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Original Article

Analysis of pesticide residues in commercially available chenpi using a modified QuEChERS method and GC-MS/MS determination

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ABSTRACT

To ensure the safety of the commercially available chenpi, a convenient and fast analytical method was developed for the determination of 133 pesticide residues in chenpi using gas chromatography-tandem mass spectrometry (GC-MS/MS). In this study, different extraction solvents, redissolution solvents and adsorbents were tested according to the recovery and purification effect to obtain a modified QuEChERS method. The samples were extracted with acetonitrile. During the clean-up step, octadecyl-modified silica (C18) and graphitized carbon black (GCB) were selected, and aminopropyl (NH_2) was used instead of primary secondary amine (PSA) because of its weaker ion exchange capacity which had little effect on the recovery of ditalimfos. Samples were quantified by matrix-matched calibration with internal standards. All pesticides showed good linearity in the respective range, both with values of $r^2 > 0.99$. The average recoveries of the pesticides spiked samples ranged from 70.0% to 112.2% with the RSDs of 0.2%–14.4%. The modified QuEChERS method was validated and applied to twenty real samples. Five pesticides were found in eight batches, but no pesticide exceeded the maximum residue limits (MRL, MRL reference to European commission).

1. Introduction

Pericarpium citri Reticulatae (chenpi), the dried pericarp of the fruit of Citrus reliculate Blanco or its cultivars, is used in medicine and food [1]. As a food, chenpi has the effect of strengthening the spleen. As a traditional herb, chenpi is widely used to treat indigestion and inflammatory respiratory tract conditions [2].

Pesticide residues are detected frequently in commercially available chenpi. Relevant literature shows that pesticides pollution in chenpi is serious [3]. Pesticides are very toxic to humans and research has shown that some pesticides have teratogenic, carcinogenic and mutagenic effects [4,5]. In 2016, Peng et al. [6] used gas chromatography to determine organophosphorus pesticides in chenpi and only 11 kinds of organophosphorus pesticides were determined by this method. Therefore, it is extremely important to establish a set of convenient and fast detection techniques for the determination of multiple pesticide residues in chenpi.

Sample preparation is a crucial step in all analytical methods and an appropriate clean-up method was developed for the extraction of pesticide residues with high selectivity, and low co-extraction. The most common sample preparation methods include solid-phase extraction (SPE) [7,8], QuEChERS [9], solid-phase micro extraction (SPME) [10,11] and gel permeation chromatography (GPC) [12–14].

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method was developed by Anastassiades et al. in 2003 [15] and it has become one of the most commonly used methods for the determination of pesticides. A typical QuEChERS method involves an extraction with acetonitrile (and water in dry commodities), followed by a phase partitioning assisted by salting out and further clean up by d-SPE. [16–19]. The method can be used to analyze many compounds, including highly polar pesticides and highly acidic compounds. It is suitable for the detection of samples with a low fat content and a high water content. Furthermore, the method has been applied to pesticide determination of many different matrices like vegetables, fruits and tea [20–22].

In the clean-up step, sorbent C18 and primary secondary amine (PSA) are used in most published methods, and florisil is used in some, but NH_2 is seldom used. NH_2 has a similar adsorption performance to PSA, while PSA contains two amino groups giving it a higher ion exchange capacity than NH_2. However, PSA sorbents result in the pH value of the final extract solutions being more than 8, which affects the stability of base-sensitive pesticides [23]

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and NH_2 can be used when PSA affects the determination of analytes.

In order to ensure food safety, in this study, a method was developed for multi-residue determination of pesticides in chenpi by GC-MS/MS and NH_2 sorbent was used in a modified QuEChERS method because of the pesticides influenced by PSA.

2. Experimental

2.1. Chemicals and other materials

Pesticide standards and the internal standard (IS), chlorpyrifos-d10 with a purity $>98\%$, were provided by Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade acetonitrile was obtained from Omni Chem (Schaumburg, IL, USA). HPLC grade acetone, ethyl acetate and n-hexane were obtained from Merck (Darmstadt, Germany). Anhydrous magnesium sulfate ($MgSO_4$) was obtained from Sigma-Aldrich (St. Louis, USA). Analytical reagent grade anhydrous sodium chloride (NaCl) was obtained from Weichen Chemical Reagent Co., Ltd (Tianjin, China). PSA, octadecyl-modified silica (C18), Florisil, graphitized carbon black (GCB) and aminopropyl (NH_2) were supplied by DIKMA Technologies (Beijing, China).

2.2. Instruments

GC-MS/MS analyses were carried out with a Shimadzu GCMS-TQ8030 (Japan). A Hitachi CF 16RN centrifuge (Japan) and an Eppendorf centrifuge 5804 (Germany) were used for the 50 mL and 10 mL centrifuge tubes, respectively, along with a BUCHI rotary evaporator (Switzerland), KQ-500DE numerical control ultrasonic cleaner (China) and Eppendorf tube (EP, China).

2.3. Preparation of pesticide standards and internal standard solutions

Individual stock standard solutions of each pesticide (1 mg/mL) were prepared by weighing pesticides and dissolving them in n-hexane. Mixed solutions of multiple pesticides (2.5 μg/mL) were prepared by combining appropriate volume of each stock standard solution and stored in a freezer ($-20\,^{\circ}C$). A suitable amount of mixed standard reserve solution was transferred into 10 mL volumetric flask, and was diluted into matrix-matched standard working solutions with concentrations of 1, 2, 5, 10, 20, 50, 100 and 200 ng/mL respectively by blank (pesticide-free) chenpi extract. The internal standard solution, chlorpyrifos-d10, was prepared at a concentration of 1 mg/mL, and then diluted to 2 μg/mL.

2.4. Sample treatment and preparation

Each batch of chenpi was obtained from different markets in China. Pesticide residues can be easily extracted from small particle samples, so before use, all samples were ground to a powder mechanically, and passed through a no. 24 mesh sieve. (The particles retained in the sieve are not included for the analysis.)

2 g samples and 100 μL internal standard (2 μg/mL) were added to 50 mL polypropylene (PP) centrifuge tubes and then 10 mL acetonitrile was used for extraction. The ultrasonic extraction was carried out for 5 min and 0.8 g anhydrous $MgSO_4$ and 0.2 g NaCl were added. Each mixture was shaken by hand for 1 min and centrifuged at 11,180 *g* (rcf) for 5 min. Then, 7 mL of the upper acetonitrile layer was transferred to a 10 mL EP tube containing 200 mg C18, 200 mg NH_2, 200 mg anhydrous $MgSO_4$ and 30 mg GCB. The solution was subjected to vortex mixing for 1 min, and then centrifuged at 7155 *g* (rcf) for 5 min, and 5 mL of the upper layer was transferred to a 50 mL round-bottom flask and evaporated to near dryness on a rotary vacuum evaporator at 40 °C. The dry residue was redissolved in 2 mL acetone for analysis by GC-MS/MS.

2.5. GC-MS/MS conditions

GC separation was performed on a DB-5MS IU capillary column (30 m × 0.25 mm × 0.25 μm; Agilent, America) and helium (purity ≥ 99.996%) was used as a carrier gas at a constant flow of 1.5 mL/min. The inlet temperature was set at 250 °C; the mode of inlet was splitless; the injection volume was 1 μL. The column temperature program is as follows: the initial temperature was maintained at 50 °C for 1 min, increased to 125 °C at a rate of 25 °C/min, raised to 230 °C at 4 °C/min, and then at 8 °C/min up to 310 °C, and held there for 3 min.

The mass spectrometer was operated with an electron impact (EI) source in multiple reaction monitoring (MRM) mode. The electron energy was 70 eV, and the ion and transfer line temperatures were set at 200 °C and 250 °C, respectively. In order to prevent instrument damage, the solvent delay was set at 3.5 min. Table 1 shows the optimized parameters of ion transition for 133 pesticide residues in chenpi.

3. Results and discussion

3.1. Optimization of extraction solvent

Acetonitrile, ethyl acetate and n-hexane are commonly used for extraction of multi-pesticide residues [24–27]. Fig. 1 shows the TIC chromatograms of negative samples extracted by different solvents. Those extracted with n-hexane had the lowest matrix; however, recoveries of dimethoate, metalaxyl, paraoxon, bromacil, isocarbophos, *E*-chlorfenvinfos, fipronil, triadimenol, *trans*-chlordane, *cis*-chlordane, fenthionsulfoxide, fensulfothion, fenthionsulfone, and azinphos-methyl were close to zero. When extracted with ethyl acetate, the recovery of *trans*-chlordane and pyridaben was less than 60%. Compared with n-hexane and ethyl acetate, acetonitrile had the strong dissolving capability for the analytes, meeting the recovery requirement. Therefore, in this study acetonitrile was used as the extraction solvent.

3.2. Selection of solvent for redissolution

Acetonitrile possesses many advantages for extraction, but the polarity of acetonitrile is high, which can damage the gas chromatography column. For the protection of chromatographic columns, before analysis, acetonitrile should be replaced. In this study, n-hexane and acetone were selected as solvents for redissolution. The recoveries of pesticides obtained with these two solvents are shown in Fig. 2.

Compared with that of acetone, the recoveries of some pesticides were lower when redissolved with n-hexane, and approximately 42% of pesticides were outside the range of 60%–120%. Dimethoate and *cis*-chlordane were close to zero. When dissolved with acetone, most of analytical pesticides satisfied the recovery requirement. So acetone was chosen as the solvent for redissolution.

3.3. Optimization of adsorbents

The use of co-extraction leads to an unsatisfactory peak shape, and an increased or inhibited response, which adversely affects the quantification. The adsorbents PSA, C18, Florisil, GCB and NH_2 were investigated to choose the most appropriate purification method.

Table 1
GC-MS/MS acquisition parameters for 133 pesticide residues in chenpi.

No.	Pesticides	Ion ratio (%)	t_R(min)	Quantitative transition		Qualitative transition	
				Precursor > product	CE/V	Precursor > product	CE/V
IS	Chlorpyrifos-D10	28.37	22.122	324.0 > 260.0	15	324.0 > 195.0	30
1	Dichlorvos	29.96	6.585	185.0 > 93.0	14	185.0 > 109.0	14
2	Mevinphos	25.09	9.585	127.0 > 109.1	9	192.0 > 127.0	9
3	Methacrifos	26.34	11.112	240.0 > 208.0	4	240.0 > 180.0	10
4	Isoprocarb	20.26	13.571	136.0 > 121.0	9	121.0 > 103.1	12
5	Propoxur	12.34	13.571	152.1 > 110.1	8	152.1 > 64.0	28
6	Ethoprophos	20.32	14.228	158.0 > 97.0	18	158.0 > 114.0	6
7	Dicrotophos	28.07	14.885	127.1 > 109.0	12	127.1 > 95.0	18
8	Phorate	28.61	15.591	260.0 > 75.0	8	260.0 > 231.0	18
9	α-hexachlorocyclohexane	21.02	15.640	218.9 > 182.9	8	218.9 > 144.9	20
10	Hexachlorobenzene	21.31	15.762	283.8 > 248.8	24	283.8 > 213.8	28
11	2,6-dichloro-4-nitroaniline	18.89	16.227	206.0 > 176.0	10	206.0 > 160.0	16
12	Dimethoate	29.65	16.276	125.0 > 47.0	14	125.0 > 79.0	8
13	β-hexachlorocyclohexane	29.41	16.794	218.9 > 182.9	8	218.9 > 144.9	20
14	Pentachloroanisole	30.00	16.917	265.0 > 237.0	15	280.0 > 265.0	10
15	Quintozene	22.09	16.917	294.8 > 236.8	16	294.8 > 264.8	12
16	γ-hexachlorocyclohexane	24.30	17.188	218.9 > 182.9	8	218.9 > 144.9	20
17	Fonofos	23.98	17.656	137.0 > 109.0	6	246.0 > 137.0	6
18	Pyrimethanil	23.67	18.050	198.0 > 183.0	12	198.0 > 156.1	24
19	Diazinon	23.34	18.075	304.1 > 179.1	10	304.1 > 162.1	8
20	δ-hexachlorocyclohexane	26.83	18.542	218.9 > 182.9	10	218.9 > 144.9	20
21	Isazofos	25.67	18.542	161.0 > 119.0	9	162.0 > 120.0	9
22	Etrimfos	23.67	18.786	292.1 > 181.1	8	292.1 > 153.1	20
23	Disulfoton	10.60	18.786	153.0 > 97.0	10	153.0 > 125.0	6
24	Tefluthrin	24.13	18.859	177.0 > 127.1	16	177.0 > 137.1	16
25	Iprobenfos	24.06	19.103	204.0 > 91.0	8	204.0 > 122.0	12
26	Pirimicarb	16.69	19.128	238.1 > 166.1	12	238.1 > 72.0	24
27	Pentachloroaniline	23.80	19.128	265.0 > 194.0	25	263.0 > 192.0	25
28	Fenchlorphos-oxon	23.63	19.372	269.0 > 254.0	20	269.0 > 224.0	25
29	Dichlofenthion	26.07	19.811	279.0 > 222.9	14	279.0 > 250.9	8
30	Chlorpyrifos-methyl	27.07	20.031	285.9 > 93.0	22	285.9 > 270.9	14
31	Acetochlor	20.12	20.031	223.1 > 132.1	22	223.1 > 147.1	10
32	Vinclozolin	29.39	20.275	285.0 > 212.0	12	285.0 > 178.0	14
33	Parathion-methyl	15.15	20.299	263.0 > 109.0	14	263.0 > 136.0	8
34	Tolclofos-methyl	20.41	20.348	264.9 > 249.9	14	264.9 > 93.0	24
35	Alachlor	29.58	20.421	188.1 > 160.1	10	188.1 > 132.1	18
36	Heptachlor	7.54	20.586	271.8 > 236.9	20	271.8 > 117.0	32
37	*N*-desethyl-pirimiphos-methyl	28.92	20.788	277.0 > 135.0	10	277.0 > 168.0	10
38	Metalaxyl	22.46	20.788	249.2 > 190.1	8	249.2 > 146.1	22
39	Fenchlorphos	22.29	20.788	284.9 > 269.9	16	284.9 > 93.0	24
40	Paraoxon	28.72	21.028	139.0 > 109.0	10	149.0 > 102.0	25
41	Prometryn	22.61	21.028	241.2 > 199.1	6	241.2 > 58.0	14
42	Pentachlorothioanisole	30.00	21.504	296.0 > 263.0	15	246.0 > 211.0	20
43	Fenitrothion	27.21	21.552	277.0 > 260.0	6	277.0 > 109.1	14
44	Pirimiphos-methyl	20.84	21.576	305.1 > 180.1	8	305.1 > 290.1	12
45	Bromacil	28.20	21.647	204.9 > 187.9	14	204.9 > 162.0	14
46	Metolachlor	23.38	22.172	238.1 > 162.1	12	238.1 > 133.1	26
47	Aldrin	13.34	2.195	262.9 > 193.0	28	262.9 > 203.0	26
48	Clorpyrifos	20.16	22.338	313.9 > 257.9	14	313.9 > 285.9	8
49	Dacthal	23.42	22.481	300.9 > 222.9	26	300.9 > 272.9	14
50	Fenthion	24.47	22.505	278.0 > 109.0	20	278.0 > 125.0	20
51	Parathion	25.33	22.672	291.1 > 109.0	14	291.1 > 137.0	6
52	Isocarbophos	26.63	22.863	289.1 > 136.0	10	289.1 > 113.0	14
53	Bromophos	29.87	23.244	330.9 > 315.9	14	330.9 > 285.9	28
54	Pirimiphos ethyl	23.99	23.544	304.0 > 168.0	10	318.0 > 166.0	15
55	Cyprodinil	26.30	23.891	224.1 > 208.1	16	224.1 > 197.1	22
56	*E*-chlorfenvinphos	29.22	23.960	323.0 > 267.0	16	323.0 > 295.0	6
57	*trans*-heptachlorepoxide	24.21	24.237	352.8 > 253.0	26	352.8 > 289.0	6
58	Fipronil	21.44	24.237	366.9 > 212.9	30	366.9 > 254.9	22
59	*Z*-chlorfenvinphos	27.49	24.422	323.0 > 267.0	16	323.0 > 295.0	6
60	Mecarbam	21.06	24.584	329.0 > 159.1	4	329.0 > 131.1	18
61	Quinalphos	25.62	24.630	298.0 > 156.0	5	298.0 > 190.0	10
62	Phenthoate	27.03	24.630	273.9 > 125.0	20	273.9 > 246.0	6
63	Procymidone	17.47	24.722	283.0 > 96.0	10	283.0 > 255.0	12
64	Triadimenol	9.37	24.791	168.1 > 70.0	10	168.1 > 112.1	4
		12.67	25.161				
65	Methidathion	22.20	25.161	145.0 > 85.0	8	145.0 > 58.0	14
66	Bromophos-ethyl	28.69	25.276	358.9 > 302.9	16	358.9 > 330.9	10
67	Methoprene	22.56	25.392	111.0 > 55.1	15	109.0 > 67.1	9
68	*o,p'*-DDE	15.41	25.415	246.0 > 176.0	30	246.0 > 211.0	22
69	Paclobutrazol	29.19	25.554	236.1 > 125.0	14	236.1 > 167.0	10
70	*Trans*-chlordane	19.56	25.754	374.8 > 263.9	28	372.8 > 336.8	10
71	Fenothiocarb KCO-3001 Panocon	7.55	25.843	160.1 > 72.0	10	160.1 > 106.1	12

(continued on next page)

Table 1 (*continued*)

No.	Pesticides	Ion ratio (%)	t_R(min)	Quantitative transition		Qualitative transition	
				Precursor > product	CE/V	Precursor > product	CE/V
72	Ditalimfos	20.77	25.977	130.0 > 102.1	12	148.0 > 130.1	12
73	N,N-Diethyl-2-(1-naphthyloxy)propanamide	22.18	26.266	128.0 > 72.1	6	271.0 > 128.1	6
74	Prothiofos	25.48	26.600	309.0 > 238.9	14	309.0 > 280.9	10
75	*Cis*-chlordane	27.66	26.823	374.8 > 338.8	8	372.8 > 265.9	22
76	Profenofos	24.54	26.823	336.9 > 266.9	14	336.9 > 308.9	6
77	Myclobutanil	21.15	27.179	179.0 > 125.0	18	179.0 > 90.1	27
78	Carboxin	29.42	27.290	235.0 > 143.1	12	235.0 > 87.0	21
79	Flusilazole	29.81	27.335	233.1 > 165.1	14	233.1 > 152.1	14
80	Buprofezin	21.48	27.380	172.1 > 57.0	14	172.1 > 131.1	6
81	*p,p′*-DDE	16.07	27.888	246.0 > 211.0	22	246.0 > 176.0	30
82	Dieldrin	22.21	27.888	262.9 > 193.0	34	262.9 > 228.0	24
83	Endrin	21.22	27.888	262.9 > 191.0	30	262.9 > 193.0	28
84	Nitrofen	27.28	27.995	282.9 > 162.0	24	282.9 > 253.0	12
85	Fenthionsulfoxide	20.42	28.509	279.0 > 109.0	20	294.0 > 279.0	10
86	Fensulfothion	29.20	28.595	293.0 > 125.0	14	293.0 > 153.0	8
87	Diniconazole	27.40	28.638	268.0 > 232.0	12	268.0 > 149.0	24
88	Fenthion-sulfone	24.24	28.766	310.0 > 105.0	15	310.0 > 109.0	20
89	*o,p′*-DDD	23.54	28.852	235.0 > 165.0	24	235.0 > 199.0	14
90	*o,p′*-DDT	23.54	28.766	235.0 > 165.0	24	235.0 > 199.0	16
91	Ethion	29.55	29.024	230.9 > 174.9	14	230.9 > 184.9	12
92	Fensulfothion sulfone	22.99	29.324	188.0 > 109.1	18	324.0 > 109.1	18
93	Famphur	18.34	29.902	218.0 > 109.0	16	218.0 > 79.0	24
94	Benalaxyl	24.19	29.981	148.0 > 77.1	27	148.0 > 105.1	18
95	Endosulfan sulfate	22.75	30.191	386.8 > 252.9	16	386.8 > 288.8	10
96	Propiconazole	26.54	30.325	259.0 > 69.0	14	259.0 > 191.0	8
		29.43	30.593				
97	*p,p′*-DDT	30.00	30.554	235.0 > 165.0	24	235.0 > 199.0	16
98	Tebuconazole	30.00	31.147	250.1 > 125.1	22	250.1 > 153.1	12
99	Piperonyl butoxide	27.48	31.739	176.1 > 131.1	12	176.1 > 117.1	20
100	Pyridaphenthion	26.92	32.223	340.0 > 199.2	9	199.0 > 77.1	30
101	Phosmet	25.23	32.332	160.0 > 77.0	24	160.0 > 133.0	14
102	Bromopropylate	23.50	32.612	340.9 > 182.9	18	340.9 > 184.9	20
103	Bifenthrin	5.87	32.736	181.1 > 166.1	12	183.1 > 153.1	8
104	Bifenazate	26.83	32.829	300.1 > 258.1	8	300.1 > 199.1	20
105	Methoxychlor	26.37	32.845	227.1 > 169.1	24	227.1 > 212.1	14
106	Fenpropathrin	12.20	33.016	265.1 > 210.1	12	265.1 > 172.1	14
107	Tebufenpyrad	24.61	33.187	333.0 > 171.1	21	318.0 > 131.2	21
108	Tetradifon	29.03	33.455	355.9 > 228.9	12	355.9 > 159.0	18
109	Phenothrin	24.35	33.522	183.1 > 153.1	14	183.1 > 168.1	14
		29.11	33.736				
110	Phosalone	21.89	33.682	182.0 > 111.0	14	182.0 > 138.0	8
111	Azinphos-methyl	21.74	33.736	160.1 > 132.1	6	160.1 > 77.0	20
112	Mefenacet	25.43	34.069	192.0 > 136.0	12	192.0 > 109.0	27
113	Mirex	13.20	34.216	272.0 > 237.0	15	270.0 > 235.0	5
114	Cyhalothrin	27.81	34.510	197.0 > 141.0	8	197.0 > 161.0	22
		28.81	34.900				
115	λ-Cyhalothrin	21.73	34.510	181.0 > 152.1	21	197.0 > 141.1	9
116	Fenarimol	28.56	34.550	251.0 > 139.0	14	251.0 > 111.0	26
117	Pyrazophos	223.60	34.710	221.1 > 193.1	12	221.1 > 149.1	14
118	Acrinathrin	24.36	34.900	289.1 > 93.0	14	289.1 > 77.0	26
		24.67	35.206				
119	Bitertanol	29.26	35.548	170.0 > 141.1	18	170.0 > 115.2	27
120	Permethrin	22.70	35.713	183.1 > 168.1	14	183.1 > 165.1	14
		24.90	35.912				
121	Coumaphos	23.63	35.759	362.0 > 109.0	16	362.0 > 226.0	14
122	Flusilazole	25.80	35.807	340.0 > 298.0	14	340.0 > 313.0	14
123	Pyridaben	20.10	35.889	147.1 > 117.1	22	147.1 > 132.1	14
124	Cyfluthrin	27.68	36.556	226.1 > 206.1	6	226.1 > 199.1	14
		24.88	36.717				
		24.11	36.792				
		23.14	36.867				
125	Boscalid	26.41	37.004	342.1 > 140.1	14	342.1 > 112.1	28
126	Cypermethrin	15.11	37.024	163.1 > 127.1	6	163.1 > 109.1	22
		17.62	37.182				
		19.05	37.252				
		11.96	37.321				
127	Quizalofop-ethyl	29.31	37.242	372.0 > 299.2	12	299.0 > 91.2	24
128	Flucythrinate	22.11	37.281	199.1 > 157.1	10	199.1 > 107.1	22
		21.41	37.568				
129	Ethofenprox	25.46	37.479	163.0 > 135.1	10	163.0 > 107.1	18
130	Phenvalerate	29.21	38.261	419.1 > 225.1	6	419.1 > 125.1	26
		29.01	38.558				
131	Tua-Fluvalinate	17.50	38.465	250.1 > 55.0	20	250.1 > 208.0	20
		16.53	38.567				

(continued on next page)

Table 1 (*continued*)

No.	Pesticides	Ion ratio (%)	t_R(min)	Quantitative transition		Qualitative transition	
				Precursor > product	CE/V	Precursor > product	CE/V
132	Difenoconazole	15.30 19.56	38.846 38.927	323.0 > 265.0	14	323.0 > 202.0	28
133	Deltamethrin	26.41 27.14	39.015 39.278	252.9 > 93.0	20	251.0 > 172.0	10

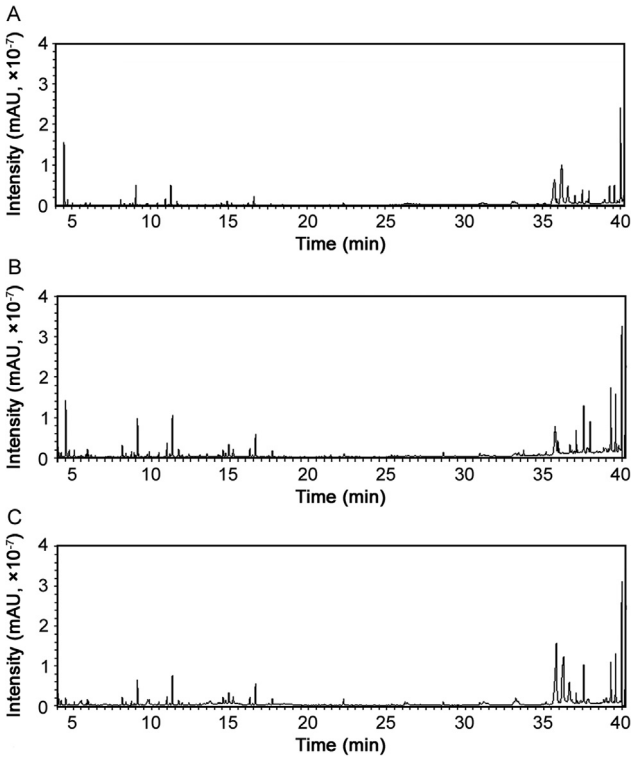

Fig. 1. Full scan chromatograms of negative samples extracted with (A) n-hexane, (B) ethyl acetate and (C) acetonitrile.

If the extraction solution was injected into the GC-MS/MS without adding adsorbents, there was clear interference of the matrix for the pesticides bitertanol, cypermethrin, flucythrinate, and difenoconazole.

The addition of Florisil for purification seemed to have no effect. C18 can be used for the reduction of lipids and non-polar interference. Because of the addition of C18, the matrices that interfered with the determination of pesticides, such as bitertanol, flucythrinate and difenoconazole, were removed.

PSA can adsorb fatty acids and pigments extracted from chenpi to improve the chromatographic peak shape of cypermethrin (Fig. 3). When the amount of PSA was 200 mg, the chromatographic peaks of cypermethrin isomers was free of interference from impurities. However, PSA clearly had an effect on the recovery of ditalimfos. This study compared the effect of the addition of 50, 100, 150, 200 mg PSA on the recovery of ditalimfos, and the results obtained are shown in Fig. 4. When the adsorbent amount was 50 mg, the recovery of ditalimfos was about 73.1%, while the recovery of ditalimfos decreased to 23.9% when the amount of PSA reached 200 mg. The main reason for this may be that PSA may increase the pH value of the final extract solutions to more than 8. According to the structure of ditalimfos (Fig. 5), ditalimfos is unstable and decomposes easily in an alkaline environment, so as the amount of adsorbent is increased, the recovery of ditalimfos is reduced.

Fig. 5 shows the structures of NH_2 and PSA. They had a similar adsorption, while PSA contains two amino groups, which resulted in a higher ion exchange capacity than NH_2. Therefore, NH_2 could not only improve the chromatographic peak shape of cypermethrin, but also have small effect on ditalimfos. When the dose of NH_2 reached 200 mg, the recoveries of pesticides were all between 72.4% and 118.6%.

The solution extracted with acetonitrile contained more pigments. GCB is widely used in the adsorption of pigments. The color of the extraction solution changed with an increase in the amount of GCB. In addition, GCB is well known for adsorbing pesticides with a planar structure, leading to unsatisfactory recoveries and poor precision. This study compared the effect of the addition of 10, 20, 30 and 40 mg GCB on the recovery of pesticides, and the results obtained are shown in Fig. 6. As the amount of GCB increased, the recoveries of some pesticides, such as hexachlorobenzene with a planar structure, decreased but were still in an acceptable range. Also, the extraction was improved when 30 mg GCB was added. In summary, 30 mg GCB was used as the adsorbent.

3.4. Validation study

Under the modified QuEChERS method conditions, a validation study was carried out to evaluate the performance characteristics of the method for multiple pesticides in chenpi by estimating the linearity, limit of quantification (LOQ), accuracy (expressed by recovery), precision and matrix effects. Validation was performed following the European Union SANTE/11945/ 2015 guideline [28].

3.4.1. Linearity

The linearity for each pesticide was assessed in matrix-matched standard solution. The calibration curves of the compounds were obtained by plotting the pesticide/IS peak area ratios against the concentration of the corresponding calibration standards at eight different levels (1, 2, 5, 10, 20, 50, 100, 200 ng/mL). The linearity results are shown in Table 2. The linearity of the method for all the pesticides was satisfactory, with correlation coefficients (r^2) higher than 0.99.

3.4.2. LOQ

The LOQ for each pesticide was defined as the lowest validated spiked level satisfying the requirement of recovery ranging from 70% to 120% and a relative standard deviation (RSD) less than 20%. Samples were spiked at two different concentrations: 0.005 and 0.01 mg/kg (6 replicates per level). The LOQ values are presented in Table 2.

3.4.3. Accuracy and precision

Recovery was evaluated at three different spiked levels of 0.05, 0.1 and 0.2 mg/kg by spiking six blank samples at each level. Precision was expressed as the relative standard deviation (RSD)

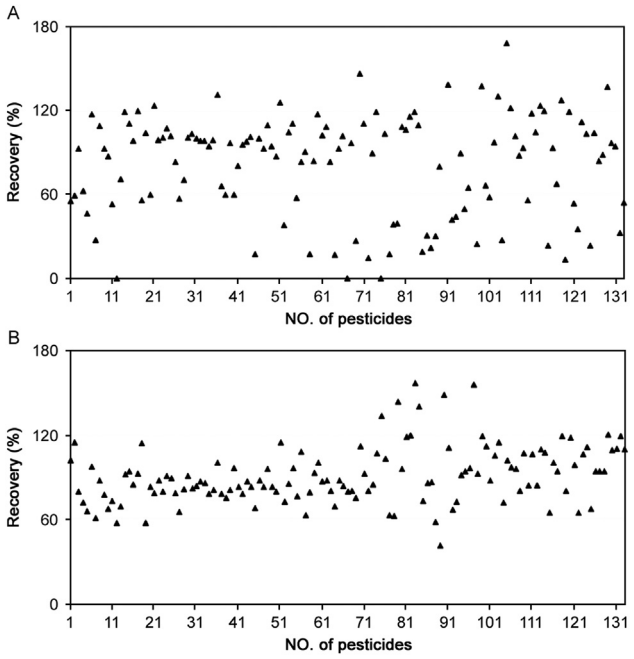

Fig. 2. Recoveries of pesticides obtained using (A) n-hexane and (B) acetone for redissolution.

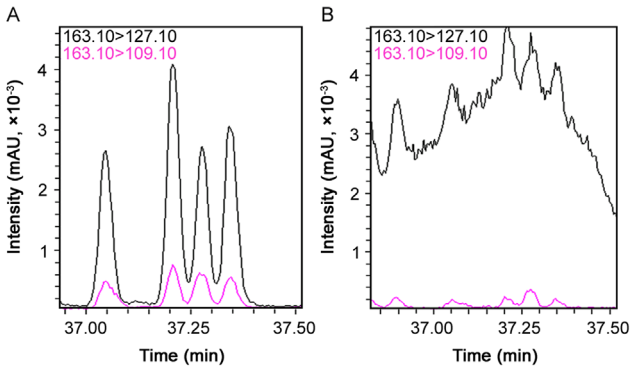

Fig. 3. Chromatogram of cypermethrin with (A) PSA adsorbent and (B) without adsorbent.

and was obtained from the six spiked samples at three spiking levels. Table 2 shows the recoveries and RSDs of all pesticides at all concentrations. The recovery of all the pesticides met the requirements of the pesticide residue determination.

3.4.4. *Matrix effects (ME)*

In this study, some pesticides, such as mevinphos, propoxur, dicrotophos and carboxine, have better chromatographic peak shapes in matrix-matched blank solutions than in pure solvent solutions because of the ME.

The ME was evaluated by the slope of the solvent calibration curve and the matrix-matched blank extract calibration curve according to the equation: ME (%) = [(slope in matrix/slope in solvent) − 1] * 100 [29]. The ME results were grouped into 3 classes: a high ME (less than −50% or higher than +50%), a medium ME (between −50% and −20% or +20% and +50%) and a low ME (between +20% and −20%). Fig. 7 shows the ME of each pesticide. Among 133 pesticides, 53% showed low ME, 32% showed medium ME and 16% showed high ME. In order to avoid the ME, matrix-matched calibration standards were used for quantification to compensate for the ME.

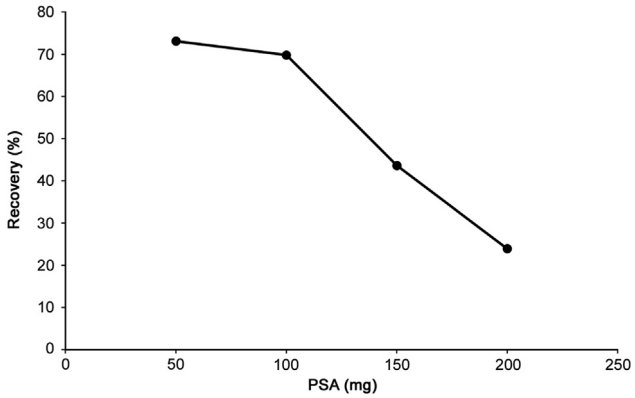

Fig. 4. Recoveries of ditalimfos with different amounts of PSA.

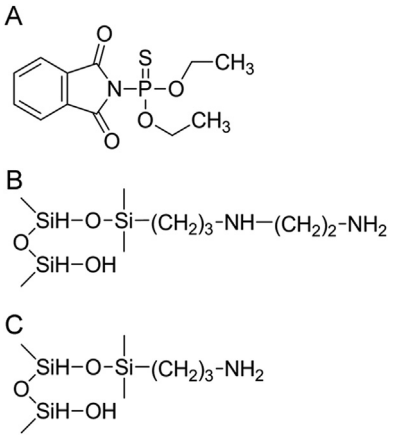

Fig. 5. The structure of (A) ditalimfos, (B) PSA and (C) NH_2.

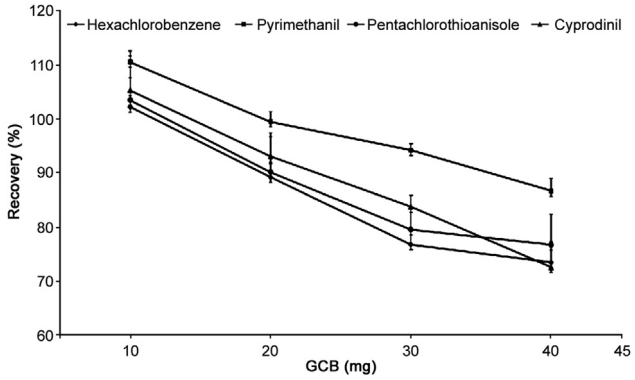

Fig. 6. Recoveries of pesticides with different amounts of GCB.

3.5. *Application to real samples*

Once the analytical methodology was validated, it was used for monitoring pesticides in chenpi samples. The established method was used for the simultaneous determination of the pesticides in twenty real samples and the results are summarized in Table 3. Chlorpyrifos, isocarbophos, methidathion, profenofos and fenpropathrin were found in eight batches, most of which were insecticides and fungicides. Insecticide clorpyrifos and methidathion were frequently detected pesticides, but no pesticide exceeded the maximum residue limits (MRL, the values of MRL for orange were taken as reference) prescribed by Regulation (EC) no. 396/2005 [30]. Clorpyrifos and methidathion are low toxicity pesticides, but the others are moderately or highly toxic pesticides, which are

Table 2
Validation results of the developed method for determination of multiple pesticides in chenpi.

No.	Pesticide	Linear range (ng/mL)	r^2	Recovery (%RSD)(%, $n = 6$)			LOQ (mg/kg)	ME(%)
				0.05 mg/kg	0.1 mg/kg	0.2 mg/kg		
1	Dichlorvos	1–200	0.9992	84.0(1.4)	90.3(2.3)	90.5(3.6)	0.005	4.3
2	Mevinphos	1–200	0.9988	85.6(2.3)	94.1(2.9)	97.2(2.3)	0.005	56.2
3	Methacrifos	1–200	0.9989	88.1(1.0)	98.9(3.0)	103.5(2.9)	0.005	21.7
4	Isoprocarb	1–200	0.9988	92.8(3.9)	92.6(1.8)	93.9(2.0)	0.005	2.5
5	Propoxur	1–200	0.9989	90.7(2.0)	93.3(2.2)	93.5(1.7)	0.005	18.8
6	Ethoprophos	1–200	0.9987	92.1(3.7)	86.5(2.0)	85.4(1.7)	0.005	14.5
7	Dicrotophos	1–200	0.9986	93.9(4.0)	87.6(3.3)	92.1(2.3)	0.005	44.0
8	Phorate	1–200	0.9981	86.6(1.2)	93.4(2.2)	93.0(1.7)	0.005	18.6
9	α-hexachlorocyclohexane	1–200	0.9989	93.4(6.4)	91.8(2.2)	94.1(2.3)	0.005	−15.5
10	Hexachlorobenzene	1–200	0.9990	71.9(2.9)	73.0(2.2)	72.0(2.5)	0.005	−19.9
11	2,6-dichloro-4-nitroaniline	2–200	0.9970	84.2(2.4)	93.0(3.8)	97.7(2.4)	0.01	62.1
12	Dimethoate	1–200	0.9984	90.7(1.6)	91.4(2.7)	91.9(1.4)	0.01	46.9
13	β-hexachlorocyclohexane	1–200	0.9988	95.5(5.2)	94.1(2.4)	95.3(2.0)	0.005	−13.2
14	Pentachloroanisole	2–200	0.9974	85.4(4.9)	78.0(2.9)	69.8(3.2)	0.005	17.5
15	Quintozene	2–200	0.9977	79.9(1.3)	84.5(1.6)	85.5(2.0)	0.005	32.7
16	γ-hexachlorocyclohexane	1–200	0.9995	92.3(7.6)	90.0(5.3)	92.0(1.7)	0.01	−7.8
17	Fonofos	1–200	0.9988	88.0(1.5)	95.5(2.8)	98.4(2.0)	0.005	11.0
18	Pyrimethanil	2–200	0.9988	77.6(1.5)	78.1(3.2)	80.7(1.8)	0.005	9.1
19	Diazinon	1–200	0.9986	92.1(1.7)	89.7(1.4)	87.9(1.7)	0.01	−0.8
20	δ-hexachlorocyclohexane	1–200	0.9986	92.8(5.9)	92.2(2.3)	94.7(2.0)	0.005	−9.3
21	Isazofos	2–200	0.9982	89.8(0.4)	96.6(3.1)	99.8(2.0)	0.005	1.3
22	Etrimfos	1–200	0.9980	93.7(5.2)	89.9(2.0)	93.4(2.2)	0.01	−18.3
23	Disulfoton	1–200	0.9976	88.1(2.4)	92.5(2.5)	95.0(2.1)	0.01	−6.9
24	Tefluthrin	1–200	0.9982	87.3(0.8)	94.1(2.5)	97.1(1.8)	0.01	−4.2
25	Iprobenfos	1–200	0.9973	85.5(3.9)	98.9(3.2)	103.0(1.9)	0.01	26.9
26	Pirimicarb	1–200	0.9980	90.0(2.3)	94.4(2.8)	97.2(2.2)	0.01	−10.5
27	Pentachloroaniline	1–200	0.9982	87.0(7.0)	71.4(3.2)	70.9(2.3)	0.005	−19.9
28	Fenchlorphos-oxon	1–200	0.9978	93.4(3.5)	91.3(3.2)	96.4(2.6)	0.005	2.2
29	Dichlofenthion	1–200	0.9983	91.3(1.1)	88.1(1.5)	87.3(2.0)	0.005	0.9
30	Chlorpyrifos-methyl	1–200	0.9981	86.6(0.6)	90.3(2.0)	90.1(2.2)	0.005	2.0
31	Acetochlor	5–200	0.9980	89.6(1.6)	98.3(3.2)	102.0(1.8)	0.01	5.4
32	Vinclozolin	1–200	0.9984	93.8(4.0)	89.5(1.2)	88.4(1.7)	0.005	−4.9
33	Parathion-methyl	1–200	0.9953	85.8(5.5)	85.5(1.2)	86.8(1.6)	0.01	70.7
34	Tolclofos-methyl	1–200	0.9984	90.0(1.9)	98.5(3.0)	103.0(2.2)	0.005	−11.3
35	Alachlor	2–200	0.9980	88.4(1.0)	97.7(2.6)	101.5(1.9)	0.01	2.2
36	Heptachlor	1–200	0.9980	83.2(1.5)	76.2(2.3)	74.5(1.8)	0.005	−10.3
37	*N*-desethyl-pirimiphos-methyl	2–200	0.9981	86.9(1.9)	99.7(3.7)	104.4(1.9)	0.005	9.6
38	Metalaxyl	2–200	0.9978	93.5(5.4)	89.1(1.7)	89.2(1.3)	0.005	−12.1
39	Fenchlorphos	1–200	0.9984	87.4(1.6)	92.5(2.0)	91.7(1.2)	0.005	−4.0
40	Paraoxon	5–200	0.9934	91.1(3.8)	89.7(4.2)	92.9(3.2)	0.01	79.7
41	Prometryn	1–200	0.9984	91.3(1.6)	88.4(1.4)	86.7(1.9)	0.005	0.2
42	Pentachlorothioanisole	2–200	0.9988	77.5(7.8)	74.0(3.3)	76.4(4.4)	0.005	−20.1
43	Fenitrothion	1–200	0.9917	82.4(4.4)	84.2(0.9)	84.4(1.5)	0.01	67.3
44	Pirimiphos-methyl	2–200	0.9980	91.6(2.2)	86.9(1.7)	86.5(1.9)	0.01	−6.5
45	Bromacil	2–200	0.9990	89.2(2.0)	93.7(2.3)	94.4(2.6)	0.01	28.7
46	Metolachlor	1–200	0.9986	89.4(1.1)	100.1(3.3)	104.6(2.1)	0.005	3.3
47	Aldrin	2–200	0.9984	92.7(6.1)	87.5(2.4)	89.7(3.0)	0.005	−20.7
48	Chlorpyrifos	1–200	0.9985	88.3(3.5)	105.5(4.9)	107.3(2.4)	0.005	1.8
49	Dacthal	1–200	0.9989	97.7(6.9)	92.0(2.1)	94.3(1.7)	0.005	−21.2
50	Fenthion	1–200	0.9986	89.8(0.8)	94.1(1.5)	92.6(1.5)	0.01	1.2
51	Parathion	2–200	0.9926	88.6(2.1)	96.2(5.0)	103.6(2.2)	0.01	69.3
52	Isocarbophos	2–200	0.9979	92.5(2.2)	96.6(3.8)	102.0(2.4)	0.005	18.5
53	Bromophos	1–200	0.9986	92.2(2.9)	90.6(1.6)	94.0(2.2)	0.005	0.3
54	Pirimiphos ethyl	1–200	0.9986	86.4(1.8)	99.4(3.8)	104.9(2.6)	0.005	6.1
55	Cyprodinil	1–200	0.9978	73.3(2.0)	70.0(5.6)	73.4(2.0)	0.005	−2.1
56	*E*-chlorfenvinphos	5–200	0.9980	95.8(5.8)	92.8(3.1)	90.6(3.0)	0.01	24.8
57	*trans*-heptachlorepoxide	5–200	0.9974	99.2(12.0)	101.1(5.0)	97.2(3.1)	0.01	−8.7
58	Fipronil	2–200	0.9970	86.5(4.1)	96.1(2.1)	95.5(1.8)	0.01	49.1
59	*Z*-chlorfenvinphos	1–200	0.9988	90.1(1.9)	88.5(1.3)	87.9(1.9)	0.01	17.3
60	Mecarbam	2–200	0.9966	86.7(6.3)	102.4(3.3)	103.2(2.4)	0.01	24.8
61	Quinalphos	2–200	0.9966	86.4(3.8)	98.5(2.7)	101.5(1.3)	0.01	4.9
62	Phenthoate	1–200	0.9976	86.4(1.0)	97.1(3.0)	102.0(2.4)	0.01	−4.4
63	Procymidone	1–200	0.9983	91.5(1.5)	92.0(1.2)	90.4(1.3)	0.01	−8.4
64	Triadimenol	1–200	0.9975	86.4(3.5)	95.3(3.5)	99.5(2.4)	0.01	29.0
65	Methidathion	1–200	0.9977	91.3(2.4)	100.4(3.4)	102.6(1.6)	0.01	29.2
66	Bromophos-ethyl	1–200	0.9984	86.9(1.4)	85.3(1.9)	84.6(1.4)	0.01	−10.1
67	Methoprene	1–200	0.9924	74.1(2.5)	96.5(4.2)	95.6(8.3)	0.01	13.0
68	*o,p'*-DDE	1–200	0.9984	87.7(2.6)	95.2(3.1)	97.2(1.7)	0.005	−14.6
69	Paclobutrazol	1–200	0.9979	84.9(2.8)	96.9(2.1)	97.7(1.4)	0.01	28.6
70	*Trans*-chlordane	5–200	0.9960	100.4(7.3)	90.1(5.5)	88.4(4.0)	0.01	−11.4
71	Fenothiocarb	1–200	0.9978	88.5(0.7)	94.1(1.9)	94.2(1.6)	0.01	51.7
72	Ditalimfos	1–200	0.9981	72.7(1.0)	83.5(4.0)	84.5(1.4)	0.005	2.5
73	Napropamid	1–200	0.9986	92.7(5.4)	92.9(2.5)	94.3(1.3)	0.005	3.6
74	Prothiofos	1–200	0.9989	90.3(2.8)	86.6(1.6)	86.1(1.7)	0.005	14.3

(continued on next page)

Table 2 (*continued*)

No.	Pesticide	Linear range (ng/mL)	r^2	Recovery (%RSD)(%, $n = 6$)			LOQ (mg/kg)	ME(%)
				0.05 mg/kg	0.1 mg/kg	0.2 mg/kg		
75	*Cis*-chlordane	5–200	0.9914	89.9(8.9)	97.9(13.1)	102.7(3.7)	0.01	24.5
76	Profenofos	1–200	0.9991	88.9(2.5)	102.1(3.9)	105.3(2.1)	0.005	34.6
77	Myclobutanil	1–200	0.9986	88.8(1.6)	96.3(2.9)	99.6(2.0)	0.01	15.8
78	Carboxin	1–200	0.9984	92.0(3.5)	93.9(2.3)	95.4(1.6)	0.01	25.4
79	Flusilazole	1–200	0.9982	88.7(1.9)	97.4(3.0)	97.8(0.9)	0.01	7.6
80	Buprofezin	1–200	0.9985	89.0(2.0)	96.8(3.5)	98.5(1.9)	0.005	1.4
81	*p,p'*-DDE	2–200	0.9992	100.0(12.3)	83.9(3.4)	79.0(2.5)	0.01	−6.7
82	Dieldrin	5–200	0.9980	92.6(6.3)	86.0(1.7)	88.2(2.8)	0.01	−9.3
83	Endrin	5–200	0.9983	94.0(7.6)	84.6(4.4)	87.0(1.3)	0.01	−8.0
84	Nitrofen	2–200	0.9933	84.6(3.2)	91.1(4.4)	97.7(2.7)	0.01	44.3
85	Fenthionsulfoxide	2–200	0.9931	89.1(1.8)	84.1(2.3)	84.2(2.2)	0.01	21.6
86	Fensulfothion	1–200	0.9997	79.2(3.6)	79.4(1.5)	81.1(2.1)	0.01	79.8
87	Diniconazole	1–200	0.9981	84.2(1.1)	83.7(2.0)	83.5(1.5)	0.005	50.0
88	Fenthion-sulfone	2–200	0.9973	90.9(2.2)	88.4(2.1)	86.3(1.4)	0.01	54.7
89	*o,p'*-DDD	1–200	0.9993	96.7(8.4)	110.8(5.1)	112.2(3.8)	0.01	69.8
90	*o,p'*-DDT	1–200	0.9964	78.8(1.1)	72.6(2.5)	77.7(1.8)	0.005	−17.8
91	Ethion	1–200	0.9971	88.9(1.6)	91.0(2.7)	92.2(1.6)	0.01	16.9
92	Fensulfothion sulfone	1–200	0.9970	88.8(1.1)	97.7(3.8)	101.6(1.9)	0.01	34.9
93	Famphur	1–200	0.9977	90.7(2.9)	92.8(3.0)	95.4(2.0)	0.005	99.3
94	Benalaxyl	1–200	0.9978	90.4(3.5)	90.6(2.2)	91.3(1.9)	0.005	8.7
95	Endosulfan sulfate	5–200	0.9979	93.4(4.9)	91.7(2.0)	87.0(1.6)	0.01	10.3
96	Propiconazole	1–200	0.9975	84.3(2.6)	96.2(3.9)	98.0(1.9)	0.005	39.9
97	*p,p'*-DDT	1–200	0.9948	75.3(4.7)	71.6(2.3)	74.6(1.7)	0.01	−9.6
98	Tebuconazole	1–200	0.9980	88.3(3.1)	90.5(2.4)	89.9(1.4)	0.005	49.1
99	Piperonyl butoxide	1–200	0.9980	85.1(2.6)	94.8(3.1)	96.7(1.8)	0.01	45.6
100	Pyridaphenthion	1–200	0.9964	83.9(4.7)	99.6(3.3)	102.7(2.0)	0.01	49.2
101	Phosmet	1–200	0.9952	85.2(1.3)	91.6(3.6)	96.1(2.2)	0.01	−2.8
102	Bromopropylate	1–200	0.9983	89.5(1.7)	90.8(1.8)	91.7(1.6)	0.005	27.1
103	Bifenthrin	1–200	0.9983	86.0(1.8)	96.8(3.8)	99.2(1.8)	0.005	26.3
104	Bifenazate	1–200	0.9962	83.3(2.9)	94.6(2.8)	95.9(1.8)	0.01	50.3
105	Methoxychlor	1–200	0.9941	78.0(3.3)	72.4(2.5)	75.2(1.7)	0.01	−10.9
106	Fenpropathrin	1–200	0.9973	91.3(2.4)	88.1(3.4)	89.8(2.0)	0.01	6.7
107	Tebufenpyrad	1–200	0.9975	88.4(1.2)	91.1(2.6)	92.9(1.9)	0.01	13.5
108	Tetradifon	2–200	0.9974	92.5(4.8)	90.1(2.8)	94.5(1.6)	0.005	−3.9
109	Phenothrin	1–200	0.9979	83.0(2.5)	91.8(4.2)	95.3(2.9)	0.01	48.3
110	Phosalone	1–200	0.9959	84.9(2.2)	94.3(3.5)	98.7(2.1)	0.01	51.8
111	Azinphos-methyl	1–200	0.9945	84.9(1.8)	80.5(1.9)	82.4(1.9)	0.01	−28.7
112	Mefenacet	1–200	0.9982	85.6(1.4)	97.2(3.8)	101(1.7)	0.005	72.8
113	Mirex	1–200	0.9985	85.0(4.9)	88.2(9.4)	86.6(4.1)	0.005	−16.1
114	Cyhalothrin	1–200	0.9950	82.5(0.2)	88.8(3.7)	93.2(1.5)	0.01	26.4
115	λ-Cyhalothrin	1–200	0.9943	81.8(2.3)	86.8(3.6)	91.2(2.3)	0.01	35.6
116	Fenarimol	1–200	0.9979	84.7(0.8)	94.0(2.5)	94.6(1.8)	0.01	23.8
117	Pyrazophos	1–200	0.9965	81.7(2.3)	86.4(4.6)	92.1(2.3)	0.01	60.3
118	Acrinathrin	2–200	0.9922	83.0(2.7)	83.0(2.4)	88.0(1.3)	0.01	−50.9
119	Bitertanol	1–200	0.9977	85.6(1.7)	90.0(3.3)	93.1(1.8)	0.01	88.7
120	Permethrin	1–200	0.9988	86.7(3.4)	94.3(4.5)	97.7(3.3)	0.005	−47.8
121	Coumaphos	1–200	0.9974	83.8(2.1)	79.4(3.6)	80.8(1.8)	0.01	59.4
122	Fluquinconazole	1–200	0.9984	86.8(2.1)	90.5(2.1)	90.2(2.0)	0.005	29.3
123	Pyridaben	1–200	0.9976	83.0(1.8)	91.6(3.2)	94.1(1.9)	0.005	28.4
124	Cyfluthrin	2–200	0.9960	80.4(2.0)	92.0(4.7)	98.6(2.6)	0.01	−49.4
125	Boscalid	1–200	0.9973	82.9(1.3)	92.3(2.2)	89.0(1.0)	0.005	64.4
126	Cypermethrin	1–200	0.9938	88.6(1.8)	92.8(5.0)	97.7(1.7)	0.01	−22.7
127	Quizalofop-ethyl	1–200	0.9964	82.7(0.9)	91.3(4.9)	95.4(2.6)	0.01	56.4
128	Flucythrinate	1–200	0.9945	81.3(1.4)	90.6(4.0)	96.4(2.0)	0.01	−39.5
129	Ethofenprox	1–200	0.9948	74.4(14.4)	85.2(10.8)	93.9(3.4)	0.01	1.3
130	Phenvalerate	2–200	0.9935	79.0(2.6)	82.8(2.7)	80.9(2.0)	0.01	−46.7
131	Tua-Fluvalinate	1–200	0.9911	79.5(0.9)	78.8(2.2)	80.1(1.4)	0.01	−36.4
132	Difenoconazole	1–200	0.9979	72.2(10.5)	90.2(7.2)	85.2(2.0)	0.01	−68.5
133	Deltamethrin	1–200	0.9905	75.5(3.8)	82.6(2.8)	86.6(2.2)	0.01	−34.3

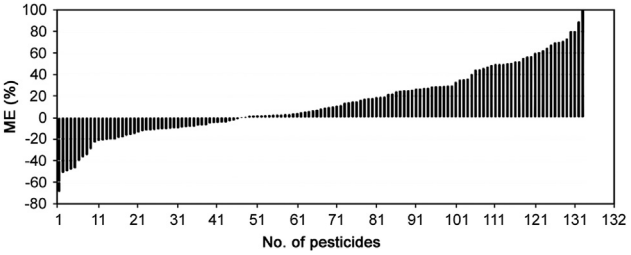

Fig. 7. Matrix effect of pesticides in chenpi.

harmful to human health. Therefore, it is important to pay attention to the appropriate use of pesticides.

4. Conclusions

A modified QuEChERS method for the determination of multiple pesticides by GC-MS/MS was developed. Several sorbents were evaluated in order to reduce the ME as much as possible. C18 and PSA were mainly used in the Original QuEChERS method. In our

Table 3
Pesticide residues found in different batches of chenpi samples and their concentrations (mg/kg).

No.	Pesticide found (mg/kg)				
	Chlorpyrifos	Isocarbophos	Methidathion	Profenofos	Fenpropathrin
2	< LOQ	n.d.	0.016	n.d.	n.d.
5	n.d.	n.d.	0.014	n.d.	n.d.
10	< LOQ	n.d.	0.016	n.d.	< LOQ
14	0.007	< LOQ	n.d.	n.d.	n.d.
16	0.008	< LOQ	< LOQ	0.007	0.221
17	0.007	0.009	0.017	0.006	0.025
18	< LOQ	< LOQ	0.013	< LOQ	0.117
20	< LOQ	< LOQ	< LOQ	n.d.	0.042
MRL	0.01	0.01	0.02	0.01	2

Note: n.d.: no residues detected. MRL: maximum residue limit.

study, PSA had an effect on the pesticide ditalimfos, which showed an unsatisfactory recovery on increasing the amount of PSA. NH_2, with a similar adsorption performance to PSA, is a substitute product of PSA for base-sensitive pesticides or pesticides which could be affected by PSA. The addition of GCB can remove pigment extracted with acetonitrile. A validation procedure was performed, which showed good results for suitability, recovery and repeatability. The developed method was applied to the determination of real samples, and some pesticides were detected, which demonstrated that it is essential to constantly monitor pesticide residues in chenpi.

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Conflicts of interest

The authors declare that there are no conflicts of interest.

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