Journal of Chromatography B, 885–886 (2012) 90–96

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

One-step extraction for gas chromatography with flame photometric detection of 18 organophosphorus pesticides in Chinese medicine health wines

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ARTICLE INFO

Article history:
Received 24 October 2011
Accepted 20 December 2011
Available online 6 January 2012

Keywords:
GC-FPD
GC–MS
One-step extraction
Organophosphorus pesticides
Chinese medicine health wine

ABSTRACT

An easy, rapid and selective gas chromatography with flame photometric detection (GC-FPD) method was established for simultaneously determining 18 organophosphorus pesticides (OPPs) in 80 Chinese medicine (CM) health wines. This method was based on a simple one-step extraction procedure using a little solvent without any further cleanup steps. The optimized extraction solvent for the pesticides is acetone:dichloromethane (1:1, V/V) with extraction recovery of 79.0–109.1% and relative standard deviation (RSD) of 0.36–12.68%, respectively. The limits of detection (LODs) of the established GC-FPD method for all investigated pesticides ranged from 1 to 15 ng mL^{-1} and limits of quantification (LOQs) from 4 to 50 ng mL^{-1}. Out of all 80 CM health wines, 18 OPPs were found in 8 samples at low concentrations of 8.2–37.9 ng mL^{-1}. These pesticides were successfully confirmed by GC–MS. This is the first report of determining OPPs in CM health wines, providing references for monitoring the quality of CM health wine in routine analysis.

1. Introduction

Chinese medicine (CM) health wines are consumed as liquor in many areas of Asia, Europe, etc. They play an important role in Asian life, culture and diet since ancient times. CM health wines, have not only high nutritive value and special flavor, but also health function. As it is well-known, the raw materials of CM health wine are various Chinese material medicas (CMMs). The major components of CM health wines are alkaloids, salts, glycosides, organic acids and volatile oils [1]. Because of increasing requirements of CMMs, organophosphorus pesticides (OPPs) are applied to these raw herbs to reduce disease and insect pests [2] in their growth and production progresses. But, the overuse of pesticides in these progresses would lead to serious pollution on CMMs, further to contaminate CM health wines.

Both the quality and safety of wine have been of growing interest for consumers all over the world [3–5], with an increasing emphasis on health risks from food in the public debate. Pesticide residues are not directly addressed into wine [6], but it is generally regulated through the different national and regional standards for natural medicines as maximum residue limit (MRLs) [7]. The European Union (EU) has set MRLs for pesticide residues in wine grapes (0.01–10 mg kg^{-1} depending on the particular pesticide) [8].

OPPs are the most frequently used pesticides worldwide. Some of them may persist in the environment to contaminate soil, air, surface and ground water. The incorrect use or overuse of OPPs may result in the residues of these compounds in agricultural products and derivative food commodities, such as wine and fruit juices [9]. So, it is necessary to detect and control the OPP residues in raw CCMs and their products including CM health wine for food and environmental safety, which plays an important role in food quality for evaluating food safety and possible risks to human health [10].

Various analytical methods including gas chromatography (GC) and liquid chromatography (LC) coupled with various detectors have been developed for the determination of pesticides in wine samples [6,10–13]. Among these methods, gas chromatography with flame photometric detection (GC-FPD) is the most frequently used techniques [14,15]. Before the analysis of pesticides by GC-FPD, an important and critical step is the sample extraction and clean-up. Different extraction and clean-up procedures, such as solid phase extraction (SPE), liquid–liquid extraction

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1570-0232/$ – see front matter.
doi:10.1016/j.jchromb.2011.12.019

(LLE) solid-phase micro-extraction (SPME), have been established for extracting numerous pesticides in wines [16]. However, SPE and LLE require large amounts of organic solvent in pretreatment, which may lead to large waste of solvent and serious contamination to the environment. SPME often results in a non-linear response due to complex matrices [17]. Also, the clean-up step may result in the loss and damage of target analytes. Therefore, a simple one-step extraction procedure using a little solvent without any further cleanup steps is a good selection.

In the present study, a rapid, reliable and simple one-step extraction for GC-FPD determination of 18 OPPs in 80 CM health wines was successfully established. Positive results were further confirmed by GC–MS. To the best of our knowledge, this is the first report of multi-residue determination of OPPs in CM health wines, providing references for monitoring the quality of CM health wine in routine analysis.

2. Experimental

2.1. Chemicals and reagents

Eighteen standard pesticides (uncertainty $\mu g\,mL^{-1}$): dichlorovos (±0.05), phorate (±0.11), dimethoate (±0.07), diazinon (±0.25), disulfoton (±0.10), parathion-methyl (±0.17), fenitrothion (±0.11), malathion (±0.11), fenthion (±0.07), durshan (±0.08), parathion (±0.07), isocarbophos (±0.05), quinalphos (±0.16), methidathion (±0.10), ethion (±0.07), triazophos (±0.19), phosmet (±0.11), and phosalone (±0.07) were purchased from the Agro-Environment Protection Institute (Tianjin, China). HPLC-grade ethyl acetate, dichloromethane, cyclohexane, *n*-hexane were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). HPLC-grade acetone was obtained from MREDA (IL, USA).

2.2. Chinese medicine health wine samples

A total of 80 CM health wine samples, which could be divided to 25 types, such as Ningxiahong (20), Chinese Jing wine (13), Lotus white wine (5), Yedaolugui wine (3), Fenglin wine (5), Diyi wine (3), Hawthorn wine (2), Yishebian wine (2), Yishewang wine (1), Yisheshengbao wine (1), Shiguogong wine (1), Cordyceps Sinensis wine (1), Sanbian wine (2), Shibu wine (1), Rhodiola rosea wine (1), Ginseng wine (1), Lucid Ganoderma wine (1), Herba Saussureae Involucratae wine (1), Tall Gastrodia Tuber wine (1), Chinese Magnoliavine Fruit wine (1), Desertliving Cistanche Herb wine (1), Ningxiner wine (2), Zhuyeqing wine (2), Jiafang wine (2), Gucixiaotongye (4), and Guogong wine (3), were purchased or collected from different markets in China. They were composed of different CMM raw materials and were stored at ambient temperature.

2.3. Standard solutions preparation

A stock standard solution of each OPP was prepared in acetone at a concentration of $100\,mg\,L^{-1}$ and stored at −20 °C in the refrigerator. The standard working solutions were daily obtained by appropriate dilution of the stock standard solution.

2.4. Sample preparation

Simple one-step extraction using a little solvent without any further clean-up step was used to extract the target OPPs from the tested CM health wine samples. 5.0 mL of sample was placed in a 15.0 mL screw cap centrifuge tube with conical bottom. 2.0 mL of extraction solvent of acetone:dichloromethane (1:1, V/V) was rapidly added into the sample using a pipettor (Eppendorf, Germany). Then, the mixture was gently shaken for several seconds by hand. A mixed solution (wine, acetone and dichloromethane) was formed in the centrifuge tube. In this step, OPPs were extracted into the fine droplets of organic solvent. The mixture was stood for a few minutes until samples and organic phase were split. The organic phase, which was sedimented at the bottom of the centrifuge tube, was evaporated by gentle nitrogen flow, then, was completely transferred into a volumetric flask to 1.0 mL.

2.5. GC-FPD condition

An Agilent Technologies (USA) 6890N gas chromatograph equipped with an FPD detector, an autosampler 7683 (Agilent) and an injector, connected to an HP ChemStation (Hewlett-Packard, Palo Alto, CA, USA), was used for determining the 18 pesticides. The capillary column was a DB-5 (30 m × 0.25 mm i.d. with 0.25 μm). Injector and detector temperatures were 220 °C and 250 °C, respectively. Oven temperature was programmed as follow: 60 °C, for 1 min, raised to 180 °C ($30\,°C\,min^{-1}$) for 5 min, raised to 200 °C ($5\,°C\,min^{-1}$) for 10 min, and raised to 250 °C ($5\,°C\,min^{-1}$) for 5 min. High-purity (over purity 99.99%) nitrogen was the carrier and make-up gas at $1.3\,mL\,min^{-1}$ and $3\,mL\,min^{-1}$, respectively. Flow relation for the FPD detector was $75\,mL\,min^{-1}$ for hydrogen and $100\,mL\,min^{-1}$ for air. Injection was performed at splitless mode with a purge time of 0.75 min.

2.6. GC–MS condition

The OPPs in the investigated samples was confirmed by GC–MS analysis using a varian 450GC-320TQ Mass Spectrometer (Bruker, Germany). The A VF-1701MS (30 m × 0.25 mm i.d. with 0.25 μm) capillary column was used. Injector temperature was 220 °C and sample injection was performed in splitless mode. Oven temperature was programmed as follows: 60 °C for 1 min, raised to 180 °C for 5 min ($30\,°C\,min^{-1}$), raised to 200 °C for 10 min ($5\,°C\,min^{-1}$), and raised to 250 °C for 10 min ($5\,°C\,min^{-1}$). High-purity (over 99.99%) helium was selected as the carrier gas. The mass conditions were set as follows: ionization mode with EI, ionization energy of 70 eV, manifold temperature at 40.0 °C, ion source temperature at 250 °C, transfer line temperature: 250 °C, full scan mode and scan range between 50.0 and 650.0 u.

3. Results and discussion

3.1. Optimization of the extraction procedure

Different parameters including extraction solvent and time were optimized to develop the simple one-step extraction of 18 OPPs in CM wine samples. Recoveries of the 18 OPPs were selected as the optimization indexes.

Firstly, different extraction solvents for 18 OPPs in CM wine samples were optimized. The recoveries of 18 OPPs from different extraction solvents including ethyl acetate, methylbenzene:acetonitrile (1:3, V/V), methylbenzene:acetonitrile:ethyl acetate (1:1:2, V/V/V), dichloromethane, and dichloromethane:acetone (1:1, V/V) were shown in Fig. 1. It could be seen that the lowest recoveries were obtained from ethyl acetate, followed by methylbenzene:acetonitrile:ethyl acetate (1:1:2, V/V/V). The recoveries from dichloromethane, methylbenzene:acetonitrile (1:3, V/V) and dichloromethane:acetone (1:1, V/V) were also satisfactory. But, the emulsification was serious using dichloromethane. On the other hand, methylbenzene was harmful to human health and the environment. So, dichloromethane:acetone (1:1, V/V) (recoveries of 79.0–109.1% for all OPPs) was optimized as the extraction solvent.

Then, different volumes (1, 2 and 5 mL) of dichloromethane:acetone (1:1, V/V) were optimized. Results showed that the recovery (59.2–96.3%) for an extraction volume of

Table 1
Calibration data (linear equation, *R*, linear range), LOD and LOQ of 18 OPPs.

Analytes	Linear equation	*R*	Linear range (ng mL^{-1})	LOD (ng L^{-1})	LOQ (ng L^{-1})
Dichlorovos	$y = 10919x - 213.21$	0.9996	0.02–2.0	1	4
Phorate	$y = 8417.6x + 5.6292$	0.9997	0.02–2.0	2	10
Dimethoate	$y = 7569.4x - 453.79$	0.9989	0.05–2.0	9	22
Diazinon	$y = 7819x + 42.636$	0.9998	0.02–2.0	3	15
Disulfoton	$y = 5252.5x + 79.358$	0.9995	0.02–2.0	5	20
Parathion-methyl	$y = 7674x - 103.7$	0.9998	0.02–2.0	5	20
Fenitrothion	$y = 7316.8x - 64.539$	0.9998	0.02–2.0	5	25
Malathion	$y = 5464.2x - 118.45$	0.9996	0.05–2.0	10	30
Fenthion	$y = 7468.9x + 35.354$	0.9998	0.02–2.0	5	20
Durshan + parathion	$y = 13699x - 0.1496$	0.9998	0.02–2.0	4	15
Isocarbophos	$y = 6785x - 220.26$	0.9994	0.05–2.0	8	30
Quinalphos	$y = 7740.7x + 10.167$	0.9998	0.02–2.0	8	30
Methidathion	$y = 6059.7x - 156.46$	0.9996	0.05–2.0	10	50
Ethion	$y = 11834x - 8.8639$	0.9998	0.02–2.0	4	15
Triazophos	$y = 6263.2x - 181.62$	0.9994	0.02–2.0	8	40
Phosmet	$y = 3934.7x - 258.43$	0.9994	0.1–2.0	9	40
Phosalone	$y = 4353.8x - 184.25$	0.9994	0.05–2.0	15	40

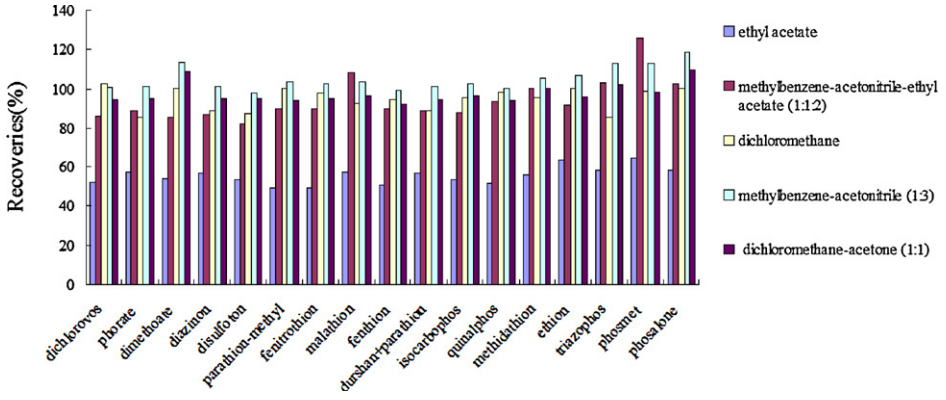

Fig. 1. Recoveries of 18 OPPs in CM wine with different extraction solvents.

1 mL were slightly lower than that of 2 mL (86.4–103.5%) and 5 mL (88.4–110.3%). Therefore, when it comes to develop eco-friendly technologies, 2 mL of the solvent was chosen for the simple one-step extraction.

Thirdly, the extraction time was studied in range of 0–60 s under other constant experimental conditions. The recovery results showed that the extraction time has no significant effect on the extraction efficiency of OPPs. So the extraction time confirmed 30 s in this study.

3.2. Calibration curves, limits of detection and quantification

The linearity of response was examined by analyzing solutions in a range of concentrations shown in Table 1. Calibration curves

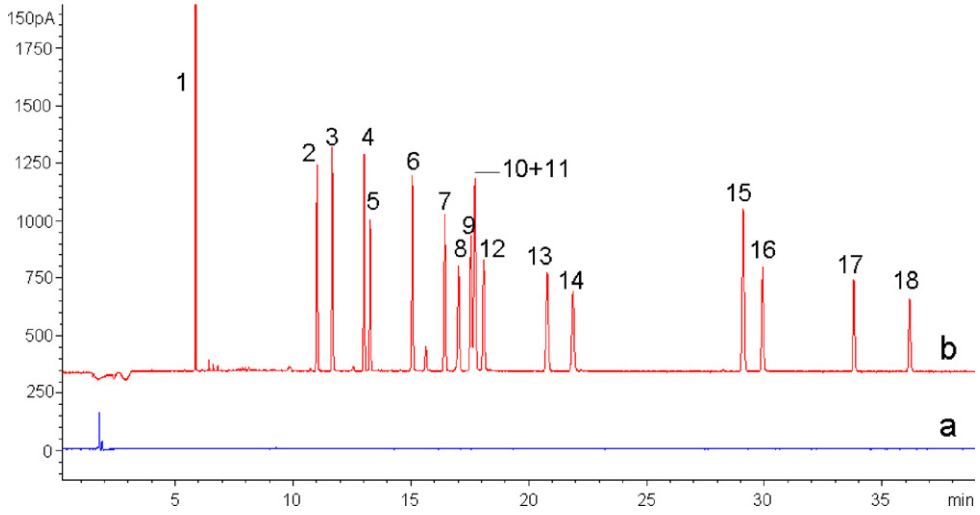

Fig. 2. GC-ECD chromatograms of (a) control sample and (b) spiked sample with 18 OPPs: 1, dichlorovos; 2, phorate; 3, dimethoate; 4, diazinon; 5, disulfoton; 6, parathion-methyl; 7, fenitrothion; 8, malathion; 9, fenthion; 10 + 11, durshan + parathion; 12, isocarbophos; 13, quinalphos; 14, methidathion; 15, ethion; 16, triazophos; 17, phosmet; 18, phosalone.

Table 2
Recoveries of 18 OPPs in three kinds of different matrix samples.

Analytes	Spiked concentration levels (mg L^{-1})	Recoveries (n = 3)					
		Ningxiahong		Chinese jing wine		Yedaolugui wine	
		Recoveries (%)	RSD	Recoveries (%)	RSD	Recoveries (%)	RSD
Dichlorovos	0.01	107.9	8.07	81.0	0.74	81.0	8.60
	0.1	104.3	1.80	90.1	2.98	85.2	2.66
	1	92.0	7.04	96.4	2.64	97.7	6.86
Phorate	0.01	103.2	4.41	79.3	2.18	81.8	6.85
	0.1	93.8	2.80	92.3	9.55	87.0	0.68
	1	83.9	7.00	92.0	2.03	93.8	4.12
Dimethoate	0.01	98.7	3.05	87.7	0.67	79.0	11.93
	0.1	105.4	1.14	96.1	10.04	109.1	1.30
	1	103.1	7.02	106.7	5.61	115.1	0.65
Diazinon	0.01	93.0	3.65	87.3	2.92	82.6	6.96
	0.1	94.1	4.64	84.6	2.41	88.6	1.40
	1	84.4	6.65	90.6	2.81	92.9	3.60
Disulfoton	0.01	97.5	5.32	87.8	3.35	79.2	3.91
	0.1	93.5	5.11	82.5	4.13	79.0	1.76
	1	83.9	7.39	90.5	2.52	92.0	2.88
Parathion-methyl	0.01	96.0	4.49	88.5	1.52	81.9	5.11
	0.1	107.3	1.39	86.8	6.43	96.6	3.77
	1	95.2	6.78	103.0	2.35	108.1	4.52
Fenitrothion	0.01	99.0	1.08	90.8	2.51	88.6	5.88
	0.1	103.6	3.14	84.3	5.78	92.2	2.03
	1	94.0	6.97	97.9	2.65	101.7	3.81
Malathion	0.01	98.4	1.84	97.3	2.37	92.3	1.67
	0.1	100.8	5.61	82.7	0.36	92.7	3.67
	1	95.6	8.41	96.3	1.96	100.1	3.62
Fenthion	0.01	102.3	2.32	92.1	3.78	80.9	3.36
	0.1	101.4	3.44	82.0	2.45	84.5	2.43
	1	91.1	7.82	92.5	1.89	96.5	2.99
Durshan + parathion	0.01	102.9	3.68	94.3	5.92	83.1	7.70
	0.1	97.6	5.40	83.1	3.27	87.2	1.60
	1	88.6	7.84	89.7	1.70	93.9	2.60
Isocarbophos	0.01	100.3	3.77	92.6	3.41	86.6	3.48
	0.1	101.1	4.08	83.8	4.27	85.0	3.17
	1	99.2	7.72	93.2	7.09	99.2	3.59
Quinalphos	0.01	107.1	1.70	94.2	4.06	79.4	7.16
	0.1	95.7	2.79	85.1	0.56	90.4	1.27
	1	95.8	7.87	89.2	2.34	92.2	3.71
Methidathion	0.01	89.1	1.42	87.5	4.43	87.3	11.49
	0.1	104.1	6.14	96.5	6.31	103.8	3.29
	1	99.1	8.37	105.1	1.61	107.9	5.97
Ethion	0.01	96.1	3.48	97.5	5.42	81.2	7.19
	0.1	97.9	6.88	90.1	6.48	92.4	0.80
	1	87.0	6.31	92.4	2.33	96.6	3.37
Triazophos	0.01	81.8	2.38	93.5	6.10	90.7	4.12
	0.1	102.8	8.40	101.5	11.06	100.8	4.32
	1	98.2	3.76	95.3	9.13	106.3	0.84
Phosmet	0.01	93.4	4.14	86.1	5.64	89.7	9.75
	0.1	108.5	1.65	100.0	3.55	107.7	0.73
	1	103.7	2.82	96.5	12.68	107.0	0.52
Phosalone	0.01	101.6	4.88	103.7	9.61	87.4	5.94
	0.1	107.9	1.89	101.2	10.52	101.2	2.07
	1	98.8	3.11	94.5	6.36	105.7	2.00

showed excellent linearity for all analytes. The calibration was checked routinely.

Limits of detection (LOD) and quantification (LOQ) were determined by injecting standard solution (n = 6) and measuring background response (noise) [18]. Results showed that the LODs of all 18 OPPs were below the MRLs.

3.3. Selectivity and precision

Selectivity was checked by injecting extracts of three kinds of different non-spiked samples. It was shown in Fig. 2 that there were no interference in samples extracts. Noise was similar regardless of the matrix.

The intra-day precision was checked by injecting extracts to be continuation of six times for the CM health wine samples spiked at 0.1 mg L^{-1} concentration level. The inter-day precision was checked by injecting extracts to be continuation of 6 days for these wine samples spiked at 0.1 mg L^{-1} concentration level. The tests were performed using the same independent preparation. Good results were obtained with RSD of 0.60–5.08% for intra-day precision and 0.28–10.72% for inter-day precision. Most of the RSD values were ≤6.38%, in agreement with the European Commission DG-SANCO (SANCO/2007/3131) [19]. The lowest RSD value (0.28%) of precision was obtained for ethion, while the highest value of 10.72% was for phosmet.

The stability was checked by injecting extracts at 0, 2, 4, 6, 10, and 12 h for the CM health wine samples spiked at 0.1 mg L^{-1} concentration level. The test was also performed using the same independent preparation. The RSD values ranged from 0.43% (for disulfoton) to 3.99% (for phosalone).

3.4. Recovery and repeatability

Recovery assays were performed with CM health wine spiked with pesticides at three concentration levels of 0.01, 0.1 and 1 mg L^{-1} for the 18 OPPs. Analyses were carried out in triplicate.

The composition of CM health wines in this study were different according to the different CMM raw materials in these samples, including single plant raw material, various plants raw materials in the wine, animals and plants mixed raw materials in the wines.

Three kinds of CM health wine, Ningxiahong, Chinese jing wine and Yedaolugui wine, which represented the common CM health wine types, were chosen to assess the method. The raw material of Ningxiahong was only one herbal raw material *Barbury Wolfberry* Fruit, while, Chinese jing wine was consisted of many kinds of herbal raw materials and Yedaolugui wine was made up of herbal and animal raw materials. The results obtained for each pesticide were different according to the type of wine, confirming the analysis method. There was a comparison between control sample and spiked sample (Yedaolugui wine, 0.1 mg L^{-1}) shown in Fig. 2.

The recoveries of all 18 OPPs in these three kinds of CM health wine were 81.8–108.5%, 79.3–106.7% and 79.0–115.1%, respectively, which were shown in Table 2. Good results were obtained with RSD values of 0.36–12.68% which were below the permissible level suggested.

The above-mentioned results showed that the developed GC-FPD method was precise, accurate and sensitive enough for simultaneously quantitative determination of 18 OPPs in 80 CM health wines.

3.5. Analysis of commercial samples

This method was applied for the determination of the 18 OPPs pesticides in 80 CM health wines. The results in Table 3 showed that a few of pesticides were detected in 8 samples, i.e. 10.0% of the analyzed samples. But, the contents of 18 OPPs in 8 positive samples, between LOQ (phosmet and methidathion) and 37.9 ng ml^{-1} (phosmet), were all below the permissible level suggested. Of the 18 OPPs, malathion, phosalone, phosmet and methidathion have been determined in most positive samples (in which OPPs have been determined). It is worth noting that high content of phosmet (37.9 ng mL^{-1}) was reported in Ginseng wine, and the highest levels of malathion (20.2 ng mL^{-1}) were in Lotus white wine samples. The OPPs, which were in CM wine samples may be came from CMMs. Depending on the type of OPPs in these samples, further work will focus on detecting the OPPs in Chinese medicine raw material of positive samples in order to controlling their content standard.

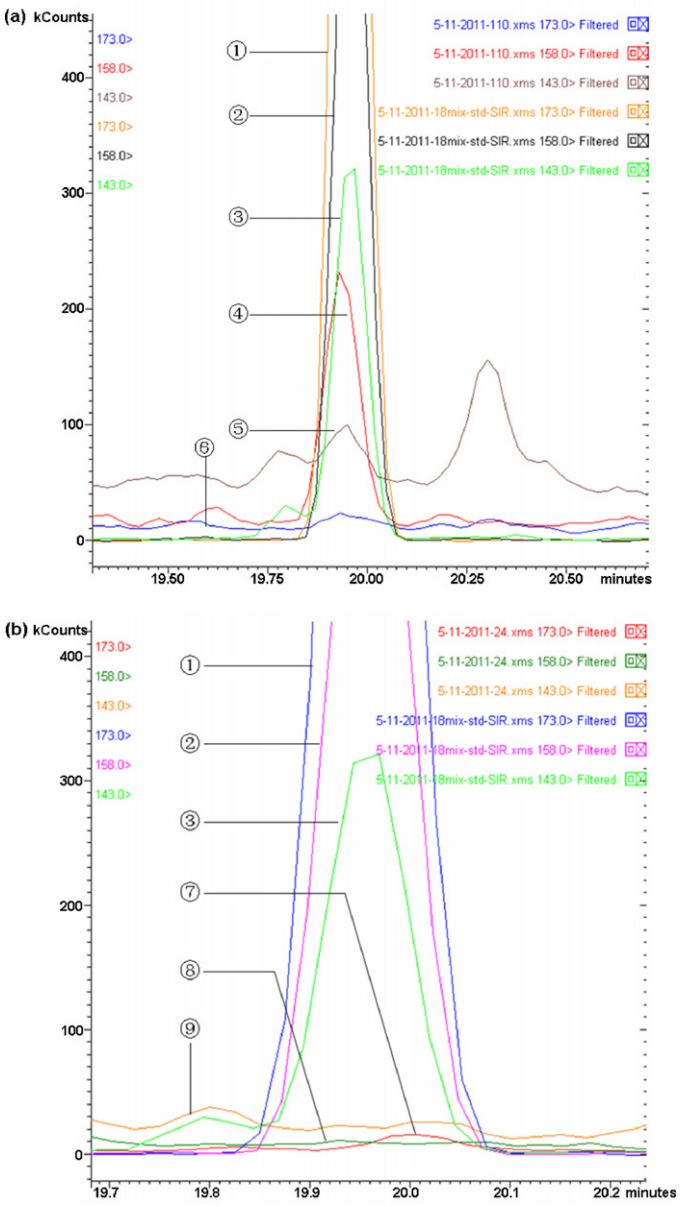

Fig. 3. Selected ion monitoring chromatogram of malathion from GC–MS confirmation of (a) the comparison between standard substance and positive sample (No. 37) and (b) the comparison between standard substance and negative sample (No. 60): (1) malathion qualitative ion (173) in standard solutions, (2) malathion qualitative ion 1 (158) in standard solutions, (3) malathion qualitative ion 2 (143) in standard solutions, (4) malathion qualitative ion 1 (158) in positive sample (No.37), (5) malathion qualitative ion 2 (143) in positive sample (No.37), (6) malathion qualitative ion (173) in positive sample (No. 37), (7) malathion qualitative ion (173) in negative sample (No. 60), (8) malathion qualitative ion 1 (158) in negative sample (No.60), and (9) malathion qualitative ion 2 (143) in negative sample (No. 60).

3.6. Confirmatory results

Various kinds of substances can be found in medicinal herbs and their related products in China, such as saponin, flavone, alkaloid, starch, volatile oil, etc. [20]. False-positive results maybe occur. Therefore, the potential to confirm positive sample by GC–MS was studied under the above-described chromatographic conditions, which was performed in the negative electrospray ionization (EI−) mode using MS scan. Fig. 3 shows the total ion chromatogram of 18 OPPs. The qualitative analysis data were listed in Table 4. Some positive samples and negative samples (in which OPPs have not been determined) were randomly selected for GC–MS analysis. The

Table 3
Contents of OPPs in 80 CM wine samples.

Sample no.	Name	Batch number	Pesticides detected	Concentration (ng mL^{-1})
1	Ningxiahong	20051122 N1036	ND	ND
2	Ningxiahong	20091029 N1043	ND	ND
3	Ningxiahong	20090303 N1019	ND	ND
4	Ningxiahong	20081115 N1009	ND	ND
5	Ningxiahong	20090131 N1017	ND	ND
6	Ningxiahong	20081112 N1009	ND	ND
7	Ningxiahong	20100330 N1059	ND	ND
8	Ningxiahong	20100525 N2062	ND	ND
9	Ningxiahong	20100119 N1017	ND	ND
10	Ningxiahong	20090123 N2014	ND	ND
11	Ningxiahong	20090217 N1014	ND	ND
12	Ningxiahong	20090810 N1028	ND	ND
13	Ningxiahong	20090330 N1230	ND	ND
14	Ningxiahong	20100525 N1062	ND	ND
15	Ningxiahong	20080523 N2013	ND	ND
16	Ningxiahong	20090530 N2031	ND	ND
17	Ningxiahong	20090120 N2014	ND	ND
18	Ningxiahong	20071021 N1018	ND	ND
19	Ningxiahong	20071013 N2012	ND	ND
20	Ningxiahong	20100510 N2032	ND	ND
21	Chinese Jing wine	20100706/61	ND	ND
22	Chinese Jing wine	20100814/03	ND	ND
23	Chinese Jing wine	20100707/02	ND	ND
24	Chinese Jing wine	20100823/07	ND	ND
25	Chinese Jing wine	20100404/52	ND	ND
26	Chinese Jing wine	20100709/61	ND	ND
27	Chinese Jing wine	20100523/62	ND	ND
28	Chinese Jing wine	20100612/56	ND	ND
29	Chinese Jing wine	20100904/33	ND	ND
30	Chinese Jing wine	20100322/08	ND	ND
31	Chinese Jing wine	20100812/01	ND	ND
32	Chinese Jing wine	20101018/10	ND	ND
33	Chinese Jing wine	20100910/47	ND	ND
34	Lotus white wine	20090321	Malathion	11.9
			Phosalone	10.4
35	Lotus white wine	20090517	ND	ND
36	Lotus white wine	20090823	Malathion	20.2
			Phosalone	9.7
37	Lotus white wine	20100110	Malathion	12.7
			Phosalone	10.6
38	Lotus white wine	20090420	Malathion	12.3
			Phosalone	10.2
39	Yedaolugui wine	20100108A	ND	ND
40	Yedaolugui wine	20090828H	ND	ND
41	Yedaolugui wine	20090824H	ND	ND
42	Fenglin wine	LGG1210822	ND	ND
43	Fenglin wine	FEY1613794	ND	ND
44	Fenglin wine	WEF1506097	ND	ND
45	Fenglin wine	20091023/06	ND	ND
46	Fenglin wine	20100520/07	ND	ND
47	Diyi wine	20070608	ND	ND
48	Diyi wine	20100320	ND	ND
49	Diyi wine	20061224	ND	ND
50	Hawthorn wine	201001312346CLS-1	ND	ND
51	Hawthorn wine	20101016	ND	ND
52	Yishebian wine	20091230	ND	ND
53	Yishewang wine	20100309	ND	ND
54	Yisheshengbao wine	20091008	Phosmet	10.0
55	Yishebian wine	20090815	Phosmet	< LOQ
56	Shiguogong wine	100303	ND	ND
57	Cordyceps Sinensis wine	20090512	ND	ND
58	Sanbian wine	20061213	ND	ND
59	Tezhisanbian wine	20090811033BJ	ND	ND
60	Shibu wine	20090217 9181707B	ND	ND
61	Rhodiola rosea wine	Home made	Methidathion	< LOQ
62	Ginseng wine	Home made	Methidathion	8.2
			Phosmet	37.9
63	Lucid Ganoderma wine	Home made	ND	ND
64	Herba Saussureae Involucratae wine	Home made	ND	ND
65	Tall Gastrodia Tuber wine	Home made	ND	ND
66	Chinese Magnoliavine Fruit wine	Home made	ND	ND
67	Desertliving Cistanche Herb wine	Home made	ND	ND
68	Ningxiner wine	20090504	ND	ND
69	Ningxiner wine	20090806	ND	ND
70	Zhuyeqing wine	201003011	ND	ND
71	Zhuyeqing wine	201004025	ND	ND

Table 3 (*Continued*)

Sample no.	Name	Batch number	Pesticides detected	Concentration (ng mL^{-1})
72	Jiafang wine	201005020	ND	ND
73	Jiafang wine	200909020	ND	ND
74	Gucixiaotongye	9180303	ND	ND
75	Gucixiaotongye	9180425	ND	ND
76	Gucixiaotongye	9180529	ND	ND
77	Gucixiaotongye	9181023	ND	ND
78	Guogong wine	9180080	ND	ND
79	Guogong wine	9180080	ND	ND
80	Guogong wine	9180073	ND	ND

Table 4
Qualitative GC–MS analysis data of 18 OPPs.

Analytes	Qualitative ion 1	Qualitative ion 2	Qualitative ion 3	time slot (min)
Dichlorvos	109	185	220	0.00–16.50
Phorate	260	121	231	0.00–16.50
Diazinon	304	179	137	0.00–16.50
Disulfoton	88	274	186	0.00–16.50
Dimethoate	125	229	143	0.00–16.50
Dursban	314	258	286	16.50–21.50
Parathion-methyl	263	233	246	16.50–21.50
Fenitrothion	278	169	153	16.50–21.50
Malathion	173	158	143	16.50–21.50
Fenthion	277	260	247	16.50–21.50
Parathion	291	186	235	21.50–29.00
Quinalphos	146	298	157	21.50–29.00
Isocarbophos	136	230	289	21.50–29.00
Methidathion	145	157	302	21.50–29.00
Ethion	231	384	199	29.00–end
Triazophos	161	172	257	29.00–end
Phosmet	160	161	317	29.00–end
Phosalone	182	367	154	29.00–end

chromatograms of positive sample (No. 37) and negative sample (No. 60) were also shown in Fig. 3. The confirmatory results were in accordance to those of GC-FPD detection.

4. Conclusions

In this study, a simple one-step extraction method using a little solvent without any further clean-up step was proposed for extracting 18 OPPs in CM health wine. The total extraction time and solvent were all limited, which improved materially the extraction efficiency. Then, GC-FPD was applied for simultaneously determining these pesticides in 80 wine samples from different sources. To the best of our knowledge, this is the first report describing the determination of 18 OPPs in CM health wine in China.

By the developed GC-FPD analytical method, 18 OPPs in Chinese medicine health wine samples were successfully detected. As a screening method, this methodology has the advantage of being simply, easy and rapid with high extraction recoveries, also the values of LOD were below the MRLs of wine grapes imposed by England and European legislation. Total analysis time is 50 min (10 min for extraction plus 39 min for chromatography). Thus, 6 samples can be prepared in less than 1 h. Due to the optimized extraction procedure and the chromatographic conditions as well as omitting any cleanup step, the method could be expanded to even further analytes depending on the availability of standards and could be used in routine analysis. It should also be noticed that positive cases should be confirmed by a complementary detection method, or the analysis performed by GC–MS.

Acknowledgements

The authors are grateful for the support from Important New Drug Research Project of the Ministry of Science and Technology of China (2009ZX09502-025, 2012ZX09301-002-001), Scientific Research Project of Traditional Chinese Medicine Vocation in 2008 of China (No. 200807042) and National Science Foundation of China (No. 81173539).

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