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Determination of pesticide residues in traditional Chinese medicinal materials Milkvetch Root

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Introduction

Traditional Chinese medicine, is a drug which has been considered to be treating the symptoms with minimal side effects, including Chinese herbal medicine and traditional Chinese medicine tablet etc.
Milkvetch Root, perennial herb, produced in Inner Mongolia, Shanxi, Gansu, Heilongjiang etc. Medicinal so far has been 2000 years of history, it can enhance immune function, protecting liver, diuresis, anti-aging and wider antibacterial effect, and so on, is widely used in traditional Chinese medicine dispensing prescription.
In the process of cultivation of Chinese herbal medicines, it's often threatened by variety of diseases, the yield and quality of medicinal materials are impacted directly which causing significant economic losses. In 1997 the national Traditional Chinese Medicine Bureau organized relevant units to carry out research on Chinese herbal medicine plant protection, the result of investigation shows that the medicinal plant diseases and insect pests prevention is the weak link for the production of Chinese herbal medicine. Plant diseases and insect pests of many types, bring severe losses. Due to the lack of knowledge about medicinal pesticide, misuse of pesticides is the prominent problem. The problem of pesticide residues in Chinese herbal medicine, a direct impact on human health, hinder the traditional Chinese medicine into the international market.
In this paper, using the SHIMADZU three triple quadrupole GC-MS realized the determination of multiple trace pesticide residues in Milkvetch Root by instrument GCMS-TQ8040, the method has high sensitivity and good accuracy.

Methods and Materials

Sample preparation:

Weigh accurately 5 g sample powder in 50 mL centrifuge tube, add 20 mL dichloromethane, vortex after 1 h soaking and ultrasonic extraction for 30 min, then centrifugates with 3000 rpm for 30 min. Keep the supernatant for purification.

Sample purification:

Florisil column was used for sample cleanup, eluted with 20 mL of n-hexane/acetone (85/15), concentrated to 1 mL and filtrated then analysed by GCMS-TQ8040.

Instrument: GCMS-TQ8040 (Shimadzu Corporation, Japan)

Experimental conditions:	
Column	: Rxi-5 MS, 30m×0.25mm×0.25μm
Column oven temp.	: 50°C(1min)-25°C/min-125°C-10°C/min-300°C(3.5min)
Injection temp.	: 250°C
Injection mode	: Splitless
Flow control mode	: Linear velocity (47.2cm/sec)
CID gas	: Argon
Detector voltage	: Tuning result+0.6kv
Interface temp.	: 250°C
Ion source temp.	: 200°C

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Figure 1. GCMS-TQ8040 triple quadrupole mass spectrometer

Result

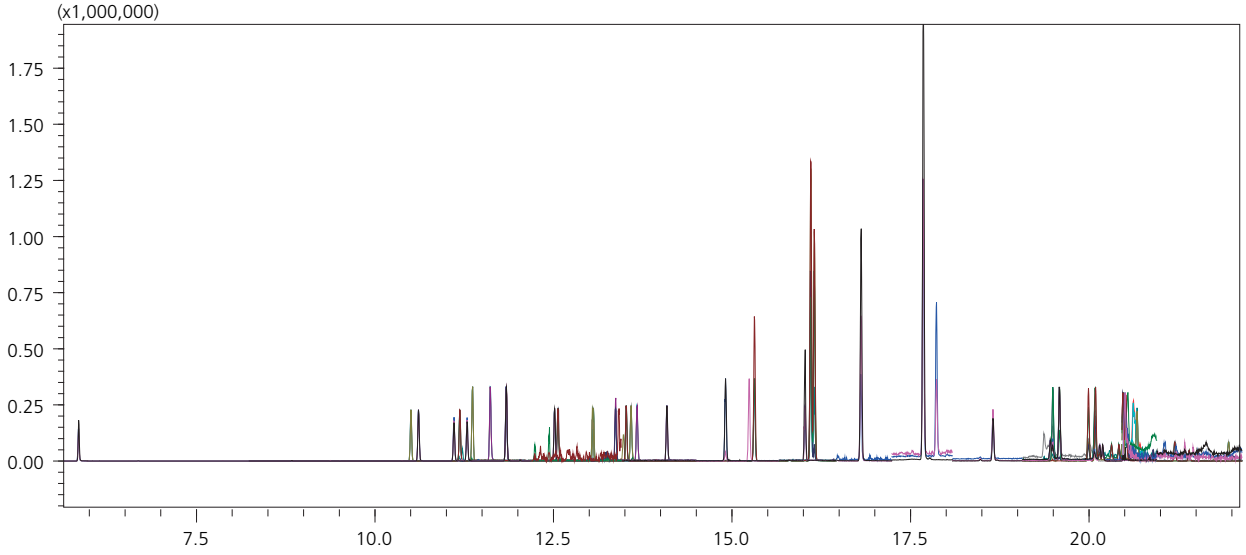

Figure 2. MRM chromatogram of standard sample (0.05 mg/L)

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Calibration curve and reproducibility

Dilute standard solution with extraction matrix. The concentrations of the solution are 5,10,50,100,500 µg/L. The correlation coefficients are shown in table 1, limited by the space, only Dichlorvos and Chlorpyrifos are shown in figure 3, their peak areas within the test ranges. Precision of the method was measured by analyzing the same sample (0.01 mg/L) six times (Table 1). The overall RSD% of analysis were below 5%.

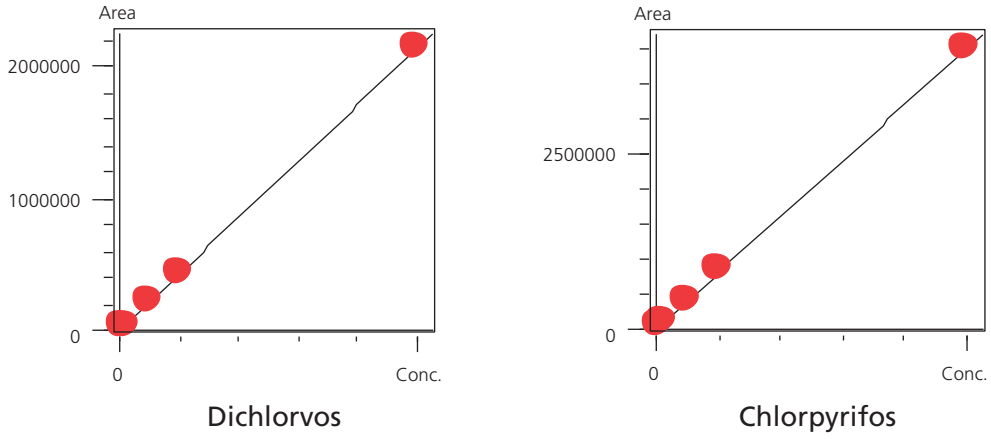

Figure 3. Calibration curve of dichlorvos and chlorpyrifos

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Table 1. Retention time, MRM parameters of compound, correlation coefficients, LOD etc.

No.	Compound name	CAS	Retention time	Quantitation ions	CE	Qualification ions	CE	Qualification ions	CE	correlation coefficients	LOD (μg/L)	RSD%	Recovery (%)	result
1	Dichlorvos	62-73-7	5.872	185.00>93.00	14	185.00>109.00	14	185.00>63.00	22	0.9999	0.057	1.463	97.808	N.D
2	alpha-HCH	319-84-6	10.604	218.90>182.90	8	218.90>144.90	20	218.90>109.00	28	0.9999	0.038	1.154	91.946	N.D
3	beta- HCH	319-85-7	11.129	218.90>182.90	8	218.90>144.90	20	218.90>109.00	28	0.9999	0.052	1.454	91.719	N.D
4	Quintozene	82-68-8	11.171	294.80>236.80	16	294.80>264.80	12	294.80>142.90	30	0.9999	0.012	1.678	105.387	N.D
5	gamma- HCH	58-89-9	11.276	218.90>182.90	8	218.90>144.90	20	218.90>109.00	28	0.9999	0.053	1.709	95.270	N.D
6	Terbufos	13071-79-9	11.371	231.00>174.90	14	231.00>128.90	26	231.00>202.90	8	0.9999	0.042	2.076	105.499	N.D
7	Chlorothalonil	1897-45-6	11.632	265.90>230.80	14	265.90>168.00	22	265.90>133.00	28	0.9999	0.084	2.616	88.976	N.D
8	delta- HCH	319-86-8	11.856	218.90>182.90	10	218.90>144.90	20	218.90>109.00	28	0.9999	0.049	2.252	89.387	N.D
9	Vinclozolin	50471-44-8	12.527	285.00>212.00	12	285.00>178.00	14	285.00>241.00	4	0.9999	0.098	2.950	92.425	N.D
10	Parathion-methyl	298-00-0	12.577	263.00>109.00	14	263.00>136.00	8	263.00>246.00	6	0.9993	0.260	4.762	110.157	N.D
11	Fenitrothion	122-14-5	13.068	277.00>260.00	6	277.00>109.10	14	277.00>228.00	14	0.9993	0.011	3.696	104.298	N.D
12	Chlorpyrifos	2921-88-2	13.371	313.90>257.90	14	313.90>285.90	8	313.90>193.90	28	0.9999	0.038	2.260	87.910	N.D
13	Parathion	56-38-2	13.528	291.10>109.00	14	291.10>137.00	6	291.10>81.00	24	0.9990	0.028	2.719	122.534	N.D
14	Triadimefon	43121-43-3	13.587	208.10>181.00	10	208.10>127.00	14	208.10>111.00	22	0.9999	0.418	4.237	101.173	N.D
15	DCBP	0-00-0	13.671	250.00>139.00	14	250.00>215.00	8	250.00>111.00	28	0.9999	0.076	1.767	86.311	N.D
16	Fipronil	120068-37-3	14.113	366.90>212.90	30	366.90>254.90	22	366.90>331.90	14	0.9998	0.082	2.503	124.105	N.D
17	alpha- Endosulfan	959-98-8	14.887	338.90>160.00	18	338.90>266.90	8	338.90>195.90	20	0.9995	0.079	3.589	97.567	N.D
18	p,p'-DDE	72-55-9	15.301	246.00>176.00	30	246.00>211.00	22	246.00>220.00	24	0.9999	0.020	1.510	86.773	N.D
19	beta- Endosulfan	33213-65-9	16.009	338.90>160.00	18	338.90>266.90	8	338.90>195.90	20	0.9999	0.878	1.954	76.519	N.D
20	p,p'-DDD	72-54-8	16.096	235.00>165.00	24	235.00>199.00	14	235.00>99.00	30	0.9990	0.030	1.321	99.207	N.D
21	o,p'-DDT	789-02-6	16.13	235.00>165.00	24	235.00>199.00	16	235.00>149.00	40	0.9999	0.053	1.755	111.830	N.D
22	p,p'-DDT	50-29-3	16.795	235.00>165.00	24	235.00>199.00	16	235.00>149.00	40	0.9990	0.025	2.011	74.462	N.D
23	Bifenthrin	82657-04-3	17.688	181.10>166.10	12	181.10>153.10	8	181.10>179.10	12	0.9992	0.055	0.845	105.677	N.D
24	Cyhalothrin-1	68085-85-8	18.5	197.00>161.00	8	197.00>141.00	12	197.00>91.00	26	0.9995	0.365	4.387	93.815	N.D
25	Cyhalothrin-2	68085-85-8	18.669	197.00>161.00	8	197.00>141.00	12	197.00>91.00	26	0.9999	0.126	4.036	116.764	N.D
26	Permethrin-1	52645-53-1	19.464	183.10>168.10	14	183.10>165.10	14	183.10>153.10	14	0.9999	0.740	3.736	110.635	N.D
27	Permethrin-2	52645-53-1	19.594	183.10>168.10	14	183.10>165.10	14	183.10>153.10	14	0.9999	0.642	4.349	93.249	N.D
28	Cyfluthrin-1	68359-37-5	20.003	226.10>206.10	14	226.10>199.10	6	226.10>151.10	28	0.9999	0.045	3.571	100.999	N.D
29	Cyfluthrin-2	68359-37-5	20.103	226.10>206.10	14	226.10>199.10	6	226.10>151.10	28	0.9999	0.044	1.269	101.738	N.D
30	Cyfluthrin-3	68359-37-5	20.161	226.10>206.10	14	226.10>199.10	6	226.10>151.10	28	0.9999	0.049	1.408	104.880	N.D
31	Cyfluthrin-4	68359-37-5	20.21	226.10>206.10	14	226.10>199.10	6	226.10>151.10	28	0.9999	0.078	4.891	102.516	N.D
32	Cypermethrin-1	52315-07-8	20.327	163.10>127.10	6	163.10>91.00	14	163.10>109.10	22	0.9999	0.031	3.744	101.067	N.D
33	Cypermethrin-2	52315-07-8	20.431	163.10>127.10	6	163.10>91.00	14	163.10>109.10	22	0.9999	0.032	4.771	100.814	N.D
34	Cypermethrin-3	52315-07-8	20.48	163.10>127.10	6	163.10>91.00	14	163.10>109.10	22	0.9999	0.054	5.019	104.511	N.D
35	Flucythrinate-1	70124-77-5	20.494	199.10>157.10	10	199.10>107.10	22	199.10>171.10	8	0.9999	0.617	5.045	118.055	N.D
36	Cypermethrin-4	52315-07-8	20.529	163.10>127.10	6	163.10>91.00	14	163.10>109.10	22	0.9996	0.051	2.675	103.894	N.D
37	Flucythrinate-2	70124-77-5	20.688	199.10>157.10	10	199.10>107.10	22	199.10>171.10	8	0.9998	0.691	2.203	115.850	N.D
38	Fenvalerate-1	51630-58-1	21.205	419.10>225.10	6	419.10>167.10	12	419.10>125.10	26	0.9999	0.048	3.863	114.964	N.D
39	Fenvalerate-2	51630-58-1	21.407	419.10>225.10	6	419.10>167.10	12	419.10>125.10	26	0.9999	0.095	3.978	102.240	N.D
40	Deltamethrin-1	52918-63-5	21.756	252.90>93.00	20	252.90>171.90	8	252.90>77.00	26	0.9998	0.481	2.550	113.103	N.D
41	Deltamethrin-2	52919-63-5	21.962	252.90>93.00	20	252.90>171.90	8	252.90>77.00	26	0.9994	0.523	4.385	111.812	N.D

Note : N.D means undetected

LOD and recovery

The limit of detection (LOD; S/N=3) of most compounds were below 0.001 mg/L (Table 1). Use commercially available Milkvetch Root for recovery test. The spiked concentration is 0.002 mg/kg and the recovery rate was 74.46 %~124.10 %, shown in table 1.

Sample analysis

Select commercially available Milkvetch Root, operate in accordance with the pretreatment processing method and analyse, the results are shown in table 1, the chromatogram is shown in Figure 4.

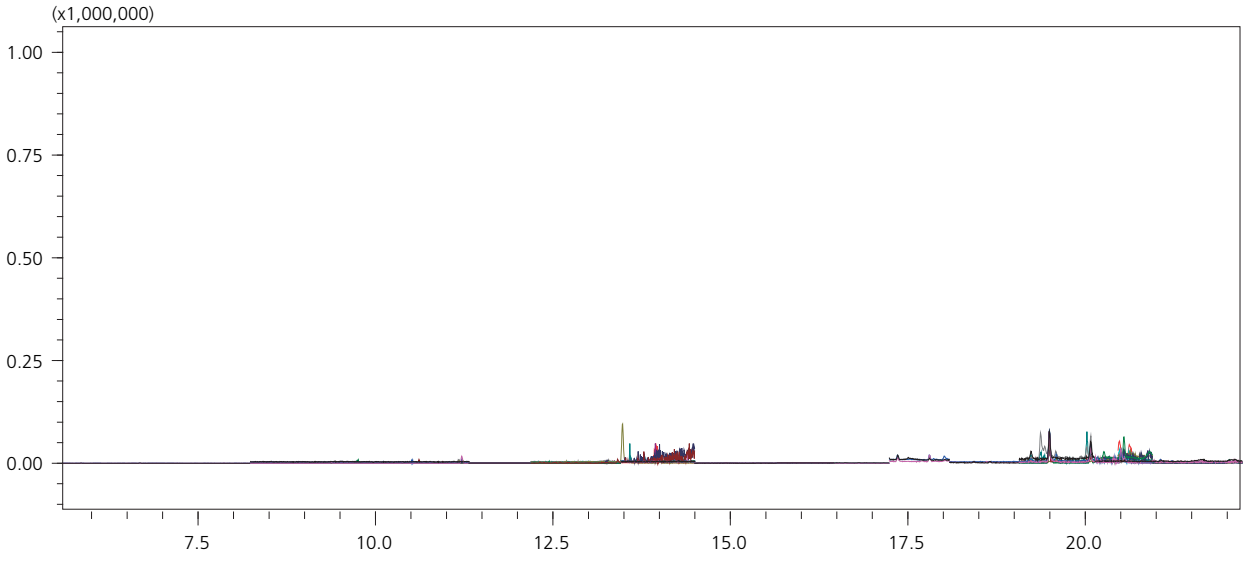

Figure 4. MRM chromatogram of sample

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Conclusions

Refer to the pesticide residues analysis method that SHIMADZU responsed to 2015 Chinese Pharmacopoeia, using SHIMADZU's triple quadrupole tandem mass spectrometry (GCMS-TQ8040), for detection of pesticide residue in new Chinese Pharmacopoeia projects, the method was established for the determination of the amount of pesticide residues in Chinese Traditional Medicine Milkvetch Root. The results of this research indicated that the relative coefficients of the 41 kinds of pesticides ranged from 1 to 500 µg/L are above 0.999. Precision of this method was measured by analyzing the same sample (0.01 mg/L) six times. The overall RSD% of analysis were below 5 %. The limit of detection (LOD; S/N=3) of most compounds were below 0.001 mg/L. Commercially available Milkvetch Root was used for recovery test, spiked concentration was 0.002 mg/kg and the recovery rate was 74.46 %~124.10 %. The developed method in this study was proved to be reliable and accurate, and permits rapid determination of pesticides can be easily applied for quality control of Milkvetch Root.

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