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Solid-phase microextraction for organochlorine pesticide residues analysis in Chinese herbal formulations

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Abstract

Solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) was used to determine pesticide residues in Chinese herbal formulations. Fibers coated with a 100-μm film thickness of poly(dimethylsiloxane) was used to extract 19 organochlorine pesticides (OCPs). The pesticides in the study consisted of α-, β-, γ- and δ-hexachlorocyclohexane, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, *o,p′*-DDT, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan (I, II and sulfate), heptachlor, heptachlor epoxide, and methoxychlor. The optimal experimental procedures for the adsorption and desorption of pesticides were evaluated. The linearity was obtained with a precision below 11% RSD for the studied pesticides expect endosulfan sulfate (21%) in a wide range from 1 to 200 ng/g. Detection limits were reached at below ng/g levels. Heptachlor epoxide was determined at a calculated limit of 0.03 ng/g. Comparison between SPME and Soxhlet extraction showed that SPME has a less than one order detection limit for residue pesticide determination. The proposed method was tested by analyzing herbal formulations from a local market for OCP multi-residues. Some residues studied were detected in the analyzed samples. The results demonstrate the suitability of the SPME–GC–MS approach for the analysis of multi-residue OCPs in Chinese herbal formulations.

Keywords: Solid-phase microextraction; Organochlorine pesticides; Pesticides

1. Introduction

The herbal plants used as medicines or food ingredients among the Chinese have been prevalent for thousands of years. Some of the present medicines were developed by synthesizing compounds from herbal plant extracts. Herbal medicines have become an important part of life in Chinese society. People use some herbal medicines as dietary supplements to improve their health. The therapeutic effectiveness of most of these herbs is accepted without any scientific or clinical investigation [1,2]. The safety in taking herbal medicines, i.e., the pharmaceutical effects and side effects of herbal remedies must be seriously considered [3,4]. Regulations for dispensing herbal remedy prescriptions are being established in the Republic of China [5], European countries [6] and the US [7]. Because pesticides are applied to a broad variety of crops to reduce loss from weeds, insects and diseases, herbal plants have a high risk of contamination from agricultural chemicals, such as organochlorine pes-

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ticides (OCPs) [8]. Some OCPs were banned in the 1970s due to their toxicity, and persistence [9]. OCPs are resistant to hydrolysis, and those that undergo photochemical reaction tend to form compounds with a persistence comparable to, or greater than, their parent compounds [10]. The pesticide residue limits for foodstuff and feed were developed by the Food and Agriculture Organization (FAO) and World Health Organization (WHO) [11,12]. Generally, herbal medicines are taken by consumers for a long time. For safety and health, the risk of herbal plants exposed to OCP contamination must be considered. It is an important task to propose limits and pesticide residue monitoring methods for herbal plants.

Determining pesticide residue amounts in ranges below ng/g is difficult and extremely complex because of the need to isolate, accurately identify and measure minute quantities in large amounts of extraneous material. Many analytical procedures for analyzing pesticides have been proposed for a wide variety of sample types [13–16]. Multidimensional analytical systems combining gas chromatography (GC) [13–15] and high-performance liquid chromatography (HPLC) [16] with multiple detectors have provided many multi-residue measurement methods. GC is the most widely adopted technique in pesticide residue analysis because it separates well, is fast and has many available selective and sensitive detectors.

The accuracy and precision of pesticide analyses depends on both sample preparation and instrument performance. Proper sampling largely determines the validity of an analytical sample for residue analysis. Previous investigations have set forth various types of extraction methods for pesticides in different matrices, including liquid–liquid extraction [17], supercritical fluid extraction [3] and solid-phase extraction [18,19]. The liquid–liquid extraction, although the most frequently used technique, produces emulsions and various extraction efficiencies for different compounds. Solid-phase extraction is extensively employed for the trace enrichment of residues from complex matrices. However, the conventional extraction methods use organic solvents that poses a threat to the environment and human health. Moreover, solvent disposal is also quite expensive. Therefore, developing a relatively simple, fast, and solvent-free extraction method for pesticide residue analysis is a relevant task.

Solid-phase microextraction (SPME), introduced by Pawliszyn, can resolve many of the above problems [20,21]. The SPME mechanism is based primarily on adsorbing analytes from aqueous solutions onto a fused-silica fiber coated with a polymeric adsorbent. After extraction, the analytes are thermally desorbed from the fiber in the hot injector block of the gas chromatograph. SPME is rapid, solventless, portable, relatively independent of instrument design. It is a tool in widespread use for the isolation, concentration and purification of analytes from complex matrices such as serum, urine, food and contaminated water [22–25]. In this study, SPME combined with GC–ECD, or GC–MS for analyzing 19 OCPs in Chinese herbal formulations was evaluated. The OCPs included hexachlorocyclohexane (HCH) isomers (α-, β-, and δ-), lindane (γ-HCH), 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*o,p′*-DDT), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-DDT), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-DDD), and 1,1-dichloro-2,2-bis(*p*-chloro-phenyl)ethylene (*p,p′*-DDE), aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan (I, II and sulfate), heptachlor, heptachlor epoxide, and methoxychlor. The optimum conditions for the SPME technique and the detection limits of this procedure for organochlorine pesticide analysis are also discussed. The proposed method's effectiveness in determining OCPs in actual samples was tested by analyzing Chinese herbal formulations sold in local markets.

2. Experimental

2.1. Reagents and materials

All solvents used were analytical or research grade. Glassware silanization was performed prior to use by soaking the glassware overnight in a toluene solution at a concentration of 10% dichlorodimethylsilane. The glassware was rinsed with toluene and methanol and then thoroughly dried for 4 h. A standard stock mixture, containing 18 chlorinated compounds (2000 μg/ml in toluene–hexane, 50:50) was purchased in 1-ml aliquots from Supelco (Bellefonte, PA, USA). *o,p′*-DDT was also purchased from Supelco. Pentachloronitrobenzene from Chem

Service (West Chester, PA) was used as the internal standard (I.S.). The standard stock mixtures were then diluted to the required concentration using methanol and spiked with the internal standard to produce standard solutions and maintained at 4°C in a refrigerator. The Ginseng ten formula (or named Ginseng and DangKuei ten combination) which is made from 10 herbs was chosen as a study sample for its complex composition. The blank Ginseng ten formula used has been monitored for the studied pesticides. The actual samples (*Cinnamon and Mahuang combination*, *minor Bupleurum combination*, *Ginseng and Astragalus combination*, *Ginseng combination*, *Paeonian radix*, *Pinellia combination*, *Rehmannia six formula*) were bought in a local drugstores in a homogeneous powder. The Chinese herbal formulations were usually dried and maintained at 4°C in a refrigerator. Herbal medicines analyzed and their compositions and sample amount for each analysis are as follows:

1. *Ginseng ten formula*: Ginseng radix (0.70 g), Atractylodis rhizoma (0.60 g), Astragali radix (0.70 g), Angelicae sinesis radix (0.60 g), Raeoniae alba radix (0.60 g), Cinnamomi ramulus (0.60 g), Hoelen poria (0.40 g), Glycyrrhizae radix (0.30 g), Ligustici rhizoma (0.40 g), Rehmanniae radix (0.70 g).
2. *Cinnamon and Mahuang combination*: Cinnamomi ramulus (1.10 g), Paeoniae radix (0.90 g), Ephedrae herba (0.90 g), Zingiberis rhizoma (0.90 g), Glycyrrhizae radix (0.90 g), Zizyphi fructus (0.50 g), Armeniacae semen (0.80 g).
3. *minor Bupleurum combination*: Scutellariae radix (0.60 g), Zizyphi fructus (0.10 g), Zingiberis rhizoma (0.60 g), Glycyrrhizae radix (0.60 g), Pinelliae tuber (1.50 g), Bupleuri radix (1.50 g), Ginseng radix (0.60 g).
4. *Ginseng and Astragalus combination*: Glycyrrhizae radix (0.90 g), Citri sinensis exocarpium (0.40 g), Angelicae sinesis radix (0.40 g), Astragali radix (1.80 g), Atractylodis rhizoma (0.50 g), Zingiberis rhizoma (0.40 g), Zizyphi fructus (0.40 g), Ginseng radix (0.50 g), Cimicifugae rhizoma (0.40 g), Bupleuri radix (0.40 g).
5. *Ginseng combination*: Ginseng radix (0.50 g), Atractylodis rhizoma (0.50 g), Astragali radix (0.50 g), Glycyrrhizae radix (0.50 g), Citri sinensis exocarpium (0.50 g), Cinnamomi ramulus (0.50 g), Angelicae sinesis radix (0.50 g), Rehmanniae radix (0.30 g), Schisandrae fructus (0.30 g), Hoelen poria (0.30 g), Paeoniae radix (0.80 g), Zingiberis rhizoma (0.30 g), Zizyphi fructus (0.30 g).
6. *Paeonian radix*: Paeonian radix (1.0 g)
7. *Pinellia combination*: Pinelliae tuber (1.50 g), Scutellariae radix (0.90 g), Zingiberis rhizoma dried (0.90 g), Ginseng radix (0.90 g), Glycyrrhizae radix (0.90 g), Coptidis rhizoma (0.30 g), Zizyphi fructus (0.90 g).
8. *Rehmannia six formula*: Moutan Radicis cortex (0.70 g), Corni fructus (1.0 g), Dioscoreae rhizoma (1.0 g), Rehmanniae radix (1.9 g), Hoelen poria (0.70 g), Alismatis rhizoma (0.70 g).

The single-component herbal medicine *Paeonian radix* was cut into very small pieces with scissors, ground into a fine powder with a mortar and pestle and homogenized.

2.2. Sampling

Chinese herbal formulation *Ginseng ten formula* (1.00 g) was loaded into 40-ml amber vials and followed by adding a known amount of OCPs (2 μg/ml, 100 μl) to prepare 200 ng/g OCPs fortified samples, and set overnight. The vials were then filled with 30 ml of water, and the vials were sealed with holed caps and PTFE-faced silicone septa (both purchased from Supelco). The SPME device consists of a reusable syringe assembly, and replaceable fiber assembly (Supelco). The fiber selected for the OCPs analysis was a fused-silica rod, 1 cm long, coated with 100 μm of polydimethylsiloxane (PDMS). The PDMS fibers were conditioned in the hot injection port of a gas chromatograph for 1 h at 250°C. Each sample was stirred vigorously during the sorption step using a 8.0-mm diameter×20.0-mm long stir bar and a stirring plate. After extraction, the needle on the SPME manual holder was set at its maximum length 4.5 cm in the GC injector and, then, the fiber was directly exposed to the hot injector for analysis. Thermal desorption of the analytes was achieved by inserting the sorbed fiber into the injection port (held at 250°C) for 5 min. In Soxhlet extraction, a 10-g herbal formulation sample was extracted with 200 ml of *n*-hexane–acetone (1:1) for 3 h. The extract was

evaporated to dryness using a rotary vacuum evaporator. The residues were redissolved in 1 ml isooctane for analysis.

2.3. Apparatus

A 30-m×0.25-mm I.D. fused capillary column DB-1301 (J&W Scientific, USA) with a stationary phase thickness of 1.0 μm was used for the chromatographic analysis. Under optimum study conditions, a Hewlett-Packard 5890 Series II (Palo Alto, CA, USA) gas chromatograph equipped with electron-capture detector (ECD) was used. The GC was operated in the splitless mode and the injector port temperature at 250°C. The combination of GC with mass spectrometer (MS) was used in quantitation and real sample analysis. Positive identification of compounds was based on comparison of GC retention times and mass spectra of authentic compounds. The GC–MS interface temperature was 270°C. A HP 5890 Series II gas chromatograph equipped with an HP 5989B MS Engine detector with EI was used for all mass spectrometric data and pesticides confirmation. The EI Mass spectrum mode was obtained at ion source 250°C, 70 eV and tuned to PFTBA (perfluorotributylamine). The mass spectra were obtained at a mass-to-charge ratio scan range of 35–450 amu. The filament emission current was set at 300 μA. For the detector, the electron multiplier was manually adjusted to 1900 eV. The solvent delay time was set at 3 min. Selected ion monitoring (SIM) mode was used in quantitation. The dwell time was set 100 ms for each ion. The helium carrier gas was held at a rate of 1 ml/min. The column temperature program was as follows: 50°C hold for 2 min, 30°C/min to 230°C hold for 5 min, 4°C/min to 280°C hold for 10 min.

3. Results and discussion

3.1. Development of SPME

The gas chromatograph equipped with electron capture detector was used to trace the optimum SPME methodology conditions. In general, the extraction efficiency is heavily dependent upon the extraction conditions. The SPME procedure is based on an equilibrium between the analyte concentration in the sample and that in the solid-phase fiber coating. Herein, the amount of an analyte extracted relied on the mass transfer of an analyte through the aqueous phase and the extraction time. Fig. 1 shows the abundance of chromatographic signals obtained for different extraction times when the fiber was employed in the extraction of OCPs in *Ginseng ten formula*. It can be observed that the signal increased with the extraction time. For most OCPs, the most abundant result was obtained at an extraction time greater than 90 min. The OCPs in the aqueous herbal formulations were extracted using a stirring bar for 90 min. Adding a salt to the sample matrix solution had varying effects on the equilibrium process, depending on the structure, analyte properties and matrix. The influence of salt on the pesticide extraction yield was investigated by adding various amounts of NaCl to the aqueous Ginseng ten formula. Three extractions were performed for every condition. Fig. 2 shows the extraction impression magnitude, as attributed to the addition of various NaCl concentrations. A diminution in extraction was obtained with an increasing concentration of NaCl from 10 to 30% (w/v) in aqueous *Ginseng ten formula* samples. These findings are in contrast to the effects obtained for some organic analytes in the literatures, in which adding salt enhances extraction [20,22]. This contribution may come from the properties of herbal medicines, which are natural products with high amounts of existing salt. The decrease in adsorption can be attributed to the addition of NaCl, which hampers the translation of pesticides, and ultimately, blocks the pesticides from being adsorbed onto the fibers. No salt was added in the experiments carried out in our study.

Decreasing the solubility of analytes in aqueous solutions will enhance the amount of analytes extracted onto the fiber. More subtle changes in sample pH may be used to provide additional solubility in the SPME process [22]. Usually analytes differ with regard to the pH at which they become an ionic form. The analyte form in the matrix affects the amount of translation, adsorption, and the extraction efficiency. In the studies, the pH of the original *Ginseng ten formula* aqueous solution was 5.3. The pH was varied from 3 to 11 and monitored to examine how pH affects the extraction. From the results in Fig. 3, the extraction for endosulfan I and endosulfan II decreased significantly by increasing

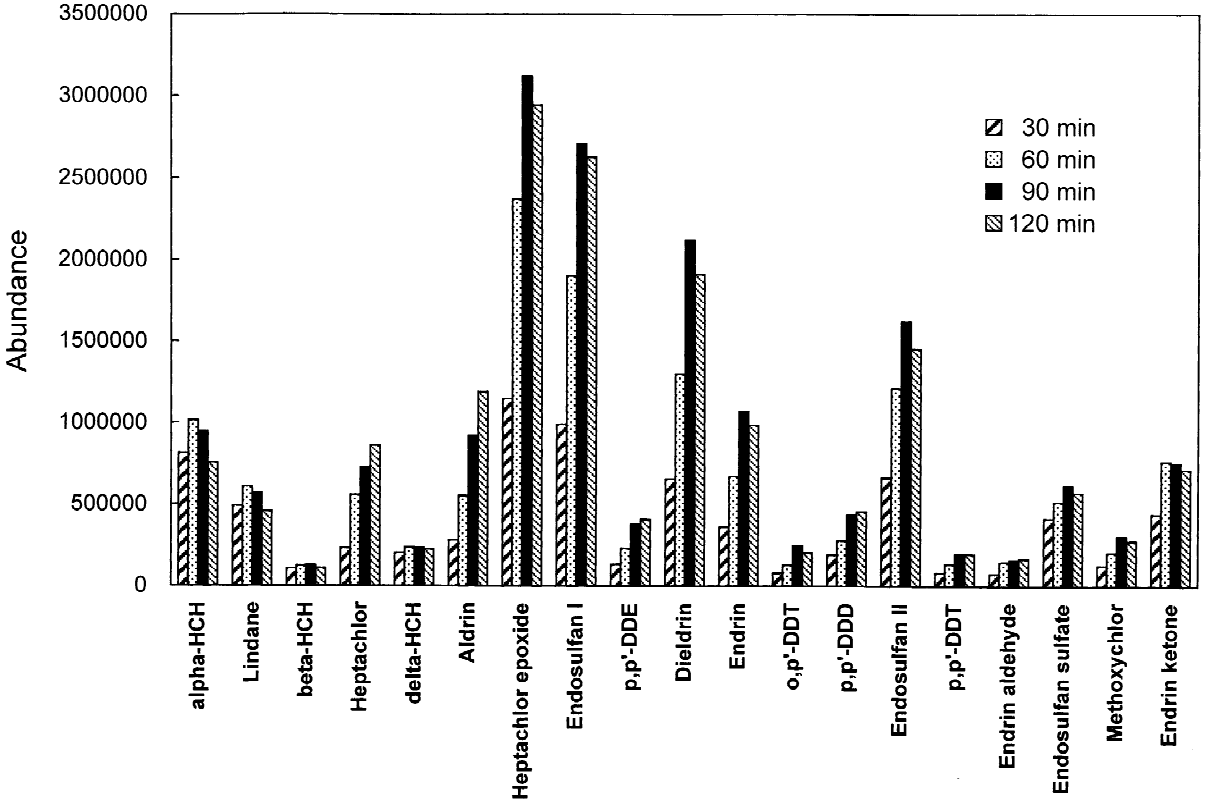

Fig. 1. Effect of extraction time on peak areas of 200 ng/g OCPs in *Ginseng ten formula* produced by SPME–GC–ECD.

the solution's pH to more than 9. The extraction of the other pesticides was not influenced significantly when the pH was changed. The organochlorine pesticides are little effected by pH because they are nonionizable compounds in aqueous solution. Therefore, extraction for pesticides in *Ginseng ten formula* samples with SPME was carried out using the original solution. The pesticide efficiency desorbed from the absorbed fiber will influence the detection sensitivity. The amounts of pesticides desorbed from the trapped fiber depended on the desorption temperature and the time the fiber is in the GC injector port. The optimum desorption conditions were also studied. Based on the results, the fiber desorbed at 250°C for 5 min was chosen for all experiments.

3.2. Analytical data

For trace analysis, GC–ECD combination is difficult for the determination analysis in the complex matrix especially for Chinese herb formulations. The high selectivity characteristic of mass spectrometer is used as the detector of GC for solving this problem. To demonstrate the reliability of this studied method, recoveries, correlation coefficients and detection limits were determined using spiked *Ginseng ten formula* samples. A gas chromatograph coupled with a mass spectrometer was used in this investigation. In the quantitative analysis, the SIM mode was performed using MS to increase sensitivity. In general, the most abundant ion is used for the ion of monitoring; the specific ion is used as the confirmed ion. In this study, some of the fragment ions of OCPs used in the literature for monitoring interfered with the background ions from herbal medicines [26]. After the background screening, the specific ion was chosen for monitoring. Table 1 lists the analytical SIM conditions for the studied pesticides. The characteristic ions were observed that were monitored in 12 groups of two to four ions, with a dwell time of 100 ms for each ion. The SPME and capillary column procedures were performed at the

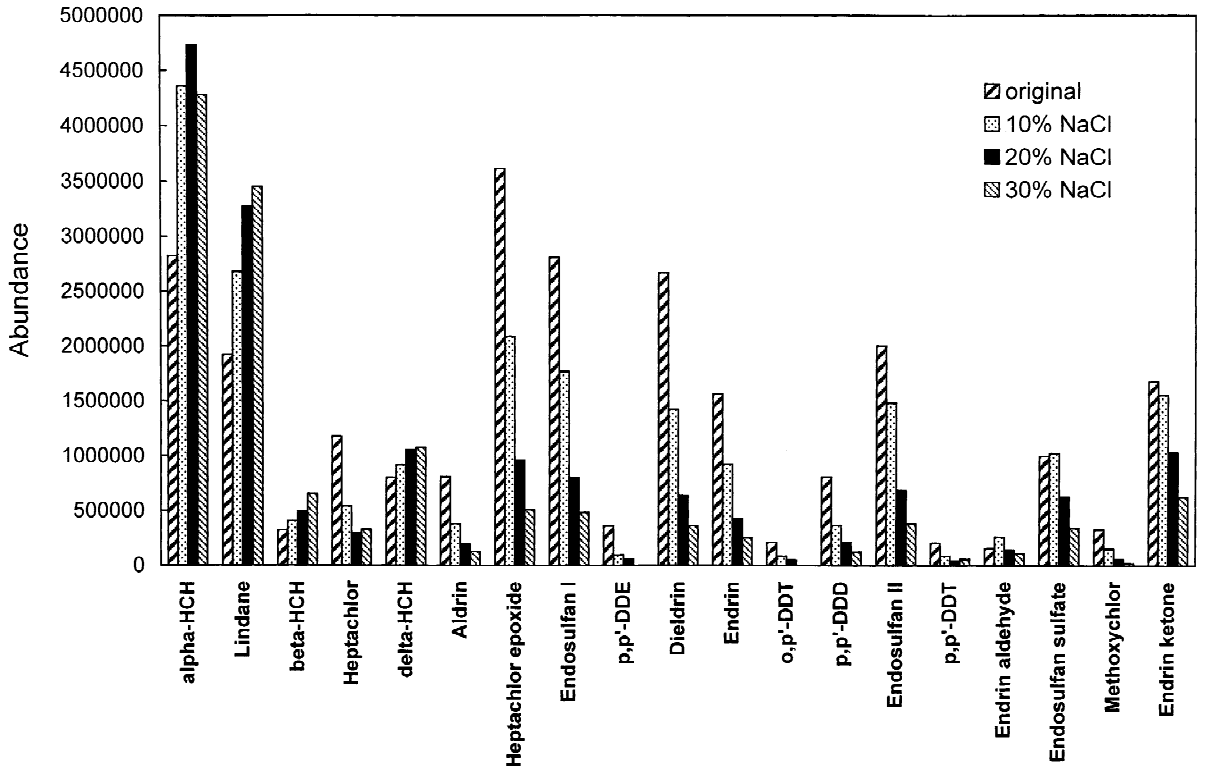

Fig. 2. Effect of different salt concentrations (10–30%, w/v, NaCl) on peak areas of 200 ng/g OCPs in *Ginseng ten formula* produced by SPME–GC–ECD.

optimal conditions. The ion chromatogram of 19 OCPs spiked at 100 ng/g in *Ginseng ten formula* are shown in Fig. 4. The peaks of all pesticides obtained were in good shape and well separated using SPME–GC–MS. A series of spiked samples containing the pesticides at various concentrations were made in the range between 1 and 200 ng/g. For the three separate experiments, the linear correlation coefficients were better than 0.991. This indicated that the fiber is linear and may be used over two orders magnitude. The linear range experiments provided the necessary information to estimate the detection limits, based on the lowest detectable peak with a signal-to-noise ratio of 3. Table 2 lists the detection limits (LODs) obtained using SPME–GC–MS. As this table indicates, the LODs for the determination of all pesticides in *Ginseng ten formula* samples are below the ng/g level. The best result was obtained for heptachlor epoxide, with a detection limit of 0.03 ng/g. Eight consecutive fiber extractions with the same concentration under the optimal conditions were performed to determine the precision of this method. The spiked sample containing 10 ng/g of each pesticide was investigated for this purpose. At room temperature, the reproducibility calculated as a relative standard deviation (RSD) varied between 3% for α-HCH and 21% for endosulfan sulfate. The precision of the SPME method was acceptable for extracting residue pesticides in herbal formulations.

3.3. Comparison with other extraction procedures

The Soxhlet extraction method was also applied to analyze pesticides in *Ginseng ten formula* samples. The concentrated extracts were analyzed using GC–MS. Table 2 lists the detection limits of the extracted pesticides. Based on the results, the detection limits reached using SPME–GC–MS are basically better than those achieved after a Soxhlet extraction using a solvent mixture of *n*-hexane–acetone (1:1). As the table indicates, the obtained LODs for all pesticides in SPME are one order less than those obtained using

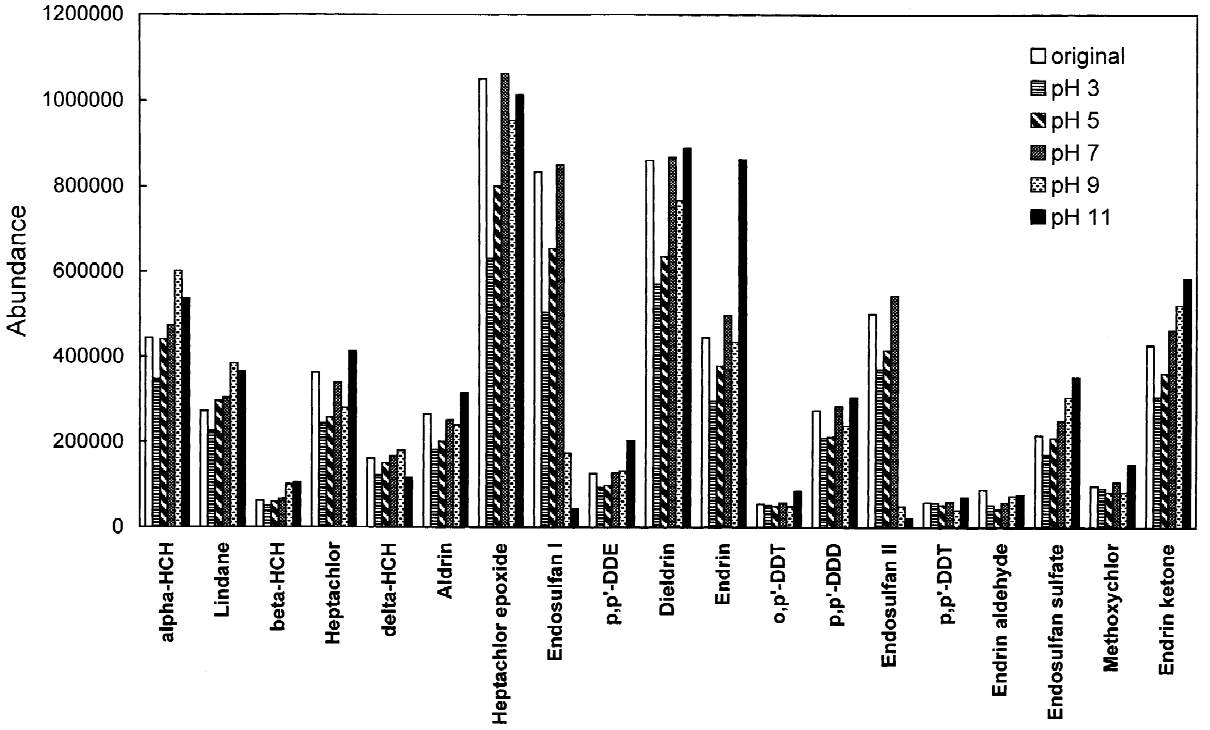

Fig. 3. Effect of different pH on peak areas of 200 ng/g OCPs in *Ginseng ten formula* produced by SPME–GC–ECD.

Table 1
The analytical SIM conditions of organochlorine pesticides

No.	Pesticide	SIM group	Start time (min)	Quantitated ion (m/z)	Confirmed ion (m/z)	t_R (min)
1	α-HCH	1	3.0	183	181	11.99
I.S.	Pentachloronitrobenzene		13.5	237	214	12.70
2	γ-HCH			181	183	13.00
3	β-HCH	2	13.5	183	109	14.22
4	Heptachlor			272	274	14.63
5	δ-HCH			183	109	15.27
6	Aldrin	3	15.6	66	263	15.80
7	Heptachlor epoxide	4	17.5	355	353	17.77
8	Endosulfan I	5	18.7	241	239	19.06
9	*p,p′*-DDE			246	318	19.53
10	Dieldrin	6	20.0	79	81	20.33
11	Endrin	7	20.8	263	245	21.20
12	*o,p′*-DDT			235	237	21.49
13	*p,p′*-DDD	8	21.8	235	237	22.07
14	Endosulfan II			197	241	22.41
15	*p,p′*-DDT	9	22.8	235	237	23.23
16	Endrin aldehyde			345	67	23.67
17	Endosulfan sulfate	10	24.3	229	272, 274	24.91
18	Methoxychlor	11	25.3	227	227	25.52
19	Endrin ketone	12	26.3	67	317	26.79

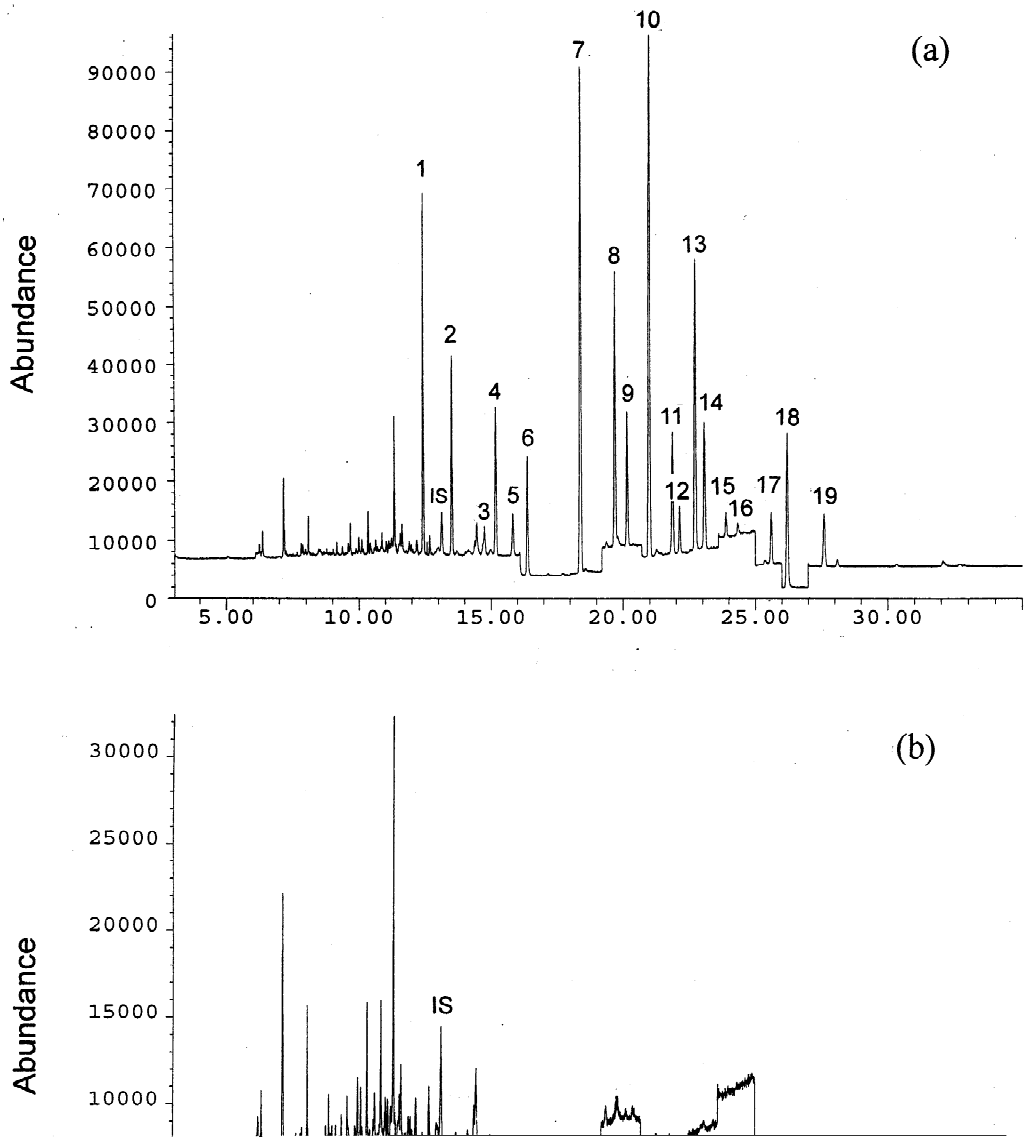

Fig. 4. The ion chromatograms of (a) spiked 100 ng/g 19 OCPs in *Ginseng ten formula* and (b) *Ginseng ten formula* blank analyzed by SPME–GC–MS. The numbers of pesticides are as listed in Table 1.

Table 2
Comparison of SPME and Soxhlet extraction methods for detection of pesticides in spiked *Ginseng ten formula*

Pesticide	SPME				Soxhlet extraction			
	Correlation coefficient[a]	Recovery (%)[b]	LOD (ng/g)	RSD (%)	Correlation coefficient[c]	Recovery (%)[d]	LOD (ng/g)	RSD (%)
α-HCH	0.996	5.6	0.1	3	0.999	81.3	1	3
β-HCH	0.994	0.5	0.5	7	0.991	91.7	2	4
Lindane (γ-HCH)	0.993	4.1	0.07	5	0.999	110.0	1	2
δ-HCH	0.992	2.2	0.1	11	0.999	114.3	4	6
Aldrin	0.994	4.1	0.2	8	0.990	90.0	2	5
Dieldrin	0.997	16.5	0.05	7	0.997	97.2	2	5
p,p-DDD	0.996	3.8	0.05	8	1.000	102.0	2	7
p,p′-DDE	0.991	1.7	0.09	8	0.996	86.5	1	7
p,p′-DDT	0.992	1.1	0.9	9	0.999	100.0	5	10
o,p′-DDT	0.991	0.8	0.3	10	0.997	106.3	1	4
Endrin	0.993	17.8	0.07	10	0.992	83.8	1	7
Endosulfan I	0.999	15.3	0.07	5	0.996	102.0	1	6
Endosulfan II	0.993	6.2	0.1	9	0.994	92.5	2	5
Endosulfan sulfate	0.998	1.9	0.6	21	0.995	92.6	2	8
Endrin aldehyde	0.996	2.2	0.7	9	0.999	85.4	2	10
Endrin ketone	0.999	5.6	0.2	5	0.993	90.1	2	9
Heptachlor	0.997	6.1	0.2	6	0.993	87.0	2	2
Heptachlor epoxide	0.993	13.3	0.03	11	0.997	97.3	2	3
Methoxychlor	0.993	15.1	0.06	10	0.997	98.8	2	6

[a] Concentration range, 1–200 ng/g.
[b] Spiked 10 ng/g.
[c] Concentration range, 10–2000 ng/g.
[d] Spiked 100 ng/g.

the Soxhlet extraction method. Although the manual SPME applied in this study for analyzing residue pesticides in herbal formulations is tedious and time consuming, many advantages are obtained in comparison with the conventional Soxhlet extraction method. The major advantages of SPME are operation simplicity and no need for organic solvents, which is very important for laboratory technician health safety. It also saves the analytical cost for solvent disposal. A high selectivity is obtained when SPME is combined with GC–MS. Therefore, SPME–GC–MS is a very useful analytical technique for trace pesticide determination in complex matrices.

3.4. Actual sample SPME

The effectiveness of the proposed method in determining multi-residue OCPs in actual samples was tested by analyzing some herbal formulations bought in a local market. The many herbal ingredients were imported from Southeast Asia. To carried out this analysis, a sample was prepared as described before and used without any added salt or pH adjustment. The SPME was performed at the described optimal conditions. The ion chromatograms of an actual herbal formulation sample are shown in Fig. 5. From the results (Table 3), including α-HCH, β-HCH, lindane, δ-HCH, aldrin, dieldrin, *p,p′*-DDE, endosulfan II, endosulfan sulfate and endrin ketone pesticides were found in the studies. The concentration of pesticides ranged from 2.2 to 119 ng/g. These results further demonstrate that the SPME–GC–MS system is highly effective in analyzing trace OCPs.

4. Conclusion

SPME is a simple, inexpensive, rapid and solvent-free sample preparation technique. The analysis selectivity method, which employs GC, can be substantially enhanced when using a high sensitivity mass spectrometer detector. This study demonstrated

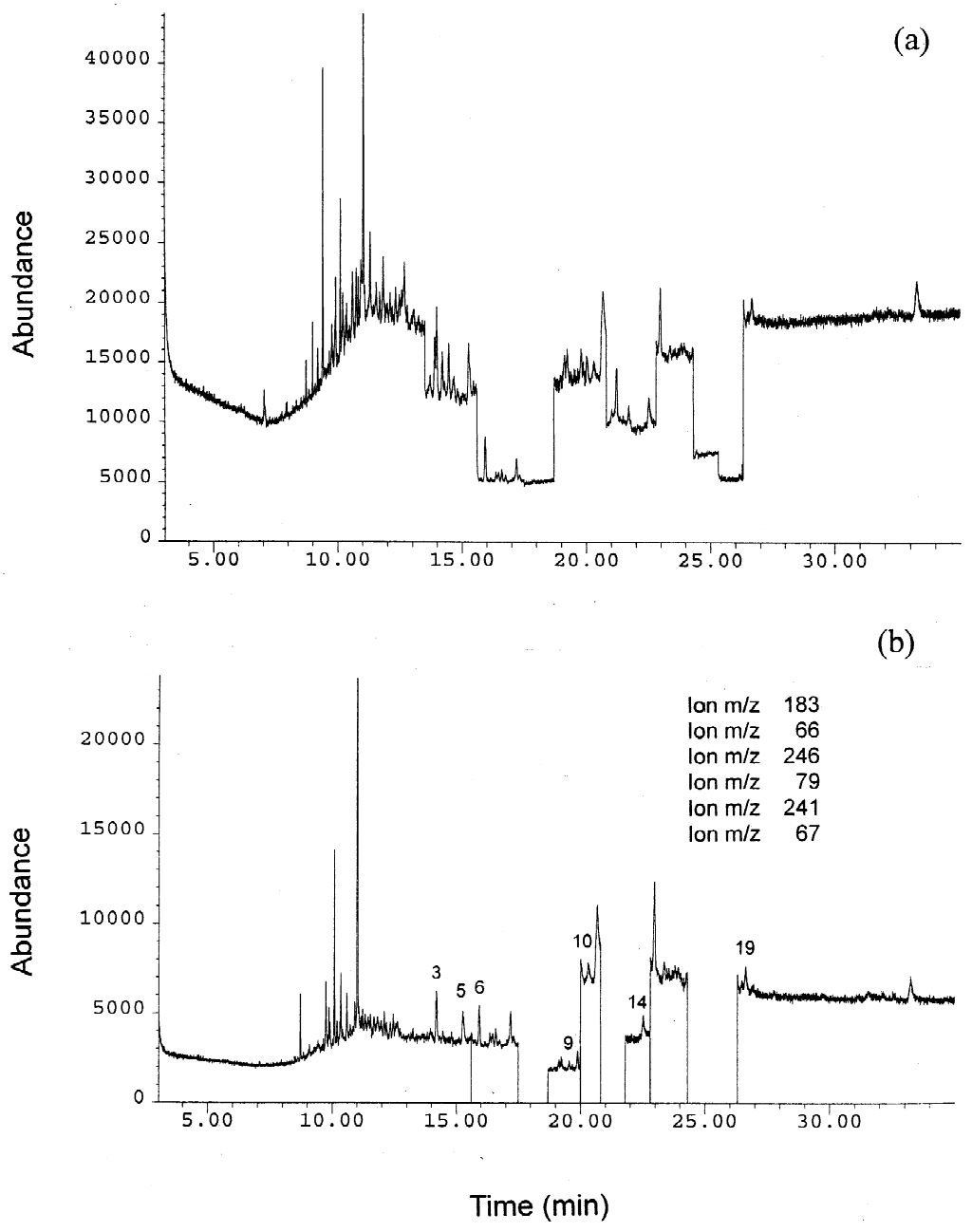

Fig. 5. Analysis of a *Ginseng and Astragalus combination* sample using SPME–GC–MS: (a) chromatogram of ion groups; (b) chromatogram of selected specific ions. The numbers of pesticides are as listed in Table 1.

that SPME, combined with GC–MS, is a precise, reproducible technique for analyzing multi-residue OCPs in Chinese herbal formulations. The optimum conditions for extraction were investigated at an equilibrium time of 90 min and desorption in a GC injector at 250°C for 5 min. This method shows a

Table 3
Pesticide concentration (ng/g) in the Chinese herbal formulations[a]

Pesticide	*Cinnamon and Mahuang*	*Ginseng and Astragalus*	*Ginseng combination*	*Minor Bupleurum*	*Paeonian radix*	*Pinellia*	*Rehmannia six*
α-HCH	ND	ND	ND	ND	6.5	ND	2.2
β-HCH	ND	119	ND	ND	ND	ND	ND
Lindane (γ-HCH)	3.7	ND	4.7	ND	13.1	6.8	ND
δ-HCH	39.3	72.3	ND	10.7	45.8	ND	ND
Aldrin	5.1	18.3	6.4	5.3	ND	ND	2.6
Dieldrin	ND	3.1	3.2	2.6	ND	ND	ND
p,p′-DDD	ND	ND	ND	ND	ND	ND	ND
p,*p*′-DDE	3.9	4.3	9.0	8.3	7.4	ND	ND
p,*p*′-DDT	ND	ND	ND	ND	ND	ND	ND
o,*p*′-DDT	ND	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND
Endosulfan I	ND	ND	ND	ND	ND	ND	ND
Endosulfan II	23.1	22.2	35.4	ND	ND	16.4	ND
Endosulfan sulfate	ND	ND	50.3	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND
Endrin ketone	ND	10.7	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND

[a] ND, below limit of detection.

precision of 3–21% (RSD), depending on the compound. Linearity is verified over a wide range. Furthermore, detection limits below the ng/g level for pesticides in herbal formulation were achieved and are better than those obtained using conventional Soxhlet extraction methods. This technique was also applied to determine pesticides in actual herbal formulation samples from a local market. The tested pesticides were in the samples were at the ng/g level. The results demonstrate the suitability of the SPME approach to analyze trace residue pesticides in herbal medicine formulations which contain high levels of interference.

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