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Quantification of multi-residue levels in peach juices, pulps and peels using dispersive liquid–liquid microextraction based on floating organic droplet coupled with gas chromatography-electron capture detection

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ABSTRACT

In this paper, polychlorinated biphenyl (PCB), organochlorine pesticide (OCP) and pyrethroid pesticides in peach was investigated by comparing their residual level in peach juice, pulps and peels using dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) combined with gas chromatography-electron capture detection (GC-ECD). Extraction conditions such as the type of extractant, volume of extractant and dispersant, salt effect and extraction time were optimized. For juice samples, the linearity of the method was obtained in the range of 10–2000 ng L^{-1},with determination coefficients > 0.99. The limits of detection (LOD) of the method were ranged between 2.8 and 18.5 ng L^{-1}. For pulp and peel samples, the developed method is linear over the range assayed, 1–20 μg kg^{-1},with coefficients also >0.99. The relative recoveries of compounds analyzed from juice, pulp and peel samples were in the range of 73–106% with a relative standard deviation between 2.6 and 11.8%. The proposed method was applied to the simultaneous analysis of residues in real peach juice, pulp and peel samples. As a result, there were no target analytes found in peach juices and pulps while 3.3 μg kg^{-1} cyhalothrin and 3.5 μg kg^{-1} fenvalerate were found in peels. The experiment results revealed that the pyrethroid residues just deposited on the peels of the fruits, but did not move into pulps and juices.

1. Introduction

In recent years, potential health risks from pesticides and other organic pollutant residues in food stuffs have become a main public concern. Pesticides such as OCP and pyrethroid pesticides have been used extensively to spray on the surface of fruits to control pest. So in our daily life, we are always persuaded to wash the fruits before consumption [1]. However, the pesticide residues tend to deposit on the fruit peels and transfer from peels into pulps and juices in long term process and cause some risk to human health [2,3]. Meanwhile, PCBs were widespread organic pollutants in air, soil and water. They are highly resistant and bioaccumulative in food chain [4], so a trace level PCBs may still exist in fruits. Therefore, determination of multi-residues in fruits as well as the comparative analysis of multi-residue mobility in different parts of fruits was an urgent need for health protection [5].

Since the investigation of multi-residue mobility required that the fruit juices, pulps and peels should be separated and compounds of different polarities, solubilities, volatilities in different parts of fruits should be simultaneously extracted and analyzed, we should develop an efficient sample pretreatment method for trace level detection [6].

Sample preparation of multi-residues analysis is normally required to isolate and concentrate compounds of interest from the sample matrix prior to chromatography analysis.

Several clean up and pre-concentration methods coupled with gas chromatography (GC) and high performance liquid chromatography (HPLC) were developed [7–9]. Supercritical fluid extraction (SFE) [10], solid-phase extraction (SPE) [2,11], disposable pipette extraction (DPX) [12], Soxhlet extraction (SE) [4], solid-phase microextraction (SPME) [13], microwave assisted solid phase microextraction (MAE-SPME) [14] and single-drop microextraction (SDME) [15] have been used for extraction of OCP pesticides, PCBs and pyrethroid pesticides in fruits by previous investigators. Matrix

Abbreviations: PCB, polychlorinated biphenyl; OCP, organochlorine pesticide; DLLME-SFO, dispersive liquid–liquid microextraction solidification floating organic; DPX, disposable pipette extraction; SDME, single-drop microextraction; MSPD, matrix solid-phase dispersion; SBSE, stir bar microextraction; EF, enrichment factor; LOD, limit of detection; LOQ, limit of quantification; GC, gas chromatograpy; ECD, electron capture detection; RR, relative recovery; RSD, relative standard deviation.

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solid-phase dispersion (MSPD) [3], headspace solid-phase microextraction (HS-SPME) [16] and stir bar microextraction (SBSE) [17] were also applied to other pesticide extraction in fruits.

In 2008, dispersive liquid–liquid microextraction (DLLME) method based on solidification of floating organic drop (DLLME-SFO) technique was developed by Leong and Huang [18,19]. In this method, the extractant has low density and low melting point, so the extractant droplets can be easily collected by solidifying it on the surface of the sample solution and the very tiny particles of the system settle down without interference with the target analytes. Moreover, this method was suitable for the extraction of non-polar organic compounds [20].

As far as our information goes, the DLLME-SFO method for simultaneous extraction and determination of PCBs, OCP and pyrethroid pesticides in juices, pulps and peels has not been reported. This work focused on the investigation of PCBs, OCP and pyrethroid pesticide multi-residues in different parts of fruit samples using DLLME-SFO. In addition, the microwave radiation extraction step was employed for the extraction of target analytes in peach pulps and peels before DLLME-SFO and thus the matrix effect was reduced effectively.

2. Experimental

2.1. Materials

2,2′,5-Trichlorobiphenyl (PCB 18), 2,4,4′-trichlorobiphenyl (PCB 28), 2,2′5,5′-tetrachloro-biphenyl (PCB 52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101), 2,2′3,4,4′5′-hexachloro-biphenyl (PCB 138), 2,2′4,4′5,5′-hexachlorobiphenyl (PCB 153), 2,2′3,4,4′5,5′-heptachloro-biphenyl (PCB 180), 2,2′3,3′4,4′5,5′6-nonachlorobiphenyl (PCB 206), bifenthrin, fenvalerate cyhalothrin, fenpropathrin were obtained from Dr. Ehrenstorfer GmbH (Augsburg, German). Aldrin, P,P′-DDD were purchased from Environmental Protection Monitoring Research Institute, Ministry of Agriculture (Beijing, China). The 0.5 $\mu g\,mL^{-1}$ individual stock solutions of the above-mentioned fourteen analytes were prepared in methanol and stored in the refrigerator. The daily standard working solutions of different concentrations were obtained by diluting the stock solutions with water. Tetradecane, hexadecane, dodecan-1-ol and undecan-1-ol were all of analytical grade and purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). HPLC-grade methanol and acetone were obtained from Tedia Company Inc. (OH, USA). Sodium chloride (Zhan yun Chemical Co. Ltd., Shanghai, China) was used in the subsequent experiment. Deionized water used was purified on a Milli-Q water purification system (Millipore Corporation, Billerica, MA, USA). Peach samples were purchased from a supermarket in Wuhan, China.

2.2. Instrument conditions

The experiments were carried out on an Agilent 6890 gas chromatography (Agilent Technologies, Palo Alto, CA, USA) equipped with electron capture detector and split/splitless injector. A DB-17 capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) was used for separation. The temperature program was from 140 °C to 260 °C at 15 °C min^{-1} and held at 260 °C for 6 min, then from 260 °C to 290 °C at 20 °C min^{-1} and held at 290 °C for 6 min. The carrier gas was nitrogen (purity 99.9995%) at a flow rate of 1.0 mL min^{-1}, the injector was operated at 300 °C and used splitless mode, the temperature of the detector was set at 300 °C and N_2 was used as a make-up gas at a flow rate of 40 mL min^{-1}, Hamilton syringe (Reno, NV, USA) was used to inject 1 μL of the sample into the GC.

The centrifuge process was produced on 80-2 centrifuge (Changzhou Guohua Electric Appliance Co. Ltd., Jiangsu, China). A blender (Midea Group Co. Ltd., China), a vacuum freezing dryer (Songyuan Huaxing Technology Development Co. Ltd., Beijing, China) and a SmithCreator™ microwave oven (Personal Chemistry AB, Uppsala, Sweden) were used for the sample preparation.

2.3. Sample preparation

The peach pulps were cut into pieces, and then put into a stainless steel blender to homogenize. After filtration, peach juice and the pulpy residues were collected separately. The peach peels were also cut into pieces and homogenized. After vacuum freeze drying, the peach pulps and peels were powdered, sieved through a 40-mesh sieve and stored in a refrigerator at 4 °C before use. The juice samples were diluted with ultra pure water in the ratio of 1:1 before use.

2.4. Extraction procedures

For peel or pulp samples, 5.0 mL acetone was added to 0.5 g spiked peach peel (pulp) samples in a microwave tube. The sealed tube was placed in a focused Smith Creator™ microwave oven with irradiation at 60 °C for 30 min. After extraction, 0.4 mL acetone in the sealed test tube was injected rapidly into a 10 mL screw cap test tube with conic bottom containing 5 mL of double distilled water. Next, 8.0 μL dodecan-1-ol was also immediately injected into the aqueous solution using a 25 μL syringe. Then the tube was in the water bath under ultrasound for 2 min. A cloudy solution (water, acetone and dodecan-1-ol) was formed in the glass test tube while the analytes were extracted into the droplets of dodecan-1-ol. The mixture was then centrifuged for 2 min at 4000 rpm, maybe a small amount of extractants are miscible with dispersants, the dodecan-1-ol phase (5 ± 0.5 μL) rose to the surface of the aqueous solution because of the lower density than that of water. The test tube was cooled in an ice bath for a few minutes and then the liquid organic droplets floating on the surface were frozen. The solidified droplet was removed with a small medicine nipper and placed into a 200 μL polychloroprene rubber tube at room temperature. Subsequently, the solid organic drop melted quickly and was diluted with methanol according to the ratio of 1:10 because of the high viscosity of dodecan-1-ol. 1 μL of the mixture was injected into GC for analysis.

For juice samples, a mixed solution of 8.0 μL dodecan-1-ol (extraction solvent) and 0.4 mL acetone (dispersive solvent) was injected rapidly into a 10 mL screw cap test tube with conic bottom containing 5 mL juice sample. A cloudy solution (water, acetone and dodecan-1-ol) was formed in the glass test tube while the analytes were extracted into the droplets of dodecan-1-ol, the subsequent procedure was the same as that of peel and pulp sample.

2.5. Validation experiments

The individual stock standard solution was prepared in methanol at a concentration of 0.5 $\mu g\,mL^{-1}$. The daily standard working solutions of 10, 20, 50, 100, 500, 1000, 2000 $ng\,L^{-1}$ for 5 mL juice samples or 1.0, 3.0, 5.0, 7.0, 10, 15, 20 $\mu g\,kg^{-1}$ for 0.5 g peel or pulp samples were obtained by diluting the stock solutions with water. In order to validate the linearity of the DLLME-SFO–GC method, a series of the above-mentioned spiked samples with different concentrations were extracted by dodecan-1-ol with the DLLME-SFO and analyzed by GC-ECD.

To investigate the extraction recoveries, juice (after dilution) samples, spiked almost at two concentrations of 10 $ng\,L^{-1}$ and 100 $ng\,L^{-1}$; peel and pulp samples, spiked nearly at two concentrations of 1.0 and 5.0 $\mu g\,kg^{-1}$, respectively, were extracted under the

optimized conditions. Each treatment was in triplicate. The relative recovery (RR) is calculated by the following equation:

$$RR = \frac{C_{found} - C_{real}}{C_{add}} \times 100$$

C_{found} represents the concentration of the analyte after adding a known amount of standard to the real sample. C_{real} is the concentration of the analyte in the real sample, and C_{add} refers to the concentration of a known amount of standard that was spiked in the real sample.

The EF (Enrichment factor) was defined as the ratio between the analyte concentration in the floated phase (C_{flo}) and initial concentration of analyte (C_0) within the sample.

$$EF = \frac{C_{flo}}{C_0}$$

3. Results and discussion

For peach pulp and peel samples, it is necessary to choose a suitable solvent to extract the fourteen non-polar priority pollutants from the solid fruit samples by microwave. Acetone was considered as extraction solvent because of its low toxicity and the effect to both polar and non-polar compounds. Meantime, acetone was suitable to act as a dispersant in DLLME-SFO. Moreover, some reports stated that fruit and vegetable extracted in acetone were usually cleaner than those obtained with other solvents [21,22].

3.1. Selection of the type and volume of extraction solvent for DLLME-SFO

To achieve optimal results, a suitable extraction solvent must be selected. The extraction solvent should meet the following requirements: (a) lower density than water, (b) low melting point, (c) low water solubility, (d) high extraction capability of target compounds and (e) good chromatographic behavior. Based on the above consideration, different kinds of extractant including dodecan-1-ol, undecan-1-ol, n-tetradecane and n-hexadecane were evaluated. For n-tetradecane (melting point: 5.8 °C) and n-hexadecane (melting point: 18 °C), their hydrophobicity was so strong that it could not be solved in the common dispersive solvent. Moreover, the organic droplet formed a thin flat shape on the surface of the solution, so it melted quickly and difficult to handle. The best result was achieved when using dodecan-1-ol (melting point: 24 °C) and undecan-1-ol (melting point: 11 °C) due to their suitable melting point and good affinity with target analytes. However, the dodecan-1-ol has a little higher extraction efficiency for all target analytes than undecan-1-ol does and dodecan-1-ol is cheaper than undecan-1-ol. So, dodecan-1-ol was selected as the best extraction solvent for further studies.

Different volumes of dodecan-1-ol (5.0, 8.0, 10.0, 15.0, 20.0, 25.0 μL) was also studied. As shown in Fig. 1, the EF values decreased while dodecan-1-ol volume increased. The volume of dodecan-1-ol less than 5.0 μL could not form droplet. The EF corresponding to 5 μL of dodecan-1-ol got the biggest value. However, the recovery ratio obtained with 5 μL of 1-docanol was only 50%, which was significantly lower than that of 8 μL of extractant (>70%). Thus, in subsequent experiments, 8 μL of dodecan-1-ol was used as the extraction solvent.

3.2. Selection of dispersant volume for DLLME-SFO

After selecting acetone as the disperser solvent, its volume should be optimized. At low volume, acetone cannot disperse extraction solvent properly and cloudy solution is not formed completely. However, at high volume, the solubility of analytes in water increases, which will result in the decrease of the extraction efficiency. To obtain optimized volume, the effect of dispersant volume on the extraction efficiency was investigated in the range of 0.2–1.0 mL (the volume of dodecan-1-ol was fixed as 8.0 μL). As shown in Fig. 2, extraction efficiency increased with the increase of the volume of acetone when it was less than 0.4 mL. Reduction in extraction efficiency was observed after the volume of acetone exceeded 0.4 mL. So, 0.4 mL was chosen as the optimum volume of the disperser solvent.

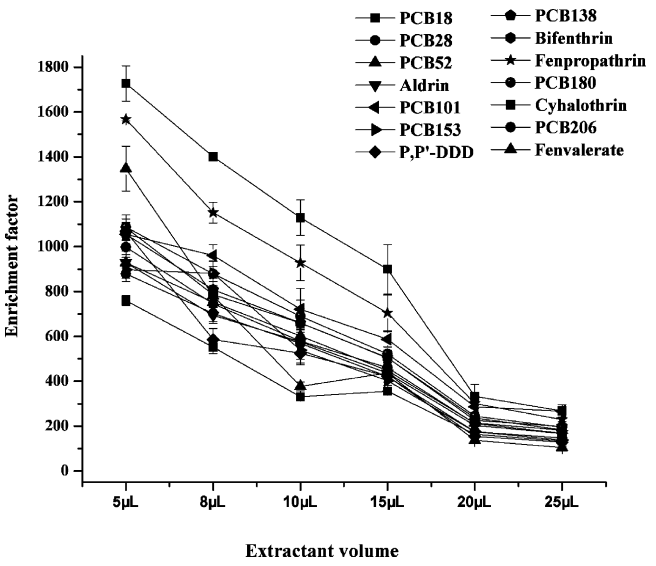

Fig. 1. Optimization of extraction solvent volume. Concentration of mixture standard solution: 1.0 μg L^{-1}, volume of the juice samples: 5 mL; extractant: dodecan-1-ol; volume of dispersive solvent (acetone): 0.4 mL; extraction time: <2 min; no salt addition; error bars represent the standard deviation of the mean enrichment factor for $n = 3$ replicates.

3.3. Effect of salt and extraction time

The influence of ionic strength is also an important factor for extraction. Generally, the increase of the ionic strength can cause a decrease in the solubility of the analytes in sample solution and an enhanced extraction efficiency. Therefore, the influence of amount of sodium chloride on the extraction efficiency was studied in the range of 0–20% (w/v). However, the experimental results showed that EFs decreased slightly with the increasing of salt amount. The reason is that the decreased solubility of floating solvent in the aqueous phase resulted in the increasing of the volume of floating phase. As a result, the peak signal of analytes and the EFs decreased slightly. Consequently, further extractions were performed in the absence of any salt.

The extraction time was defined as the ultrasonic time after the mixture of extractant and dispersant was added into the samples. Ultrasound can accelerate the formation of fine cloudy solution, increase extraction efficiency and reduce extraction time. The effect of extraction time on the extraction efficiency was examined in the range of 0–3 min. The analytes were extracted into the fine droplets of dodecan-1-ol for about 2 min and the extraction equilibrium reached quickly. Therefore, 2 min was chosen for the further experiments.

3.4. Method validation

In order to validate the proposed method, the linearity, precisions, limits of detection (LOD) and limits of quantification (LOQ) were evaluated for peach juice, pulp and peel samples. As can be

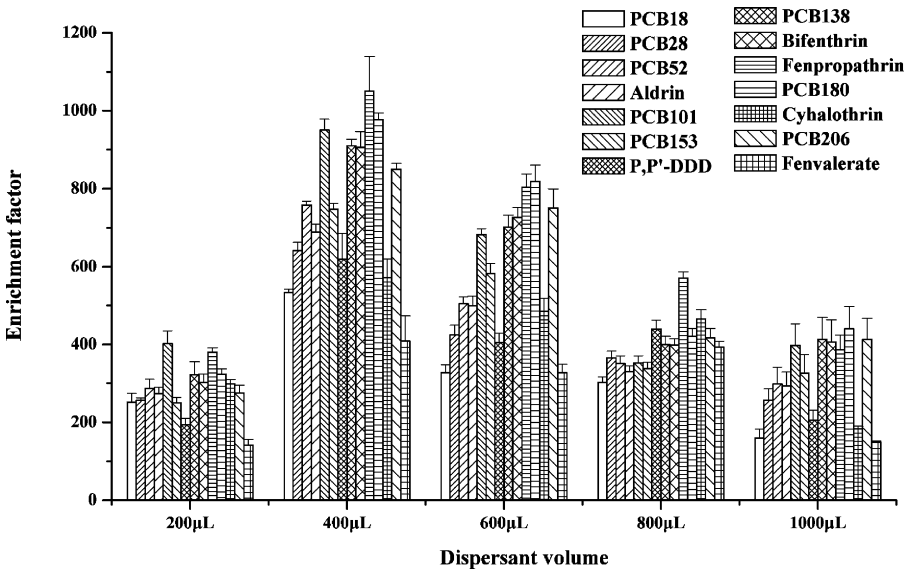

Fig. 2. Optimization of dispersive solvent volume. Concentration of mixture standard solution: 1.0 μg L^{-1}. Volume of the juice sample: 5 mL; volume of extractant (dodecan-1-ol) 8 μL; dispersive solvent: acetone; extraction time: <2 min; no salt addition; error bars represent the standard deviation of the mean enrichment factor for $n = 3$ replicates.

Table 1
Linearity equation, linearity, limits of detection, limits of quantification and repeatability of DLLME-SFO for peach juices.

Analytes	Linear equation	R	Linearity[a] (ng L^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})	EF[a]	RSD[b] (%) ($n = 6$)
PCB18	$Y = 2.38 \times 10^3 x - 60.34817$	0.9959	50–2000	18.5	48.0	540	4.5
PCB28	$Y = 11.47 \times 10^3 x - 94.2108$	0.9938	10–2000	3.0	10.0	663	5.4
PCB52	$Y = 7.81 \times 10^3 x + 17.6316$	0.9984	10–2000	3.0	9.8	747	4.3
PCB101	$Y = 16.09 \times 10^3 x + 653.1077$	0.9957	10–2000	3.2	10.7	917	6.0
PCB138	$Y = 22.82 \times 10^3 x - 553.6163$	0.9949	20–2000	6.7	22.0	905	5.0
PCB153	$Y = 18.43 \times 10^3 x - 372.4236$	0.9974	10–2000	3.9	9.6	745	4.1
PCB180	$Y = 36.40 \times 10^3 x - 1031.3119$	0.9942	10–2000	3.7	12.2	985	6.7
PCB206	$Y = 30.77 \times 10^3 x - 510.4267$	0.9959	10–2000	3.2	9.5	861	4.0
Aldrin	$Y = 29.69 \times 10^3 x - 723.0565$	0.9962	10–2000	2.8	9.3	699	5.0
P,P′-DDD	$Y = 12.33 \times 10^3 x - 442.3170$	0.9912	10–2000	3.1	10.2	673	10.7
Bifenthrin	$Y = 7.39 \times 10^3 x - 126.6934$	0.9956	10–2000	3.1	10.4	928	4.4
Fenpropathrin	$Y = 5.68 \times 10^3 x + 146.0219$	0.9959	10–2000	3.5	11.6	1089	8.5
Cyhalothrin	$Y = 5.73 \times 10^3 x - 72.0840$	0.9957	10–2000	4.0	10.6	681	13.5
Fenvalerate	$Y = 2.79 \times 10^3 x - 66.8505$	0.9950	50–2000	16.3	53.8	409	18.4

[a] Extraction conditions: juice sample volume, 5 mL; dispersive solvent (acetone) volume, 0.4 mL; extraction solvent (1-dodecanol) volume, 8 μL (sediment phase 5 ± 0.5 μL); no salt addition, room temperature; extraction time: <2 min.
[b] Relative standard deviation.

Table 2
Linearity equation, linearity, limits of detection and limits of quantification of microwave assisted DLLME-SFO for peach peels.

Analyte	Linear equation	R	Linearity[a] (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	RSD (%) ($n = 6$)
PCB18	$Y = 38.5436 \times 10^3 x - 1.2316$	0.9995	3–20	1.10	3.63	5.6
PCB28	$Y = 375.02279 \times 10^3 x - 352.6813$	0.9883	1–20	0.25	0.83	6.7
PCB52	$Y = 257.6688 \times 10^3 x - 151.0822$	0.9900	1–20	0.27	0.89	4.5
PCB101	$Y = 453.1284 \times 10^3 x + 468.7206$	0.9968	1–20	0.34	1.12	4.3
PCB138	$Y = 693.0042 \times 10^3 x - 636.9021$	0.9950	1–20	0.27	0.89	5.2
PCB153	$Y = 577.4002 \times 10^3 x - 444.8316$	0.9906	1–20	0.30	0.99	4.7
PCB180	$Y = 1206.0514 \times 10^3 x - 962.5208$	0.9954	1–20	0.37	1.12	5.8
PCB206	$Y = 1095.6071 \times 10^3 x - 513.5246$	0.9957	1–20	0.34	1.12	5.9
Aldrin	$Y = 915.9159 \times 10^3 x - 473.9528$	0.9945	1–20	0.30	0.99	7.0
P,P′-DDD	$Y = 502.5368 \times 10^3 x - 172.7581$	0.9827	1–20	0.28	0.92	9.8
Bifenthrin	$Y = 250.9079 \times 10^3 x - 148.3753$	0.9941	3–20	1.70	5.61	6.4
Fenpropathrin	$Y = 289.7699 \times 10^3 x - 121.6459$	0.9947	1–20	0.30	0.99	7.6
Cyhalothrin	$Y = 1583.4972 \times 10^3 x + 4041.9518$	0.9931	1–20	0.32	1.06	10.5
Envalerate	$Y = 848.06121 \times 10^3 x + 2541.1988$	0.9987	1–20	0.26	0.86	12.3

[a] Extraction conditions: (1) MAE: the mass of sample: 0.5 g spiked peach peel samples in a microwave tube; extraction solvent: 5 mL acetone; extraction temperature: 60 °C; extraction time: 30 min. (2) DLLME-SFO: water sample volume: 5 mL; extraction solvent (1-dodecanol) volume: 8 μL; dispersive solvent (acetone, the extraction solvent in MAE) volume: 0.4 mL; room temperature; extraction time: <2 min.

Table 3
Linearity equation, linearity, limits of detection and limits of quantification of microwave assisted DLLME-SFO for peach pulps.

Analyte	Linear equation	R	Linearity[a] ($\mu g\,kg^{-1}$)	LOD ($\mu g\,kg^{-1}$)	LOQ ($\mu g\,kg^{-1}$)	RSD (%) ($n=6$)
PCB18	$Y=95.9055\times10^3x-19.5622$	0.9935	3–20	0.89	2.97	4.7
PCB28	$Y=434.4619\times10^3x-359.8529$	0.9878	1–20	0.36	1.08	6.5
PCB52	$Y=286.2133\times10^3x-24.9033$	0.9909	1–20	0.28	0.92	5.5
PCB101	$Y=491.3491\times10^3x-21.0109$	0.9949	1–20	0.31	1.02	6.8
PCB138	$Y=928.5314\times10^3x-574.9877$	0.9919	1–20	0.38	1.14	5.6
PCB153	$Y=908.7323\times10^3x-806.7101$	0.9906	1–20	0.33	1.08	4.6
PCB180	$Y=1518.4195\times10^3x-913.4270$	0.9944	1–20	0.29	0.96	7.8
PCB206	$Y=1298.777\times10^3x-583.6724$	0.9953	1–20	0.26	0.86	5.3
Aldrin	$Y=1192.700\times10^3x-921.0023$	0.9947	1–20	0.23	0.76	6.4
P,P′-DDD	$Y=832.7581\times10^3x-1018.0265$	0.9987	1–20	0.32	1.05	8.6
Bifenthrin	$Y=424.8585\times10^3x-440.9287$	0.9975	3–20	1.75	5.77	7.4
Fenpropathrin	$Y=229.9079\times10^3x-63.0537$	0.9954	1–20	0.28	0.92	6.5
Cyhalothrin	$Y=533.8269\times10^3x-392.5755$	0.9815	1–20	0.37	1.22	11.3
Envalerate	$Y=249.9248\times10^3x+47.1079$	0.9685	1–20	0.28	0.92	12.1

[a] Extraction conditions: (1) MAE: the mass of sample: 0.5 g spiked peach peel samples in a microwave tube; extraction solvent: 5 mL acetone; extraction temperature: 60 °C; extraction time: 30 min. (2) DLLME-SFO: water sample volume: 5 mL; extraction solvent (1-dodecanol) volume: 8 μL; dispersive solvent (acetone, the extraction solvent in MAE) volume: 0.4 mL; room temperature; extraction time: <2 min.

Table 4
The relative recoveries of peach juice, pulp and peel spiked with different concentrations of PCBs, OCP and pyrethroid pesticides.

Analytes	Juice (% ±RSD, $n=3$)		Pulp (% ±RSD, $n=3$)		Peel (% ±RSD, $n=3$)	
	50 ng L^{-1}	100 μg L^{-1}	3 μg kg^{-1}	10 μg kg^{-1}	3 μg kg^{-1}	10 μg kg^{-1}
PCB18	96 ± 5.6	98 ± 3.2	92 ± 9.6	104 ± 4.7	84 ± 7.8	106 ± 4.2
PCB28	91 ± 5.8	99 ± 4.2	82 ± 6.4	94 ± 4.8	80 ± 5.9	103 ± 4.6
PCB52	89 ± 6.1	97 ± 5.4	93 ± 2.6	104 ± 4.4	81 ± 4.8	105 ± 3.2
PCB101	82 ± 5.2	101 ± 3.9	83 ± 6.3	98 ± 4.9	85 ± 5.1	105.0 ± 4.2
PCB138	97 ± 5.8	97 ± 5.8	90 ± 5.8	96 ± 4.7	91 ± 5.4	94.0 ± 3.8
PCB153	79 ± 4.9	100 ± 3.6	73 ± 5.2	94 ± 3.7	83.6 ± 4.6	103 ± 3.4
PCB 180	80 ± 5.1	102 ± 4.2	90 ± 4.8	105 ± 3.3	93.6 ± 3.8	98 ± 3.2
PCB206	93 ± 7.6	87 ± 4.8	79 ± 8.6	88 ± 5.1	88 ± 6.2	91 ± 4.9
Aldrin	96 ± 4.5	91 ± 4.2	77 ± 11.8	84 ± 3.8	92 ± 4.5	97 ± 3.6
P,P′-DDD	91 ± 5.4	93 ± 4.8	87 ± 8.9	89 ± 3.8	82 ± 4.1	96 ± 5.2
Bifenthrin	93 ± 5.5	91 ± 5.2	79 ± 5.9	88 ± 6.2	90 ± 3.8	92 ± 4.5
Fenpropathrin	86 ± 6.4	92 ± 4.5	91 ± 6.2	93 ± 6.7	86 ± 4.5	88 ± 7.6
Cyhalothrin	89 ± 6.1	92 ± 5.2	93 ± 5.8	79 ± 5.3	81 ± 4.2	86 ± 3.5
Fenvalerate	91 ± 5.1	86 ± 3.2	78 ± 4.5	81 ± 4.1	92 ± 4.8	94 ± 5.2

seen in Table 1, for the juice samples. The linearity of the method was evaluated using a series of samples with seven different concentrations being extracted by 8 μL undecan-1-ol with DLLME-SFO and analyzed by GC-ECD. Good linearities ranging from 0.9912 to 0.9984 was obtained for all of the target analytes. The EFs for 5 mL of sample solution containing the fourteen target analytes were between 494 and 606. As can be seen in Tables 2 and 3, for the peach pulps and peels, linearity of pulp and peel samples evaluated by spiking fourteen target analytes were observed in the range of 3–20 μg kg^{-1} for PCB 18 and bifenthrin, and 1–20 μg kg^{-1} for the rest twelve target analytes. The correlation coefficient ranged from 0.9827 to 0.9995. The LOD (calculated as three times the signal-to-

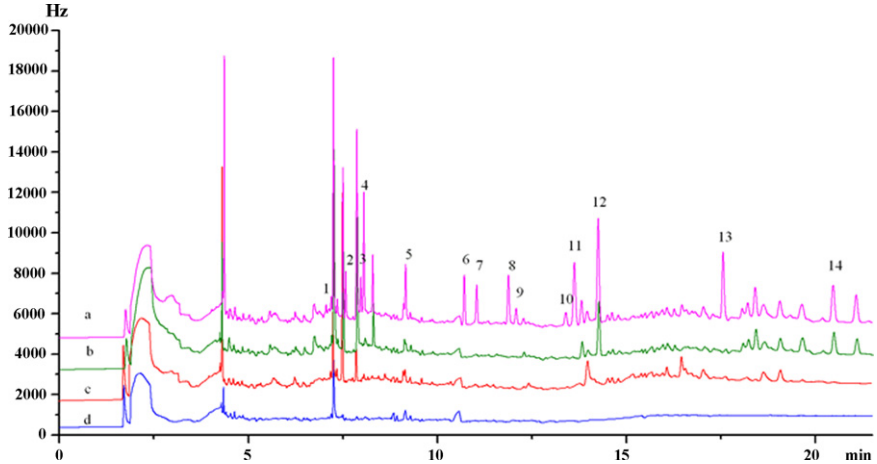

Fig. 3. Chromatographs of peach peel samples spiked with 10.0 μg kg^{-1} (a), blank peach peel samples (b), blank peach pulp samples (c), and blank peach juice samples (d). The samples were analyzed via DLLME-SFO–GC-ECD. Peak identification: (1) PCB 18, (2) PCB 28, (3) PCB 52, (4) aldrin, (5) PCB 101, (6) PCB 153, (7) P,P′-DDD, (8) PCB 138, (9) bifenthrin, (10) fenpropathrin, (11) PCB 180, (12) cyhalothrin, and (13) PCB 206, and (14) fenvalerate.

noise) and LOQ (calculated as ten times of the signal-to-noise) were obtained for all target analytes.

3.5. Application of the method

The developed method was applied to determination of eight PCBs, two OCPs and four pyrethroid pesticides in real peach juice, pulp and peel samples. The relative recoveries of the fourteen target analytes in the real samples at the different concentration levels are summarized in Table 4. Fig. 3 depicts the attained chromatograms peach peel samples spiked with 10.0 $\mu g\,kg^{-1}$ (a), blank peach peel samples (b), blank peach pulp samples (c), blank peach juice samples (d). As shown in Fig. 3, the results indicated that peach juices and pulps sample were free from target analytes while peach peels suffered from contamination of 3.3 $\mu g\,kg^{-1}$ cyhalothrin and 3.5 $\mu g\,kg^{-1}$ fenvalerate. Although PCB 101 can be detected in blank juice, peel and pulp samples, but it cannot be quantified. This means that pyrethroid pesticides have not transferred from peels into juices and pulps.

4. Conclusion

In this paper, DLLME-SFO–GC-ECD method was successfully developed for the determination of three class multi-residues in peach juices, pulps and peels. High enrichment factors (EFs), satisfied sensitivity and recoveries were obtained for all the target multi-residues in different parts of fruit samples. Experiment results demonstrated that the DLLME-SFO was a simple, quick, effective, accurate and reliable extraction method for multi-residues in juices, pulps and peels. Furthermore, it can be concluded that the pesticides commonly deposited on peels of the fruits.

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