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Short Communication

Rapid method for the determination of multiple pyrethroid residues in fruits and vegetables by capillary column gas chromatography

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Abstract

A rapid and economical simplified multi-residue method is described for the determination of multiple pyrethroid insecticides in fruits and vegetables. The residues are extracted from crops with methanol and the crop co-extractives are removed by toluene partitioning and Florisil–charcoal minicolumn chromatography. The final extract is analysed by capillary column gas chromatography with electron-capture detection. The recoveries were determined by fortifying six different crops (apples, oranges, cabbages, pears, peppers and tomatoes) with eleven pyrethroids (Py-115, allethrin, biphenthrin, fenpropathrin, cyhalothrin, permethrin, cyfluthrin, flucythrinate, fluvalinate, fenvalerate and deltamethrin) at three levels, 0.01–0.07, 0.10–0.70 and 1.0–7.0 mg/kg. Three determinations were made at each level for each crop. Recoveries of the eleven pyrethroids ranged from 70.4 to 110.0% at the three different levels. The practical determination limit of the method was in the range 3.0–30.0 μg/kg for all the pyrethroid insecticides. The proposed method had major advantages that simplified steps were achieved for the extraction and the clean-up, the solvent consumption was reduced and the analysis time was shortened.

1. Introduction

Various pyrethroids are widely used as agricultural insecticides around the world. The development of a multi-residue method for the determination of these insecticides in crops is indispensable to routine work. Well known multi-residue approaches have been applied successfully to analyses for organohalogens [1], organophosphates [1,2] and carbamates [3,4] in agricultural products. The pyrethroid insecticides differ from the oganophosphates and the carbamates, as each of them is actually a mixture of more than one isomer, and some pyrethroids consist of eight possible isomers [5]. Therefore, it is more difficult to develop a multi-residue method for pyrethroids. However, several methods have been published for the multi-residue determination of pyrethroids in agricultural products [5–8].

Various methods for the extraction and clean-up of individual or several pyrethroids in crops have been described. The solvent systems included acetone–hexane [5,9,10], acetone–dichloromethane [6,11], acetone–light petroleum [7,8], acetonitrile–hexane [12], methanol–

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toluene [13,14] and acetonitrile–light petroleum [15]. The different types of adsorbent used included Florisil [7,9,12,15], silica gel [5], alumina [6,16], Bio-Beads SX-3 [9,15], alumina–Florisil [10], Florisil–charcoal [13,14] and activated charcoal–magnesia–diatomaceous earth [6]. Most of these procedures for extraction and clean-up require large volumes of solvents and time-consuming evaporation of the organic solvents before further clean-up and analysis either to concentrate the residues or to remove solvents that interfere with selective detection.

Of the extraction and partitioning systems investigated, we found that methanol–toluene extraction and Florisil–charcoal minicolumn clean-up did not essentially have these drawbacks. It was originally used in a comprehensive multi-residue method for various compounds including two pyrethroids [13,14]. In this work, this technique for extraction and clean-up was appropriately modified, and it was successfully extended to the determination for multiple pyrethroid residues in fruits and vegetables.

2. Experimental

2.1. Instrumentation

A Hewlett-Packard Model 5890A gas chromatograph equipped with a ^{63}Ni electron-capture detector, a split–splitless capillary column injection port, a Model 7673A automatic sampler and a Model 3393A reporting integrator was used. The injection port temperature was 280°C and the detector temperature 300°C. Both the carrier gas and make-up gas were methane–argon (10:90).

Fused-silica capillary columns were supplied by Hewlett-Packard: (i) HP-1 (2.65 μm), 5 m × 0.53 mm I.D., as an analytical column, carrier gas flow-rate 5.0 ml/min, make-up gas flow-rate 60.0 ml/min, column temperature programme initially 230°C for 2 min and increased at 2°C/min to 260°C, held for 5 min; (ii) Ultra 2 (0.17 μm) (cross-linked 5% phenyl–methylsilicone), 25 m × 0.32 mm I.D., as a confirmation column, carrier gas flow-rate 1.2 ml/min, make-up gas flow-rate 54.0 ml/min, column temperature programme initially 50°C for 0.5 min, increased at 20°C/min to 210°C, held for 12 min, and increased at 1°C/min to 250°C, held for 8 min.

2.2. Reagents

Standard solutions of the insecticides in toluene (100 μg/ml) were prepared for deltamethrin (98.0%), cypermethrin (97.0%), fenpropathrin (92.3%), fenvalerate (94.1%), biphenthrin (94.3%), cyhalothrin (97.0%), permethrin (91.1%), flucythrinate (94.2%), fluvalinate (90.6%), cyfluthrin (93.8%), allethrin (92.3%) and Py-115 (93.7%). These insecticides were obtained from Roussel-Uclaf Nanjing Office (Nanjing, China), FMC Far East (Beijing, China), Shell China (Beijing, China), ICI China (Beijing, China) and Shanghai Midwest Pesticide Factory (Shanghai, China).

Methanol and toluene were redistilled in all-glass apparatus prior to use and procedural blanks were analysed by gas chromatography with electron-capture detection before sample analysis.

Charcoal (20–40 mesh), acid-washed and activated as described by Bolygó and Zakar [6], and Florisil (60–100 mesh), activated as described by Holland and McGhie [13], were used.

2.3. Extraction, clean-up and analysis

Place 50.0 g of chopped sample and 50 ml of methanol in a homogenizer jar and homogenize sample for 2 min at high speed. Vacuum filter the homogenate through a 12-cm perforated Büchner funnel containing filter-paper, collecting the filtrate in a 250-ml filter flask. Re-homogenize the filter cake with 50 ml of methanol and filter. Measure the volume of the combined filtrates. Transfer a portion of filtrate equivalent to 20 g of sample into a 250-ml separating funnel and add 10 ml of toluene followed by 60 ml of water containing 10% (w/v) NaCl. Shake well for 2 min and let the layers separate. Prepare a chromatographic minicolumn: on top of a glass-wool plug add 0.5 g of Florisil followed by 0.04 g of activated charcoal and 1.5 g of anhydrous

Table 1
Recoveries of pyrethroids from various crops

Compound	Added (ppm)	Average recovery ± S.D. (%)[a] and R.S.D. (%)[b]					
		Apples	Oranges	Pears	Peppers	Cabbages	Tomatoes
Py-115	0.01	107.2 ± 3.9 (3.6)	98.6 ± 4.2 (4.3)	89.1 ± 2.7 (3.0)	96.4 ± 5.6 (5.8)	101.1 ± 3.2 (3.2)	97.2 ± 1.6 (1.7)
	0.10	88.3 ± 2.8 (3.2)	96.7 ± 1.9 (2.0)	81.4 ± 3.2 (3.9)	86.2 ± 1.5 (1.7)	83.9 ± 2.7 (3.2)	97.5 ± 3.0 (3.1)
	1.00	92.6 ± 3.4 (3.7)	90.3 ± 4.0 (4.4)	83.2 ± 3.7 (4.5)	80.5 ± 2.9 (3.6)	91.6 ± 1.4 (1.5)	102.3 ± 3.9 (3.8)
Allethrin	0.01	95.4 ± 3.6 (3.8)	110.0 ± 3.1 (2.8)	98.4 ± 2.7 (2.7)	92.8 ± 4.3 (4.6)	89.7 ± 3.1 (3.5)	99.3 ± 3.0 (3.0)
	0.10	87.0 ± 1.5 (1.7)	81.9 ± 1.7 (2.1)	90.3 ± 2.3 (2.5)	86.4 ± 3.4 (3.9)	92.5 ± 3.1 (3.4)	89.3 ± 2.0 (2.2)
	1.00	88.4 ± 2.1 (2.4)	91.0 ± 3.5 (3.8)	80.1 ± 2.7 (3.4)	83.6 ± 1.9 (2.3)	92.1 ± 0.9 (1.0)	94.5 ± 3.3 (3.5)
Biphenthrin	0.02	80.3 ± 1.9 (2.5)	87.6 ± 2.5 (2.9)	85.0 ± 2.7 (3.2)	90.3 ± 4.6 (5.1)	96.1 ± 1.8 (1.9)	82.1 ± 3.9 (4.8)
	0.20	92.3 ± 3.5 (3.8)	89.0 ± 3.3 (3.7)	93.5 ± 2.4 (2.6)	107.5 ± 4.2 (3.9)	78.5 ± 1.9 (2.4)	79.0 ± 3.7 (4.7)
	2.00	83.2 ± 1.7 (2.0)	78.9 ± 2.1 (2.7)	97.0 ± 3.7 (3.8)	73.4 ± 2.6 (3.5)	81.4 ± 3.1 (3.8)	81.2 ± 0.9 (1.1)
Fenpropathrin	0.02	82.2 ± 2.0 (2.4)	79.8 ± 2.9 (3.6)	91.5 ± 0.7 (0.8)	75.3 ± 3.2 (4.3)	84.0 ± 1.6 (1.9)	96.4 ± 1.8 (1.9)
	0.20	80.7 ± 3.7 (4.6)	87.0 ± 1.9 (2.2)	77.4 ± 2.9 (3.9)	98.3 ± 1.7 (1.8)	83.8 ± 2.9 (3.5)	82.9 ± 1.9 (2.3)
	2.00	90.4 ± 1.2 (1.3)	101.1 ± 3.0 (3.0)	86.5 ± 0.7 (0.8)	85.8 ± 2.8 (3.3)	102.3 ± 1.6 (1.6)	81.4 ± 3.4 (4.2)
Cyhalothrin	0.01	95.6 ± 2.9 (3.1)	99.3 ± 1.7 (1.7)	89.6 ± 2.3 (2.6)	78.6 ± 2.4 (3.1)	85.7 ± 1.6 (1.9)	78.6 ± 2.2 (2.8)
	0.10	82.9 ± 1.6 (1.9)	106.7 ± 1.6 (1.5)	78.9 ± 0.8 (1.0)	96.4 ± 3.2 (3.3)	84.3 ± 3.1 (3.7)	82.9 ± 3.0 (3.6)
	1.00	79.6 ± 0.9 (1.1)	101.3 ± 3.1 (3.1)	85.7 ± 3.1 (3.6)	87.1 ± 1.8 (2.1)	96.4 ± 1.9 (2.0)	81.4 ± 4.5 (5.5)
Permethrin	0.07	80.9 ± 1.1 (1.4)	81.4 ± 1.7 (2.1)	82.9 ± 3.0 (3.6)	93.4 ± 2.3 (2.5)	92.9 ± 2.9 (3.1)	86.3 ± 1.3 (1.5)
	0.70	79.7 ± 1.7 (2.1)	102.3 ± 3.4 (3.3)	92.0 ± 1.9 (2.2)	106.5 ± 3.7 (3.5)	79.4 ± 1.9 (2.4)	80.7 ± 2.1 (2.6)
	7.00	83.6 ± 2.6 (3.1)	81.9 ± 2.6 (3.2)	98.4 ± 3.5 (3.6)	80.1 ± 1.5 (1.9)	81.3 ± 3.6 (4.4)	91.0 ± 1.7 (1.9)
Cyfluthrin	0.03	84.2 ± 3.5 (4.2)	83.3 ± 3.6 (4.3)	86.2 ± 1.5 (1.7)	78.0 ± 3.2 (4.1)	75.0 ± 3.4 (4.5)	86.3 ± 3.6 (4.2)
	0.30	80.0 ± 0.9 (1.1)	89.7 ± 1.9 (2.1)	87.9 ± 2.0 (2.3)	86.7 ± 1.7 (2.0)	82.1 ± 2.6 (3.2)	89.5 ± 1.5 (1.7)
	3.00	92.5 ± 2.9 (3.1)	77.0 ± 3.0 (3.9)	83.6 ± 3.3 (4.0)	82.1 ± 2.6 (3.2)	79.1 ± 2.7 (3.4)	97.9 ± 4.1 (4.2)
Flucythrinate	0.04	79.1 ± 2.5 (3.2)	93.3 ± 2.1 (2.3)	80.3 ± 3.1 (3.9)	81.0 ± 3.1 (3.8)	84.6 ± 2.5 (3.0)	80.0 ± 1.9 (2.4)
	0.40	89.5 ± 3.7 (4.1)	98.7 ± 3.6 (3.7)	82.4 ± 1.6 (1.9)	89.4 ± 2.4 (2.7)	90.0 ± 1.7 (1.9)	86.7 ± 2.3 (2.7)
	4.00	94.6 ± 1.1 (1.2)	87.9 ± 2.7 (3.1)	97.3 ± 2.7 (2.8)	90.3 ± 3.6 (4.0)	77.4 ± 2.8 (3.6)	81.1 ± 3.1 (3.8)

Table 1 (*continued*)

Compound	Added (ppm)	Average recovery ± S.D. (%)[a] and R.S.D. (%)[b]					
		Apples	Oranges	Pears	Peppers	Cabbages	Tomatoes
Fenvalerate	0.04	90.0 ± 4.1 (4.2)	76.9 ± 2.8 (3.6)	104.2 ± 4.3 (4.1)	80.4 ± 1.9 (2.4)	88.2 ± 3.3 (3.8)	106.3 ± 3.9 (3.7)
	0.40	95.2 ± 2.1 (2.2)	84.3 ± 1.7 (2.0)	91.0 ± 1.5 (1.7)	83.4 ± 0.8 (1.0)	85.4 ± 2.1 (2.5)	90.6 ± 2.1 (2.3)
	4.00	82.1 ± 3.0 (3.7)	82.1 ± 3.1 (3.8)	88.4 ± 2.6 (2.9)	91.3 ± 3.1 (3.4)	78.0 ± 3.6 (4.6)	83.2 ± 2.7 (3.3)
Fluvalinate	0.04	79.4 ± 1.8 (2.3)	79.4 ± 3.0 (3.8)	90.5 ± 3.1 (3.4)	83.0 ± 3.3 (4.0)	77.3 ± 4.2 (5.4)	81.6 ± 2.9 (3.6)
	0.40	96.9 ± 2.7 (2.8)	88.5 ± 2.3 (2.6)	79.3 ± 1.8 (2.3)	92.4 ± 1.5 (1.6)	83.6 ± 3.0 (3.6)	87.4 ± 0.8 (0.9)
	4.00	82.3 ± 3.4 (4.1)	83.2 ± 1.9 (2.3)	82.2 ± 3.6 (4.4)	80.0 ± 2.9 (3.6)	80.6 ± 2.9 (3.6)	109.4 ± 3.8 (3.5)
Deltamethrin	0.04	98.2 ± 2.3 (2.3)	72.3 ± 2.8 (3.9)	75.4 ± 2.9 (3.9)	92.1 ± 1.7 (1.8)	78.4 ± 2.7 (3.4)	81.0 ± 2.7 (3.3)
	0.40	94.3 ± 1.7 (1.8)	80.5 ± 1.2 (1.5)	88.6 ± 2.3 (2.6)	86.5 ± 1.1 (1.3)	88.1 ± 0.7 (0.8)	96.9 ± 1.1 (1.1)
	4.00	77.6 ± 2.9 (3.7)	89.2 ± 4.0 (4.5)	77.1 ± 3.2 (4.2)	90.3 + 2.6 (2.9)	82.3 ± 1.9 (2.3)	85.4 ± 4.0 (4.7)

[a] $n = 3$.
[b] R.S.D.s in parentheses.

Na_2SO_4. Prewash the minicolumn with 20 ml of toluene. Add 5 ml of the toluene layer from the separating funnel and collect the eluate in a sample tube. Elute with an additional 5 ml of toluene and adjust thc total eluate volume to a suitable level for gas chromatography. Tentatively identify the residue peaks according to the retention times. Measure peak areas or peak heights and determine the residue content by comparison with that obtained from a known content of appropriate reference material.

3. Results and discussion

The efficiency of extraction and clean-up of the modified procedure was satisfactory, as no interfering peaks were observed on the chromatogram of the different samples under the selected conditions. However, organochlorine compounds such as HCB, BHC, heptachlor, aldrin, heptachlor epoxide and DDT would also be extracted together with the pyrethroid insecticides, if present in the sample. We found that the retention times of the pyrethroids on the capillary columns described as above were considerably longer than those of organochlorines. It took *ca.* 3 min for the organochlorines to be eluted from the column before the pyrethroid insecticides, except for Py-115 and allethrin, which has almost the same retention times as isomers of BHC and DDT, respectively. This problem could be resolved by the confirmatory method described below.

The proposed method validation was based on the recovery of different insecticides from the selected crops. Six fruits and vegetables were fortified with eleven pyrethroids at 0.01–0.07, 0.10–0.70 and 1.0–7.0 mg/kg levels, using 50 g

of each sample and adding *ca.* 1 ml of methanol containing an appropriate amount of each of the insecticides. One unfortified portion and three fortified portions of each sample were analysed at one time. The recovery data obtained are given in Table 1. A chromatogram of these compounds is shown in Fig. 1. Linear calibration graphs were obtained from 0.005 to 3.0 ng for the eleven insecticides. The practical determination limit of the method was in the range 3.0–30.0 μg/kg for all the insecticides.

In order to increase the reliability of peak identification on the basis of wide-bore capillary gas chromatographic data, especially in the presence of interferents originating from crop samples or possible cross-interference from either some pyrethroids or organochlorine compounds present together, we also examined separations on a high-resolution narrow-bore capillary column. An example of the analysis of an apple sample spiked with 12 pyrethroids is given in Fig. 2. As can be seen in Figs. 1 and 2, all isomers of each insecticide appeared as a single peak on the chromatogram from the wide-bore column, except for flucythrinate, whereas they were all separated as isomeric peaks on the narrow-bore column. This should not only enhance the resolution but also confirm the presence of various pyrethroids. For example, biphenthrin and fenpropathrin had the same retention time on the wide-bore column but were completely resolved with the narrow-bore column.

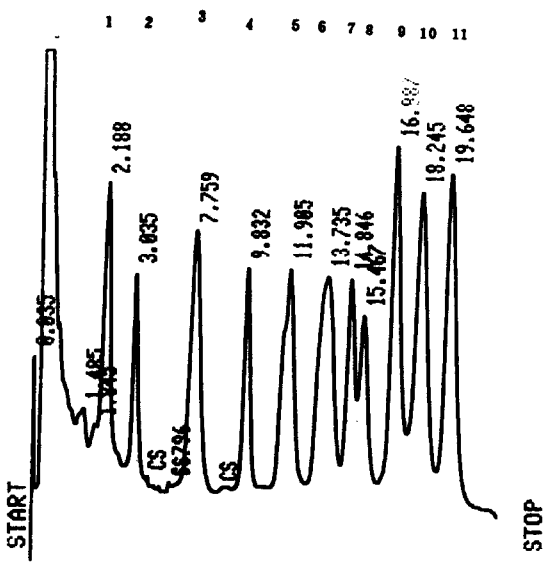

Fig. 1. Chromatogram of a spiked apple extract using the wide-bore capillary column. Peaks: 1 = Py-115 (0.10 mg/kg); 2 = allethrin (0.10 mg/kg); 3 = biphenthrin (0.12 mg/kg) + fenpropathrin (0.12 mg/kg); 4 = cyhalothrin (0.15 mg/kg); 5 = permethrin (0.70 mg/kg); 6 = cyfluthrin (0.35 mg/kg); 7, 8 = flucythrinate (0.40 mg/kg); 9 = fenvalerate (0.40 mg/kg); 10 = fluvalinate (0.40 mg/kg); 11 = deltamethrin (0.40 mg/kg). For chromatographic conditions, see text; injection volume, 1 μl. Values at peaks indicate retention times in min.

Cyfluthrin, cypermethrin and flucythrinate consist of four, four and two isomers, respectively. They can be eluted separately as one, one and two peaks with the wide-bore capillary column. However, cyfluthrin and cypermethrin were not resolved and the peak of cypermethrin and the first isomeric peak of flucythrinate overlapped when present together in the samples. The three insecticides were eluted separately as four, four and two peaks with the narrow-bore capillary column, and their isomeric peaks were well resolved, except for the last isomeric peak of cypermethrin and the first isomeric peak of fluthrinate, which overlapped. However, these problems have no effect on the identifications of the various pyrethroids. Therefore, the wide-bore capillary column was used as the analytical column and the narrow-bore capillary as the confirmation column. By this means it was easy to determine multiple residues of the pyrethroids in fruits and vegetables.

In conclusion, the method described is relatively simple, rapid and economical, and is suitable for multi-residue analyses for pyrethroid insecticides in non-fatty samples.

4. Acknowledgements

The authors gratefully thank ICI China, FMC Far East and Shell China for providing reference pesticides.

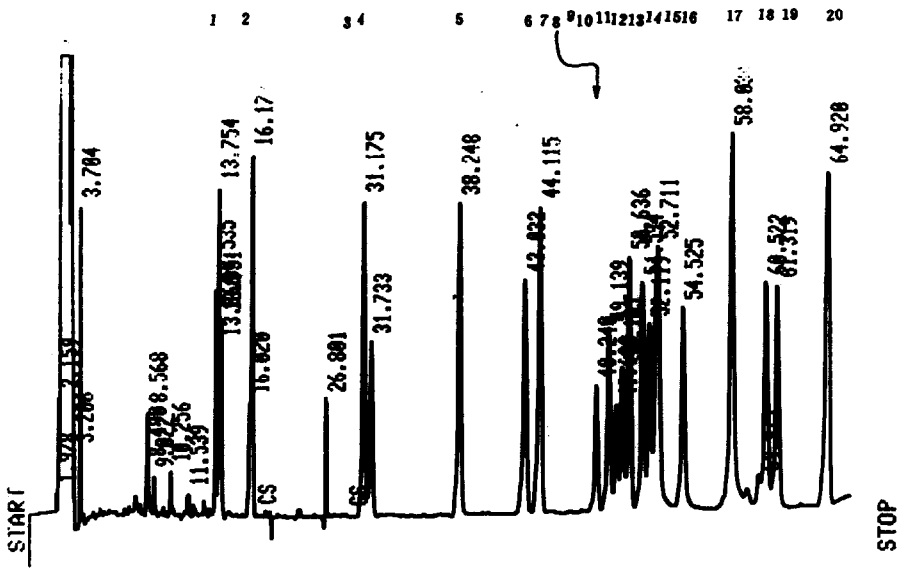

Fig. 2. Chromatogram of a spiked apple extract using the narrow-bore capillary column. Peaks: 1 = Py-115; 2 = allethrin; 3 = biphenthrin; 4 = fenpropathrin; 5 = cyhalothrin; 6, 7 = permethrin; 8, 9, 10, 11 = cyfluthrin; 12, 13, 14 = cypermethrin; 15 = cypermethrin + flucythrinate; 16 = flucythrinate; 17 = fenvalerate; 18, 19 = fluvalinate; 20 = deltamethrin. For chromatographic conditions, see text; injection volume, 1 μl. Spiked sample concentrations as in Fig. 1, plus cypermethrin (0.40 mg/kg). Values at peaks indicate retention times in min.

5. References

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