pesticides [2]. Similarly, human beings would face the same risk of neurotoxic potential of OPPs. The maximum residue limits (MRLs) allowed for different OPPs in the National Standards for Pesticide Residue of China was presented in the report [3]. Although most samples will contain concentrations below the MRLs allowed for pesticides, the analytical control is likely to continue.

Hence, there is an increasing demand for developing methods for the determination of such contaminations in food and environment. For the analysis of OPPs in food and environmental water samples, sample preparation are required in order to isolate the analytes from the complex matrices, remove interfering compounds and achieve a sufficient sensitivity. Jose et

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al. [4] and Stefan and Jozef [5] have been reviewed recently on the sample preparation, chromatographic separation systems and detection techniques for the determination of pesticide residues in beverage and water. It is obvious that the analytical methods based on gas chromatography (GC) or liquid chromatography (LC) are the most applied technique for the pesticide determination and sample preparation is the critical step for pesticide analysis.

OPPs can be extracted from aqueous matrices using a variety of conventional techniques. Most common techniques for extracting pesticides are liquid–liquid extraction (LLE) and solid-phase extraction (SPE). These techniques are time consuming, expensive and, especially in relation to LLE, hazardous to health due to the high volume of potentially toxic solvents used. Because of the disadvantages of conventional extraction techniques, solvent free sample preparation methods or those employing less organic solvents are becoming more and more important.

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation, and the minimization of organic solvent used. Solid-phase microextraction (SPME), liquid-phase microextraction (LPME) and stir bar sorptive extraction (SBSE) are easy and fast techniques, which avoid or used only microliters of toxic solvents.

SPME is a solvent free sample preparation technique, and has been widely used for the detection of contaminants in the environmental samples [6–12]. The concentration capability of SBSE was better than SPME because the film of PDMS phase that covers the bar is thicker, it has also been used for organic compounds analysis recently [13–18]. Liquid-phase microextraction is a fairly new method of sample preparation, initially proposed by Jeannot and Cantwell in 1996 [19]. It is a miniaturized implementation of conventional liquid–liquid extraction in which only microliters of solvents are used instead of several hundred milliliters in LLE. It is quick, inexpensive and can be easily automated.

The methodologies that evolved from this approach fall into two categories: single-drop microextraction and hollow fiber liquid-phase microextraction (hollow fibre LPME). The extractant phase of SDME is a drop of an organic solvent, and in hollow fiber LPME system, a hollow fiber impregnated with an organic solvent is used to accommodate or protect microvolumes of acceptor solution.

There are two modes of SDME sampling: direct SDME and headspace SDME (HS-SDME). The direct SDME consists of suspending a microdrop of organic solvent at the tip of a syringe, which is immersed in the aqueous sample. HS-SDME is very similar to direct SDME except that microdrop of high boiling extracting solvent is exposed to the headspace of a sample. Today, both modes have been successfully used for the extraction of organic pollutants such as organochlorine pesticides [20,21], organophosphorous pesticides [22,23], endosulfan [24], dialkyl phthalate esters [25], *s*-triazine herbicides [26], and organotin compounds [27], from a variety of matrices [20–27]. It has been demonstrated that LPME shows comparable extraction efficiency and reproducibility as the widely used SPME technique.

It should be noted although SDME has been increasingly used for the extraction and concentration of pesticides from simple aqueous samples [20–24,26] since 1996, to best of our knowledge, it has not been used in the analysis of pesticide residues in fruit juice, the complex matrices of such products may cause interference in the extraction procedure.

In this work, a SDME procedure was developed for the analysis of six OPPs in water and fruit juice by gas chromatography with flame photometric detection (GC-FPD). Two types of direct SDME: static single-drop microextraction (static SDME) and cycle-flow single-drop microextraction (cycle-flow SDME) were comparatively studied. The experimental parameters affecting the extraction of the studied pesticides, such as selection of organic solvent, organic drop volume, sample stirring, salt addition, temperature, and sampling time, were assessed and optimized. Finally, the procedure of static SDME was applied for the determination of OPPs in the water and fruit juice samples.

2. Experimental

2.1. Standard solutions and chemicals

Pesticide standards dichlorvos (National Standard Number of China: GSB G23023-92), phorate (National Standard Number of China: GSB G23019-92), fenitrothion (National Standard Number of China: GSB G23012-92), malathion (National Standard Number of China: GSB G23018-92), parathion (National Standard Number of China: GSB G23009-92) and quinalphos (National Standard Number of China: GSB G23062-94) were obtained from Agro-Environmental Protection Institute of Ministry of Agriculture (Tianjin, China). Individual pesticide standard stock solutions of 100 μg/mL in acetone were prepared and a mixed standard solution containing 1 μg/mL of each of the pesticides was prepared in acetone from the individual standard stock solutions. The stock standard solution was stored in refrigerator at 4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with doubly distilled water to the required concentrations.

Hexane, toluene, cyclohexane, tetrachloromethane and other reagents used were of analytical reagent grade. Doubly distilled water was used throughout this work.

2.2. Preparation of samples

The apple, pear and orange commercially available were used. A WM-98C-II Jinweima blender (Shunde, Guangdong) was used to comminute and homogenize the fruit samples. After filtration, the fruit juice was spiked with 50 and 200 ng/mL of OPPs. For validation, fortified juice samples were analyzed after 1/100 dilution with water.

Water sample was obtained from East Lake (Wuhan, China). Original water was used for spiking experiments. The spiked water samples were obtained by spiking 2 and 5 ng/mL of OPPs in above lake water sample.

2.3. Static single-drop microextraction

The experimental set-up of static SDME is the same as that reported in [28]. A commercially available 10 μL microsyringe (Gaoge, Shanghai) was used for microextraction. Single-drop microextraction was performed in a 3 mL vial. The vial was placed on a 85-2A constant temperature magnetic stirrer (Ronghua, Jiangsu). This technique is performed by suspending 1.5 μL drop of organic solvent on the tip of a 10 μL microsyringe immersed in the stirred 2 mL aqueous solution. The analytes partition between the bulk aqueous phase and the organic solvent microdrop. Following sample extraction, the magnetic stirrer was switched off and the drop was withdrawn into the syringe. The needle was then removed from the vial. One microliter was injected directly into the GC-FPD for analysis.

2.4. Cycle-flow single-drop microextraction

The set-up of cycle-flow SDME system is similar to the continuous-flow SDME system with a modification that the waste outlet of tubing was put into the sample reservoir, and the sample volume was set as 2 mL [29]. When the extraction chamber has been filled with the sample solution, a 10 μL microsyringe was used to take extraction solution and push out 1.5 μL of extraction solution to form a drop above the PFA tubing outlet in extraction chamber. As the fresh sample solution flowed around the single drop circularly at the flow rate of 0.4 mL/min by an HL-2 pump (Qingpu, Shanghai), the trace analytes were kept extracting into the solvent drop from the sample solution. The volumes of sample solution in the sample reservoir, connecting tubing, and extraction chamber were about 1.2, 0.6, and 0.2 mL, respectively. After the extraction was finished, the drop was withdrawn by the microsyringe. One microliter was injected directly into the GC-FPD for analysis.

2.5. GC-FPD analysis

Pesticide residues were determined using a Agilent 6890N Network GC system fitted with an FPD operated in the phosphorus mode at 250 °C. The analytical column was a 30 m × 0.32 mm HP-5, with a film thickness of 0.25 μm. The 1 μL SDME extract was injected into the GC-FPD in splitless mode at 250 °C. The column oven temperature was held at 125 °C for 2 min, then programmed at 75 °C/min to 200 °C for 1 min, 10 °C/min to 220 °C and held for 3 min. N_2 carrier gas was maintained at a flow rate of 1.6 mL/min. H_2 75 mL/min and air 100 mL/min were used as combustion gases.

3. Results and discussion

3.1. Optimization of static SDME

In order to perform the microextraction of OPPs from aqueous samples efficiently, several parameters that influence on the extraction efficiency should be studied and optimized. Such factors included solvent type and drop volume, stirring rate, extraction time, sample pH and temperature, and effect of salt concentration.

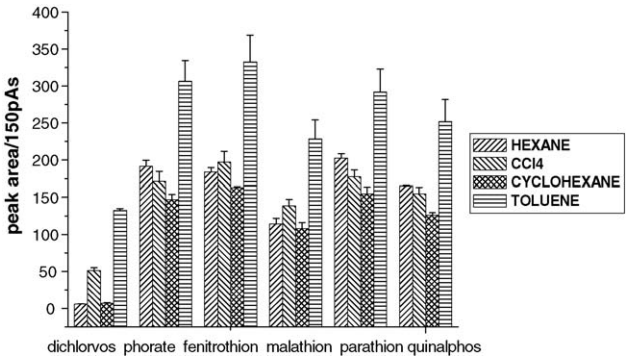

Fig. 1. Effect of extraction solvent on static SDME efficiency ($n = 3$). Conditions: OPPs standard mixture solution with individual concentration of 10 ng/mL, 10 min extraction with 1.5 μL of solvent at a stirring rate of 500 rpm, injection volume 1.0 μL.

3.1.1. Solvent type and drop volume

Selection of a suitable solvent is very important for achieving good selectivity and improving extraction effciency. The extraction solvent had to meet the following requirements: the solvent must have low water solubility, extract analytes well and have good drop stability when stirring and low level of toxicity [28]. In this study, four different solvents, hexane, toluene, cyclohexane and tetrachloromethane were tested for the microextraction of OPPs and Fig. 1 shows the effect of the extraction solvent on extraction effciency. As could be seen, toluene gave the best extraction efficiency for all tested target analytes. It was also found in our experiment that toluene is more stable and less toxic than other organic solvents tested. Toluene is also a very suitable solvent for pesticide GC injection [30]. Thus, toluene was chosen as the extraction solvent in the static SDME.

Generally, the use of a large organic drop results in an increase of the analytical response of the instrument. However, larger drops are difficult to manipulate and are less reliable. In addition, the analytes get into the drop through the diffusion process, the larger the drop volume, the longer the time to reach the equilibrium. Therefore, in order to increase the sensitivity of the SDME procedure, the organic drop volume must be optimized experimentally. The influence of drop volume on the extraction efficiency was also evaluated. It could be seen that the analytical signal for all OPPs increased with increasing the drop volume from 1.0 to 1.5 μL, then leveled off, and after 2.0 μL the peak areas for all OPPs except for dichlorvos decreased with the further increase of drop volume. Considering the facts that large volume of organic drop will result in the shrinking of the organic drop, drop volume of 1.5 μL was employed in further static SDME experiments.

3.1.2. Stirring rate

Sample stirring increases extraction efficiency and reduces extraction time, as the partitioning equilibrium of analytes in both aqueous and organic phases is established more rapidly. To evaluate the effect of stirring, sample solutions were contin-

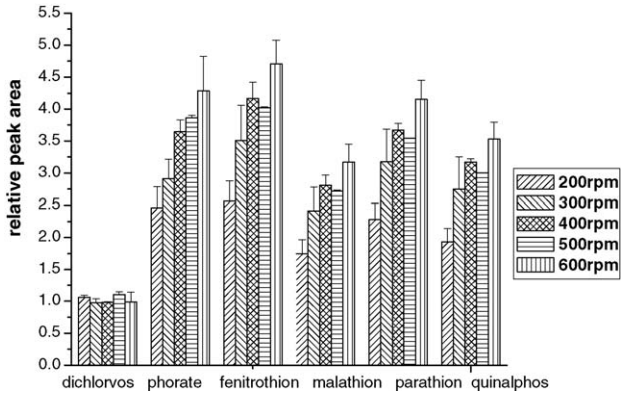

Fig. 2. Effect of stirring rate on static SDME efficiency ($n = 3$). Conditions: OPPs standard mixture solution with individual concentration of 10 ng/mL, 20 min extraction with 1.5 μL of toluene, injection volume 1.0 μL. Relative peak area: relative vs. peak area of TBP (I.S.).

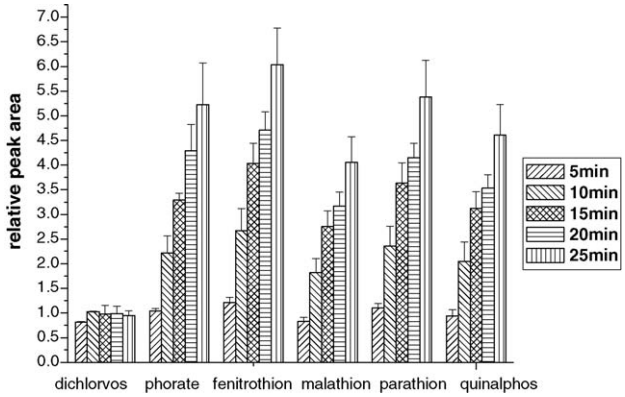

Fig. 3. Effect of extraction time on static SDME efficiency ($n = 3$). Conditions: OPPs standard mixture solution with individual concentration of 10 ng/mL, 1.5 μL toluene as extraction solvent, stirring rate of 600 rpm, injection volume 1.0 μL. Relative peak area: relative vs. peak area of TBP (I.S.).

uously agitated at different stirring rates and the experimental results are given in Fig. 2. As can be seen, the peak areas of all the analytes increase with the increase of stirring rate from 200 to 600 rpm (except for dichlorvos, no obvious increase). According to the film theory [31], the aqueous phase mass transfer coefficient β_{aq} increases with increasing stirring speed, because faster stirring decreases the thickness of the diffusion film δ_{aq}. Agitation of the sample enhances extraction and reduces the time to thermodynamic equilibrium. However, after the sample stirring rate was above 700 rpm, although extraction efficiency was better for some analytes, air bubble formation frequently occurred, leading to quantification problems. And higher stirring rates will also result in drop dislodgement and drop dissolution especially for prolonged extraction times. Hence, a stirring rate of 600 rpm was chosen in further work.

3.1.3. Extraction time

The effect of extraction time on extraction efficiency was investigated with the time varying from 5 to 25 min. For all target analytes except for dichlorvos (the equilibrium was reached in 10 min), the relative peak areas increase with the increase of extraction time and the equilibrium was reached after 25 min (Fig. 3). One of the possible reasons for this may be the slow equilibrium rate between the sample solution and the organic drop. SDME will attain the maximum sensitivity after the equilibrium between aqueous and organic phase has been achieved. However, SDME is not an exhaustive extraction technique, and it is similar to LLE and SPME in that it is based on the analyte's partitioning between the aqueous sample and the organic solvent. Therefore, when using SDME it is not practical to takes a longer time to reach the complete equilibrium which is not necessary for analytical methods with extraction time and other extraction parameters remaining constant. And moreover, a prolonged extraction time may result in drop dissolution and have a high incidence of drop loss. Therefore, the extraction time for all subsequent experiments was standardized at 20 min. In order to get better precision, tributyl phosphate (TBP) was added into toluene to be used as an internal standard.

3.1.4. Sample pH

Generally, the natural sample shortly after collection was acidified to avoid the degradation of organic compounds. However, the ionization form of certain analytes will change with the change of pH and thereby affecting their water-solubility and extractability. In this work, the effect of sample pH on OPPs extraction was investigated by varying the pH values from 1 to 7. It was found that a better extraction efficiency was obtained for all tested OPPs at pH 5–6. At pH higher than 6, the peak area for the tested OPPs was decreased. The OPPs had a reduced extraction efficiency at more alkaline pH range. These compounds are known to decompose at an alkaline pH. On the basis of these results, a pH of 5–6 (the usual pH for environmental water) can be used for further analysis.

3.1.5. Extraction temperature

The effect of extraction temperature on extraction efficiency was investigated. The experimental results showed that the extraction efficiency of most OPPs increase with increase in extraction temperature. This can be explained by the fact that an increase in extraction temperature would increase the OPPs diffusion coefficient. Although the equilibrium would achieve faster at a higher extraction temperature, it will result in the formation of air bubbles. Hence, the room temperature (20 ± 2 °C) was used for sample analysis.

3.1.6. Effect of salt concentration

Addition of salt (such as NaCl or Na_2SO_4) to the sample may have several effects on single-drop microextraction [28]. It can improve the extraction of analytes since high ionic strength due to the salt addition reduces their water solubility. However, the presence of salt was found to restrict extraction of analytes. It was assumed that apart from the salting-out effect, the presence of salt caused another effect and changed the physical properties of the extraction film, thus reducing the diffusion rates of the analytes into the drop. The effect of salt concentration on the extraction efficiency of OPPs was illustrated in Fig. 4. As can be seen, the addition of salt has a remarkable effect on the extraction of analytes, but this effect was different for differ-

Table 1
Comparison of the static SDME and cycle-flow SDME

OPPs	Concentrations after static SDME (ng/mL)	Concentrations after cycle-flow SDME (ng/mL)	Enrichment factor	
			Static SDME	Cycle-flow SDME
Dichlorvos	232.3	149.6	23	15
Phorate	971.2	16.13	97	2
Fenitrothion	1093	56.33	109	6
Malathion	990.1	141.4	99	14
Parathion	999.4	27.60	99	3
Quinalphos	971.9	23.87	97	2

Static SDME conditions: standard mixture solution with individual concentration of 10 ng/mL, extraction 20 min with 1.5 μL toluene at stirring rate 600 rpm; cycle-flow SDME conditions: extraction 15 min with 1.5 μL toluene at sample flow of 0.4 mL/min.

Table 2
Analytical performance data for six OPPs by static SDME-GC-FPD

OPPs	Equation	Correlation coefficient	Linearity (ng/mL)	Detection limit (ng/mL)	R.S.D. (%)	LOD of other methods (ng/mL or ng/g)
Dichlorvos	$y = 0.1086x - 0.02824$	0.9995	1.0–50	0.56	10.0	0.10–6.0 [22,32–34]
Phorate	$y = 0.4082x - 0.04029$	0.9999	0.5–50	0.22	4.1	0.20–10 [10,35]
Fenitrothion	$y = 0.4538x + 0.00332$	0.9998	0.5–50	0.35	1.7	0.011–50 [10,23,33,35–38]
Malathion	$y = 0.3082x + 0.03596$	0.9997	0.5–50	0.26	3.5	0.073–50 [10,23,33,35,36,38,39]
Parathion	$y = 0.3979x + 0.02198$	0.9998	0.5–50	0.21	3.5	0.049–1.7 [10,22,40]
Quinalphos	$y = 0.3530x + 0.02985$	0.9995	0.5–50	0.37	3.6	0.004–50 [37,38]

ent analytes. With the exception of dichlorvos, the extraction efficiency for the tested OPPs decrease with the adding NaCl concentration changing from 0 to 30% (m/V). In contrast, the extraction efficiency for dichlorvos increase with the increase of adding NaCl concentration from 0 to 30% (m/V). Based on the above experimental results, sample direct analysis without the salt addition was employed in this work.

3.2. Comparison of static SDME and cycle-flow SDME

Two types of SDME, both static SDME and cycle-flow SDME were evaluated to efficiently extract OPPs. For this purpose, some important extraction factors affecting the extraction efficiency of OPPs by cycle-flow SDME such as nature of microextraction solvent, solvent volume, extraction time and sample flow rate were also studied and optimized.

Similar to static SDME, the solvent toluene can give the best extraction efficiency for the tested target analytes, so toluene was selected for further cycle-flow SDME experiments. With the use of toluene as extraction solvent, the effect of other parameters on the extraction of six OPPs in the cycle-flow SDME was studied and the results showed that no significant influence of drop volume on the extraction efficiency of OPPs with the drop volume varying from 1.5 to 2.5 μL, but the extraction efficiency increases with the increase of sample flow rate, which indicated that higher flow rate provided more effective extraction of analytes. This is quite similar to the results obtained in the static SDME in which the extraction efficiency of analytes

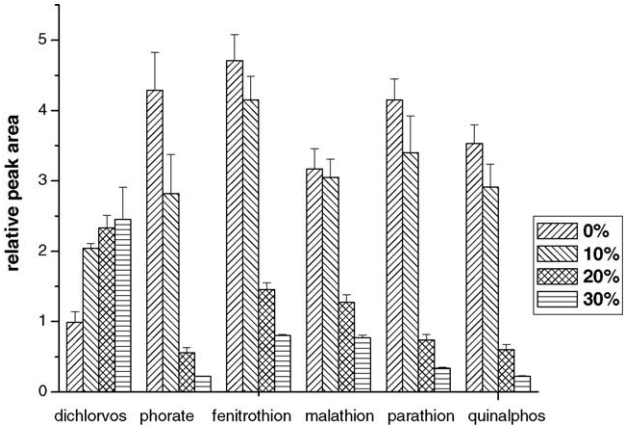

Fig. 4. Effect of NaCl concentration on static SDME efficiency ($n = 3$). Conditions: OPPs standard mixture solution with individual concentration of 10 ng/mL (add different amount of NaCl), 20 min extraction with 1.5 μL toluene at a stirring rate of 600 rpm, injection volume 1.0 μL. Relative peak area: relative vs. peak area of TBP (I.S.).

Table 3
Six OPPs recoveries in East Lake water samples at the two spiked levels

OPPs	Added (ng/mL)	Found (ng/mL)	Recovery (%)	R.S.D. (%)
Dichlorvos	2	1.97	98.6	0.7
	5	4.62	92.4	2.4
Phorate	2	1.81	90.7	8.5
	5	5.32	106.5	2.7
Fenitrothion	2	1.81	90.8	5.4
	5	4.94	98.9	3.3
Malathion	2	1.82	91.4	4.6
	5	4.89	97.7	2.7
Parathion	2	1.83	91.7	6.1
	5	4.84	96.9	2.7
Quinalphos	2	1.91	95.5	6.8
	5	4.97	99.4	0.6

increase with the increase of stirring rate. The same as in static SDME, no equilibrium was attained in the cycle-flow SDME for most studied pesticides (except for dichlorvos) in 20 min. Based on these experimental results, the extraction solvent of 1.5 μL toluene, sample flow rate of 0.4 mL/min and the extraction time of 15 min were selected as the optimal cycle-flow SDME conditions.

Under the optimized conditions, the enrichment factors for six OPPS in both static SDME and cycle-flow SDME were determined and the results are given in Table 1. The enrichment factor, defined as the ratio of peak area of target analytes after and before extraction. As could be seen in Table 1, the enrichment factors for six OPPs in cycle-flow SDME, generally, were much smaller than that in static SDME, which means a poorer sensitivity will be obtained in former. More specifically, in cycle-flow SDME the highest enrichment factor of 15 and 14 was obtained for dichlorvos and malathion, respectively, which was still lower than the lowest enrichment factor of 23 obtained for dichlorvos in static SDME. For the rest analytes such as phorate, fenitrothion, parathion and quinalphos, only 2–6-fold of enrichment factors were obtained in cycle-flow SDME, while the enrichment factors of nearly 100-fold were got in static SDME for the tested OPPs (except for dichlorvos 23-fold). The possible reason for this is that extraction dynamic of the six OPPS is slow in the cycle-flow SDME, and only at the strong stirring they can be extracted efficiently like in static SDME.

For the real sample analysis, the quantitative analysis was carried out in the mode of static SDME due to its better analytical sensitivity.

3.3. Validation

The validation was performed for six OPPs with tributyl phosphate as internal standard. Fig. 5(a–c) show the typical chromatograms obtained for the mixed standard OPPs solution, spiked lake water and apple juice samples after static SDME.

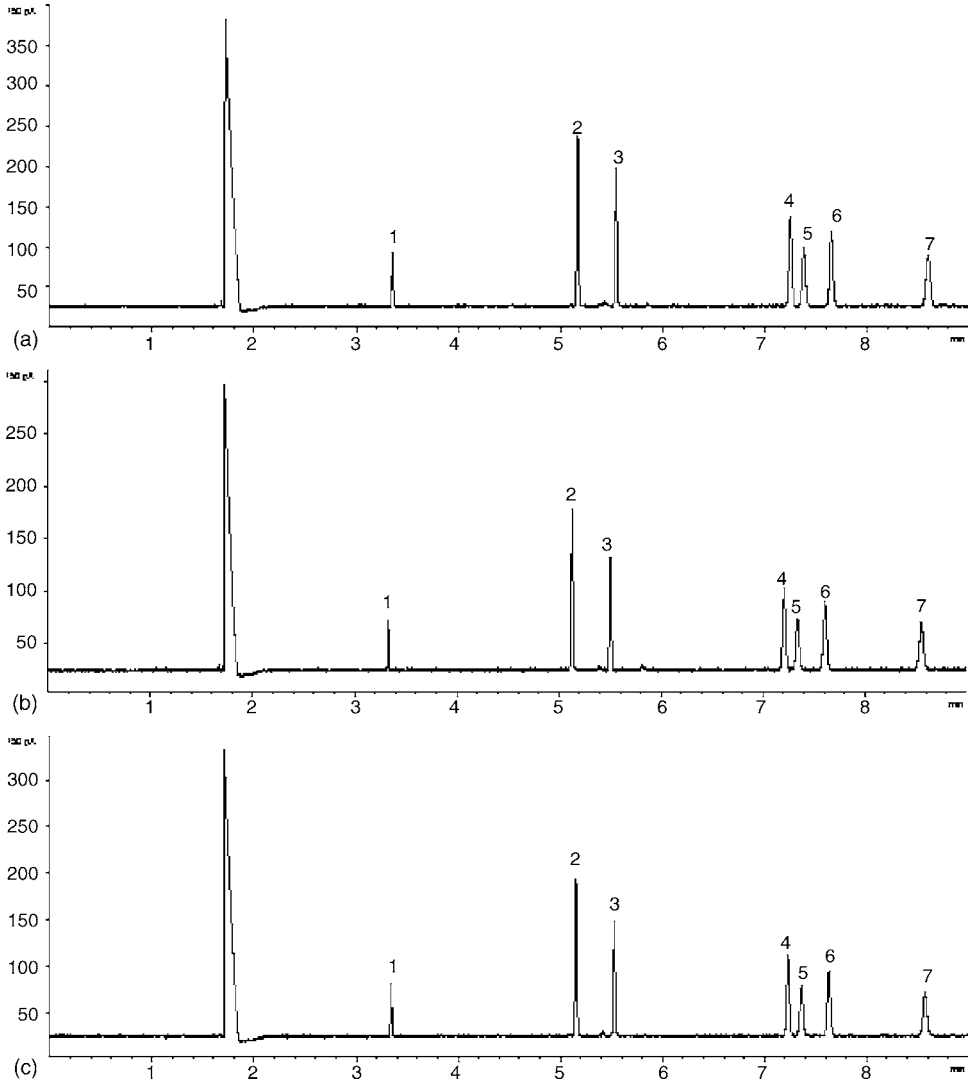

Fig. 5. Chromatograms of six OPPs after static SDME. (a) Chromatogram of the mixed standard OPPs solution with individual concentration of 2 ng/mL; (b) chromatogram of lake water, spiked to 2 ng/mL; (c) chromatogram of apple juice, spiked to 200 ng/mL (analysed after 1/100 dilution). (1) dichlorvos; (2) TBP (internal standard); (3) phorate; (4) fenitrothion; (5) malathion; (6) parathion; (7) quinalphos. Conditions: 20 min extraction with 1.5 μL of toluene at a stirring rate of 600 rpm, injection volume 1.0 μL.

The results concerning precision, limits of detection (LODs), linear dynamic range and calibration data are listed in Table 2.

The linear response range was examined over the concentration range of 0.5–50 ng/mL for all tested OPPs and a high level of linearity over the range of 0.5–50 ng/mL (except for dichlorvos 1.0–50 ng/mL) with correlation coefficients (r) ranging from 0.9995 to 0.9999 were obtained in water. The limits of detection were obtained adding standard solutions to the water and determining the minimum amount of each analyte required to give a S/N = 3, after applying the static SDME method. They were found to be in the range of 0.21–0.56 ng/mL for the six studied OPPs. Table 2 also listed the LODs data reported in literatures for a comparison. As could be seen, the LODs obtained by this method are lower than the LODs reported in references [32,33,35,38–40], but a little bit higher than that given in references [10,22,23,34,36,37]. However, the proposed method is sensitive enough to determine the OPPs in the environmental water and fruit juice samples. The precision of the experimental procedure was evaluated under the optimum extraction conditions. This yielded a standard deviation (R.S.D.) of between 1.7 and 10.0% for a total of three replicates.

3.4. Application

According to the literature [41], the complexity of the fruit matrix makes it difficult to obtain a quantitative extraction of pesticides, but the decrease in concentration of the interfering components by a dilution of the sample makes it possible for the quantification of pesticides. Therefore, for the analysis of pesticides in fruit juice matrices, a 100-fold dilution of fruit juice samples was performed prior to its analysis. For the water sample analysis, no dilution was required.

3.4.1. Analysis of water and fruit juice samples

Static SDME procedure was applied for determining six OPPs (dichlorvos, phorate, fenitrothion, malathion, parathion and quinalphos) in the water sample from East Lake (Wuhan, China) and fruit juice samples after 1/100 dilution with water. None of the six OPPs was detected in the water and fruit juice samples.

3.4.2. Analysis of spiked samples

East Lake water samples were spiked at concentration of 2 and 5 ng/mL with the standard mixture solution containing 1 μg/mL of each pesticide. Samples from each level were extracted in three replicates by static SDME. We compared the real concentration added and the concentration values obtained by interpolation in the calibration graphs prepared by spiking the pesticides in water and extracting them by static SDME. The recovery of the method was defined as the percentage ratio between concentration of analyte found and concentration of analyte added. And the results were listed in Table 3. As could be seen, the recoveries for the six OPPs were between 90.7 and 106.5% with an R.S.D. of less than 8.5%.

After filtration, samples of 100 mL fruit juice (apple, pear and orange juice) were spiked at concentration of 50 and 200 ng/mL with the individual standard stock solutions of 100 μg/mL,

Table 4
Six OPPs recoveries in fruit juice samples at the two spiked levels

OPPs	Apple juice				Pear juice				Orange juice			
	Added (ng/mL)	Found (ng/mL)	Recovery (%)	R.S.D. (%)	Added (ng/mL)	Found (ng/mL)	Recovery (%)	R.S.D. (%)	Added (ng/mL)	Found (ng/mL)	Recovery (%)	R.S.D. (%)
Dichlorvos	50	n.d.	–	–	50	n.d.	–	–	50	n.d.	–	–
	200	197.46	98.7	11.8	200	218.32	109.2	3.0	200	173.14	86.6	13.3
Phorate	50	44.58	89.2	9.1	50	41.65	83.3	9.7	50	48.00	96.0	4.6
	200	227.19	113.6	1.8	200	193.53	96.8	13.4	200	190.27	95.1	12.7
Fenitrothion	50	45.04	90.1	13.3	50	38.83	77.7	8.2	50	49.69	99.4	0.6
	200	197.18	98.6	4.5	200	166.38	83.2	10.2	200	177.96	89.0	5.8
Malathion	50	48.90	97.8	11.9	50	51.28	102.6	7.3	50	52.48	105.0	0.5
	200	200.27	100.1	3.6	200	171.25	85.6	11.8	200	180.27	90.1	10.1
Parathion	50	50.33	100.6	9.6	50	50.81	101.6	6.8	50	53.67	107.3	1.0
	200	202.46	101.2	5.6	200	171.96	86.0	5.5	200	178.03	89.0	9.1
Quinalphos	50	40.88	81.8	1.7	50	41.12	82.2	1.2	50	45.03	90.1	3.8
	200	204.86	102.4	0.8	200	168.65	84.3	2.3	200	175.67	87.8	8.4

Analysed after 1/100 dilution with water; n.d., not detected.

respectively. One milliliter was further diluted to 100 mL. Table 4 lists the OPPs recoveries for the spiked fruit juice samples after extraction in three replicates by static SDME. It demonstrated that the recoveries for all OPPs spiked samples were between 77.7 and 113.6% with an R.S.D. of less than 13.4%, only an exception for the sample spiked with 50.0 ng/mL dichlorvos in which no dichlorvos was detected.

Dilution of samples is adequate to determine low levels of most pesticides because of the low limits of detection of the method. The method was validated in a wide range for the pesticides studied.

4. Conclusion

Two types of direct SDME, both static SDME and cycle-flow SDME, were comparatively studied in this work. Some important experimental parameters affecting the extraction efficiency of OPPs were also studied and optimized. The enrichment factors for six OPPs in static SDME were nearly 100-fold (except for dichlorvos 23-fold), which were much better than that in cycle-flow SDME. For the sample analysis, the quantitative analysis was carried out in the mode of static SDME due to its better analytical sensitivity. A 100-fold dilution of fruit juice samples is adequate to determine levels of most pesticides below the MRLs because of the low limits of detection of the method.

The optimized static SDME technique in conjunction with GC-FPD is a fast, simple and economical procedure for analysis of OPPs in the water and fruit juice samples, does not require any preliminary sample preparation step and reduce the volume of (toxic) solvents used. The method is precise, reproducible and has a high level of linearity over a wide range of analyte concentrations.

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