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Determination of Multiple Pyrethroid Insecticides in Chrysanthemum Flower

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Abstract A simplified method for determining four pyrethroid insecticides (fenpropathrin, cypermethrin, fenvalerate, and deltamethrin) in the Chinese herbal medicine (chrysanthemum flower) is described. Standards were fortified into chrysanthemum flower (5g) with three levels, 1, 0.1 and 0.01mg/kg. The pyrethroid insecticides are extracted with petroleum ether and cleaned-up with neutral aluminum oxide. The extracts are analyzed by gas chromatography equipped with electron capture detector (ECD). Analysis of fortified chrysanthemum flower (n= 5) shows mean recoveries ranged from 86%～104% at 1 mg/kg level, 87%～95% at 0.1 mg/kg level and 81%～99% at 0.01 mg/kg level. The minimum detector response ranged form 8.3×10^{-4}～2.8×10^{-3} ng and minimum detectable concentration ranged from 0.83～2.82 μg/kg. The method is rapid, simple, sensitive and is applicable to the determination of fenpropathrin, cypermethrin, fenvalerate, and deltamethrin in chrysanthemum flower.

Key words Chrysanthemum flower; Multiresidue; Pyrethroid; Insecticide

1 Introduction

Chrysanthemum flower (*Chrysanthemum morifolium* Ramat) is one of the Chinese herbal medicines that are popularly used in China and some other Asian countries such as Japan, Malaysia, Singapore and Korea. The medicine chrysanthemum flower could reduce fever, improve vision, calms and reduce excitement and irritation, clear away toxic substance, treat febrile disease, release toxins and brighten the eyes, decrease the irascibility. Chrysanthemum flower also became popular in USA and some European countries, and it has been exported in large amounts to such countries. Normally there are some regulations and restrictions in the export of the agricultural products regarding pesticide residues. FAO and WHO have prescribed residues limits for some pyrethroid in agricultural and livestock products but no limit has been set for Chinese herbal medicine which became very popularly in many countries. Methods for the analysis of residues of individual pyrethroid compounds in a variety of crops have been presented[1～3]. Some other methods focusing in the simultaneous determination of pyrethroid multiresidue techniques in fruits, vegetables, and grains also been published[4～8]. There are no reports on multiple insecticide residues in chrysanthemum flower. The objective of this research paper is to

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describe an easy, rapid, economic, and sensitive method for determining the residues of multiple pyrethroid insecticides in chrysanthemum flower.

2 Experimental

2.1 Apparatus

Shimadzu GC-9A gas chromatography (Shimadzu Corp., Kyoto, Japan) equipped with ^{63}Ni electron capture detector (ECD) and with a 1.5 m × 3.0 mm id glass column packed with 5% OV-101 on 60～80 mesh Chromosorb W. AW-DMCS. Operating condition: both injector port and detector, 300 ℃; column, 270 ℃; carrier gas (N_2), flow rate 75 mL/min, injection volume 2 μL. DC-200 high speed blender (Shanghai, China). Haake SWB20 mechanical shaker (Germany). SBXZ-1 rotary vacuum evaporator (Shanghai, China). Shimadzu C-R3A Data processor (Shimadzu Corp., Kyoto, Japan).

2.2 Reagents

Redistilled petroleum ether (at 30～60 ℃) (Hangzhou, China). Anhydrous sodium sulfate, heated 8 h at 450 ℃ and stored in a tightly capped bottle until used (Lan qi, China). Neutral aluminum oxide (reagent grade), using 5% water deactivated (previously activated 6 h at 650 ℃) and stored in a tightly capped bottle until used (Shanghai, China). Pesticides: fenpropathrin (98.3%), cypermethrin (98%), fenvalerate (99%), and deltamethrin (98%). All obtained from Sumitomo China Chemical Ltd (China). The standard solutions are individually prepared in petroleum ether at 100～120 μg/mL concentration. The mixed standard solutions were prepared by mixing suitable volumes of individual standard solutions and diluting with petroleum ether for the recovery study.

2.3 Sample preparation

Four kilograms (total of 80 bags, each bag contain 50 g) of chrysanthemum flower was collected from different market, after thoroughly mixing, 0.5 kg of total amount was covered by plastic bags and kept in the refrigerator prior to use (within 24 h of sampling).

2.4 Extraction

Five grams of sample were weighed into a blender cup, fortification standard was added and the sample was allowed to equilibrate for 12 h. The fortified samples then blended for 2 min with 80 mL petroleum ether. The content of the blender jar was transferred into erlenmeyer flask, and the jar was then rinsed with two 40 mL portions of petroleum ether, and add the washings to the same erlenmeyer flask. The erlenmeyer flask was placed on the mechanical shaker and shaked for 2 h. Filter the extracts through glass funnel containing 5 g anhydrous sodium sulfate. Collect the filtrate into a 250 mL round bottom flask. Rinse the erlenmeyer flask with two 10 mL portions of petroleum ether. Pass the rinsing through the same funnel containing anhydrous sodium sulfate and collect them in the round bottom flask with the organic extracts. Evaporate contents of the flask to about 5 mL volume on a rotary evaporator at 40 ℃.

2.5 Clean-up

Chromatographic Cleanup Column——25 cm × 1.5 cm id glass column was used for the clean-up procedure. The column was prepared by adding anhydrous sodium sulfate (2 cm), neutral aluminum oxide (5 g), anhydrous sodium sulfate (2 cm), then prewashed by 20 mL petroleum ether-ethyl acetate (95+ 5). The concentrated extracts were transferred from round bottom flask into the chromatographic cleanup column. The round bottom flask rinsed with two 5 mL portion of petroleum ether and the washings was added to the column. The pyrethroid residues were eluted with 80 mL petroleum ether, the eluate then collected into 250 mL round bottom flask. The eluate fractions was evaporated at 40 ℃ with rotary evaporator and diluted to 10 mL.

3 Results and Discussion

To meet the objectives for the surveillance and monitoring of insecticides residue in Chinese herbal medicine samples, we have developed a new sensitive routine method for pyrethroid insecticide, which is described here. We have applied that method to evaluate the levels of the above insecticides in the chrysanthemum flowers. As a first step petroleum ether extraction of the samples, followed by clean up procedure, using neutral aluminum oxide. This system afforded good conditions for the gas chromatographic analysis of four pyrethroid insecticides at 10^{-12} level. Validation of the method for the insecticides was performed by spiking in the laboratory with four pyrethroid insecticides at various concentration levels. The recovery was determined with samples of 5 g chrysanthemum flower fortified with pesticide standards at three concentration levels of 0.01, 0.1 and 1 mg/kg. The results of a series of fivefold experiments for each concentration level are presented in Table 1. Mean recoveries of all pyrethroid insecticides at the 1 mg/kg level of fortification were between 86%～104%, Recoveries at 0.1 mg/kg level of fortification were 87%～95%. At the lowest level of fortification (0.01 mg/kg), recoveries were 81%～99%. Recoveries were higher than 80% in all cases. Coefficients of variation were lower than 7% and there by meet the requirements for pesticide residue Fig. 1 shows chromatograms of insecticide standards (A), control (C), and extracted sample (B) which was spiked with 0.01 mg/kg of the four pyrethriod insecticides. Peaks were measured by height. Control samples of chrysanthemum flower shows no significant insecticide residues when chromatographed at different concentration levels. Fenpropathrin, cypermethrin, fenvalerate, and deltamethrin were identified by comparison of their retention times to the standards. Table 2 shows the retention times of these insecticides. An external standard method was used to determine the linearity of response of the detector, to calculate the percentages of the insecticides recovered and to evaluate the level of the residues in chrysanthemum flower samples. The minimum detectable levels (MDL) and the minimum detectable concentration given in table 2 were estimated from standard pesticide concentrations. It is right therefore that the monitoring of their residue levels in food and the environment should continue.

Table 1 Mean % recovery and relative standard deviation of pyrethroid in chrysanthemum flower samples at 0.01, 0.1 and 1 mg/kg fortification level (n= 5)

Insecticide	Fortification level/mg·kg^{-1}	Recovery (%)	*CV* (%)
fenpropathrin	1.034	95.54	4.19
	0.103	87.74	6.84
	0.010	99.11	6.05
cypermethrin	1.220	102.2	4.89
	0.122	89.56	4.47
	0.012	90.24	5.54
fenvalerate	1.000	104.69	5.73
	0.100	95.59	4.18
	0.010	81.47	6.14
deltamethrin	1.220	86.95	4.60
	0.122	94.65	5.28
	0.012	94.36	5.30

Table 2 The minimum detector response and minimum detectable concentration of pyrethroid

Insecticide	Retention time/min	Minimum detectable response/ng	Minimum detectable concentration/μg·kg^{-1}
fenpropathrin	2.64	8.3×10^{-4}	0.83
cypermethrin	5.70	2.2×10^{-3}	2.18
fenvalerate	7.37	2.5×10^{-3}	2.50
deltamethrin	9.25	2.8×10^{-3}	2.82

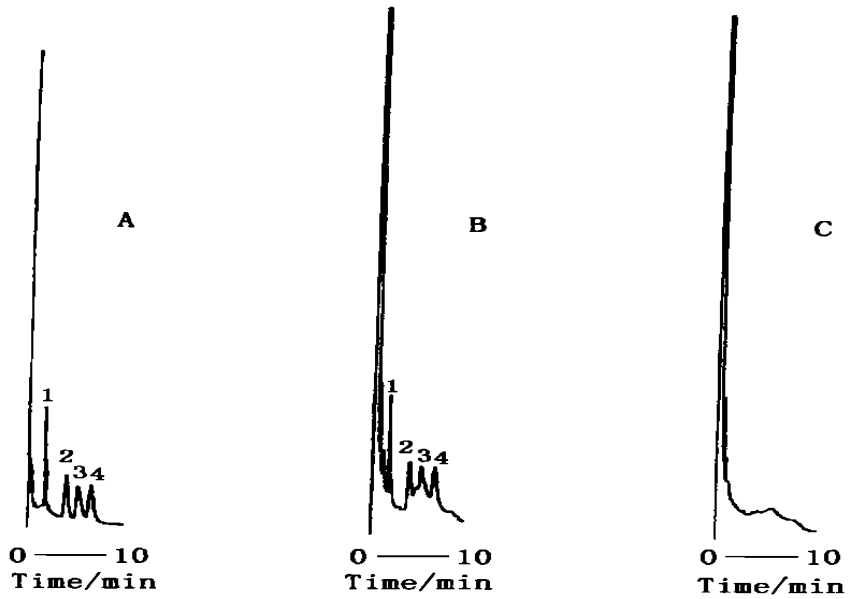

Fig. 1 Representative gas chromatograms of pyrethroids

A: insecticide standards B: chrysanthemum flower sample fortified with pyrethroid (0.01 mg/kg). C: control chrysanthemum flower. Peak identities are fenpropathrin (1), cypermethrin (2), fenvalerate (3), and deltamethrin (4).

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菊酯类农药在中草药白菊花中的多残留分析方法研究

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摘　要　报道了采用气相色谱仪、电子捕获检测器同时测定 4 种菊酯类农药(甲氰菊酯、氯氰菊酯、氰戊菊酯和溴氰菊酯)在中草药白菊花中的残留分析方法。添加浓度分别为 1.0、0.1、0.01 mg/kg, 白菊花中的回收率分别为 86%～104%, 87%～95% 和 81%～99%, n= 5, 最低检测量 8.3×10^{-4}～2.8×10^{-3}ng。该方法简便、准确、分离效果好、回收率高。

关键词　白菊花; 多残留分析; 菊酯类农药