



Short communication

## Simultaneous determination of nine pyrethroids in indoor insecticide products by capillary gas chromatography

Hongyuan Yan<sup>a,b</sup>, Fengxia Qiao<sup>b,c</sup>, Minglei Tian<sup>b</sup>, Kyung Ho Row<sup>b,\*</sup>

<sup>a</sup> College of Pharmacy, Hebei University, Baoding, 071002, China

<sup>b</sup> Department of Chemical Engineering, Inha University, Incheon, 402751, Republic of Korea

<sup>c</sup> Department of Chemistry, Baoding University, Baoding, 071000, China

### ARTICLE INFO

#### Article history:

Received 15 August 2009

Received in revised form

27 September 2009

Accepted 29 September 2009

Available online 7 October 2009

#### Keywords:

Pyrethroids

Active ingredients

Mosquito coils

Aerosol products

Capillary gas chromatography

### ABSTRACT

A gas chromatographic method was developed for simultaneous determination of nine pyrethroids (permethrin, transallethrin, beta-cypermethrin, prallethrin, tetramethrin, transfluthrin, cyphenothrin, phenothrin, imiprothrin) in indoor insecticide products using dibutyl phthalate and iso-octyl phthalate as two internal standards. Parameters affecting the extraction and separation efficiency were investigated. Good linear fit curves were obtained in a range of 0.4–900 mg/l with correlation coefficients >0.999. The proposed method was successfully applied for the determination of pyrethroids in mosquito coils and two aerosol products. The recovery of transallethrin in mosquito coils at three spiked levels was 96.8% with relative standard deviation less than 2.7%. The recoveries of transallethrin, tetramethrin, permethrin and cyphenothrin in aerosol products were 97.2%, 96.4%, 94.3%, 94.6% with RSD less than 2.3%, 2.8%, 3.1%, 2.9%, respectively.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Pyrethroid drugs are widely used indoors to control household pests, such as flies, mosquitoes, termites, and other harmful insects [1]. Recently, many synthetic pyrethroids as new products have been put into production with a rapidly increasing sale, now accounting for a quarter of the world market of pesticide drugs. The separation and determination of pyrethroid drugs is of great significance to regulate the quality of final products sold in the market and monitor their side effects on humans [2]. Therefore, a rapid, accurate and sensitive method is required for the assay of different household insecticide products.

Several methods had been developed for the analysis of pyrethroid products, including spectrophotometry [3], immunoassay [4,5], capillary electrophoresis [6], gas chromatography (GC) [7,8], GC–mass spectrometry (MS) [9] and liquid chromatography (LC) [10] using mainly liquid–liquid extraction and solid-phase extraction for the sample preparation. Chromatographic techniques were considered as the best methods to determine pyrethroids in complicated sample matrices.

Simonaitis and Call [11] determined the residues of benzyl furoseamide permethrin in corn and wheat by GC-FID with n-

pentane as extraction solvent and Florisil adsorbent. Chocholous et al. [12] developed a sequential injection system equipped with miniaturized 10 mm monolithic column for determination of fenoxycarb and permethrin in veterinary pharmaceutical foams and sprays. Vazquez et al. [13] determined seven pyrethroids in cucumber and watermelon using LC combined with post-column derivatization. Cheng et al. [14] developed a neutral alumina-based matrix solid-phase dispersion procedure for determination of two pyrethroids in porcine tissues.

The aim of this work was to develop a capillary gas chromatographic method with dibutyl phthalate and iso-octyl phthalate as two internal standards for the separation and determination of the common active ingredients in different household pyrethroid products (mosquito coils and two kinds of aerosol insecticides) in local market.

### 2. Experimental

#### 2.1. Chemicals

Permethrin, transallethrin, beta-cypermethrin, prallethrin, piperonyl butoxide, D-tetramethrin, transfluthrin, cyphenothrin, phenothrin, imiprothrin were obtained from Yangnong Chemical Co. Ltd. (Yangzhou, China). Dibutyl phthalate (IS1) and iso-octyl phthalate (IS2) were purchased from Huaxin Reagent Co. (Baoding, China). All the other reagents used in the experiment were of the highest grade commercially available.

\* Corresponding author. Tel.: +82 32 860 7470; fax: +82 32 872 0959.  
E-mail address: [rowkho@inha.ac.kr](mailto:rowkho@inha.ac.kr) (K.H. Row).

## 2.2. Instrumentation

GC analysis was performed using a Shimadzu GC-2014 system equipped with a split/splitless injector and an FID detector (Shimadzu, Japan). An N-2000 chromatography data workstation (Zheda Zhineng Co. Ltd., Hangzhou, China) was used as data acquisition system. The capillary column was KB-1 (30 m × 0.25 mm × 0.25 μm) and the flow rate was set at 1.5 ml/min with a split ratio of 10. The temperature-programmed mode was as follows: the initial oven temperature was 180 °C for 3.0 min and then increased at 10 °C/min to 240 °C for 10 min, finally increased 20 °C/min to 270 °C for 13 min. The injection port and detector temperature was set at 250 and 270 °C, respectively.

## 2.3. Sample preparation and assay procedure

Each stock solution (10 mg/ml) of permethrin, transallethrin, beta-cypermethrin, prallethrin, tetramethrin, transfluthrin, cyphenothrin, phenothrin, imiprothrin was prepared individually in acetone and then combined to get the mixed standard solution containing 0.1 mg/ml IS1 and IS2. The mixed standard solution was diluted using 0.1 mg/ml internal standard solution by stepwise dilution method to get nine working standard solutions with different concentrations (0.4–900 mg/l).

The mosquito coil products (five double disks, smoke-free) purchased from local market were ground and then 5.0 g of the powder thus obtained was put into conical flask. After adding 20 ml internal standard solution and stirring at 2000 rpm for 10 min, the solution was centrifuged at 3000 rpm for 5 min and then filtered for further chromatographic analysis. The aerosol insecticide products (600 ml, Canned) obtained from local market were homogenized by shaking for 3.0 min, then 40 ml liquid content was poured into a beaker followed by ultrasonic treatment for 15 min to remove projectile agents. After adding 2.0 ml internal standard solution and vortexing for 5 min, the solution was filtered using a 0.45 μm filter membrane and stored for the chromatographic analysis. The blank samples of mosquito coils and aerosol products (same sample matrix without analytes) obtained from their manufacturers were dealt with using the same pretreatment procedure.

## 3. Results and discussion

### 3.1. Separation model for the nine pyrethroids

Due to different polarities and wide boiling range of the nine pyrethroids, temperature-programming was used in a range of 90–275 °C. The optimum conditions are described in Section 2.2. The chromatogram of the nine pyrethroids (0.04 mg/ml) in Fig. 1 shows that all analytes were completely resolved within 20 min. Piperonyl butoxide (PB), the common synergist used in household insecticide products also can be fully separated from the nine pyrethroids. Multiple peaks based on the isomers appeared on the chromatogram of the most pyrethroids. Different compounds including dibutyl phthalate, isobutyl phthalate, mesitylene phosphate ester, iso-octyl sebacate, octyl phthalate ester and iso-octyl phthalate ester were investigated as potential internal standards. Considering the retention times and resolutions, dibutyl phthalate and iso-octyl phthalate were selected as internal standards.

### 3.2. Optimization of the extraction process

Various parameters affecting the extraction efficiency (extractants, extractant volume, stirring rate, and extraction time) were

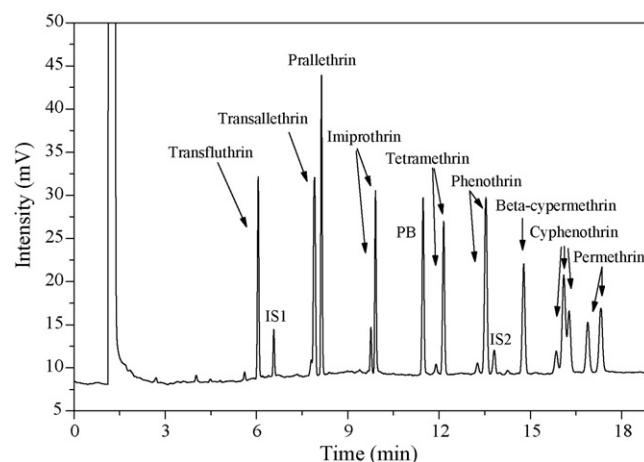


Fig. 1. Chromatogram of the nine pyrethroids samples.

investigated. Different extractants including acetone, ethanol, isopropanol, n-hexane, and ethyl acetate were investigated for the mosquito coils (0.50 mg/g). The best extraction efficiency was obtained with 20 ml of acetone (recovery of 96.8%,  $n = 5$ ).

The extraction efficiency increased when the extraction time was increased from 5 to 10 min and remained constant using extended extraction time. Hence 10 min was applied as extraction time for further work. The extraction efficiency increased when the stirring rate was increased to 2000 rpm. No further increase was found reasonable: the optimum stirring rate was 2000 rpm. 15 min of ultrasonic treatment is enough to get extraction equilibrium and remove projectile agents from the samples matrix.

### 3.3. Validation of the proposed method

Calibration curves were constructed using the ratio of peak areas of analytes with the internal standard measured at nine increasing concentrations, in a range of 0.4–900 mg/l. Good linearity was obtained for all analytes. The regression equations are shown in Table 1. The inter-assay precision and accuracy were determined by analyzing spiked samples at three-concentration levels within the calibration curves on five different days ( $n = 5$ ). The intra-assay precision and accuracy was determined by analyzing seven replicates of the spiked samples at three-concentration levels, extracted on the same day ( $n = 7$ ). Intra-assay and inter-assay precision expressed as the relative standard deviation (RSD) of concentrations calculated from the three spiked samples were less than 2.5% and 3.1%. Based on a signal-to-noise ratio of 3, the limits of detection (LOD) ranged from 0.04 to 0.11 mg/l for the nine pyrethroids, respectively. Five blank samples were also extracted and analyzed under same procedure for assessment of the potential

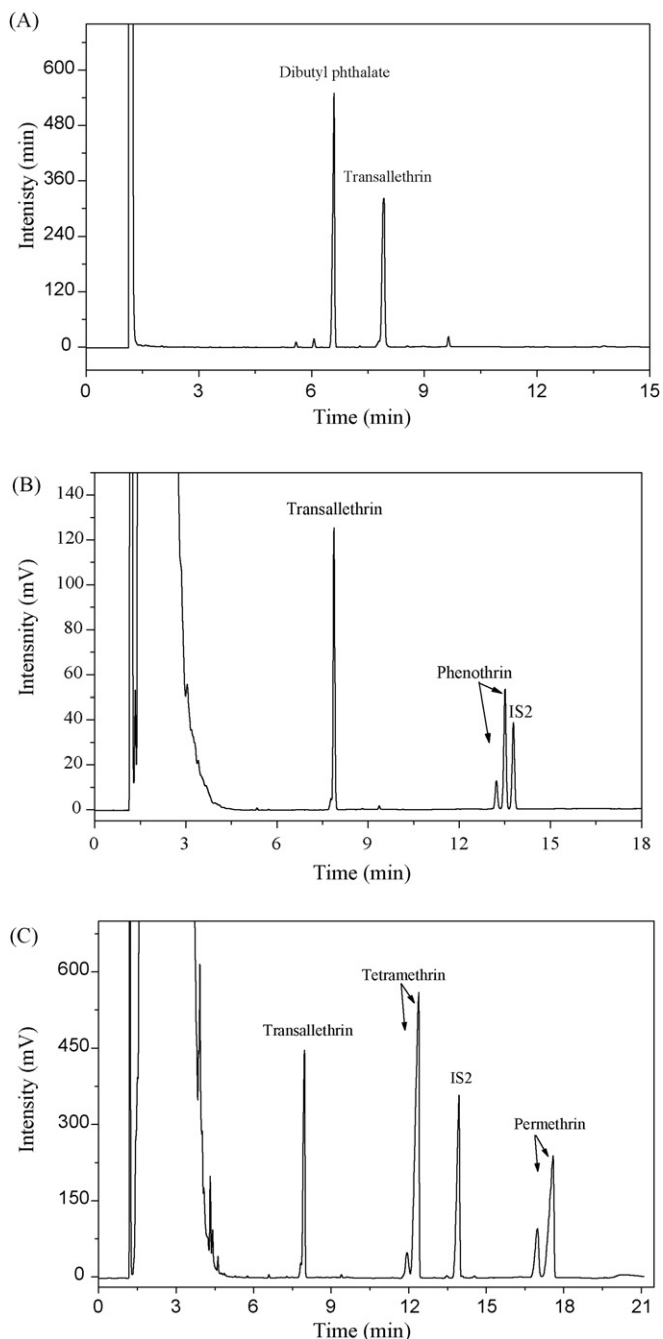
Table 1  
The linearity equation and LOD of the nine pyrethroids.

| Pyrethroids       | Regression equation   | $r^2$  | LOD (S/N = 3) |
|-------------------|-----------------------|--------|---------------|
| Permethrin        | $Y = 115.62X + 0.020$ | 0.9997 | 0.10 mg/l     |
| Transallethrin    | $Y = 132.24X - 0.013$ | 0.9996 | 0.05 mg/l     |
| Beta-cypermethrin | $Y = 69.79X + 0.076$  | 0.9991 | 0.11 mg/l     |
| Prallethrin       | $Y = 125.32X - 0.102$ | 0.9990 | 0.07 mg/l     |
| Tetramethrin      | $Y = 109.42X + 0.153$ | 0.9995 | 0.08 mg/l     |
| Transfluthrin     | $Y = 79.86X - 0.026$  | 0.9991 | 0.09 mg/l     |
| Cyphenothrin      | $Y = 145.57X - 0.045$ | 0.9999 | 0.07 mg/l     |
| Phenothrin        | $Y = 139.37X + 0.044$ | 0.9997 | 0.04 mg/l     |
| Imiprothrin       | $Y = 88.63X - 0.107$  | 0.9990 | 0.06 mg/l     |

IS1 was used for transfluthrin, transallethrin, prallethrin, and imiprothrin; IS2 was used for piperonyl butoxide, tetramethrin, permethrin, beta-cypermethrin, cyphenothrin, and phenothrin.

**Table 2**  
Pyrethroids contents and recoveries in mosquito coils and aerosol products ( $n=5$ ).

| Samples                 | Analytes       | Content (mg/g) | RSD (%) | 1.0 mg/g     |         | 3.0 mg/g     |         | 6.0 mg/g     |         |
|-------------------------|----------------|----------------|---------|--------------|---------|--------------|---------|--------------|---------|
|                         |                |                |         | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) |
| Mosquito coils          | Transallethrin | 1.740          | 0.92    | 96.0         | 1.7     | 97.3         | 1.9     | 96.5         | 2.4     |
|                         | Transallethrin | 2.181          | 1.77    | 95.4         | 1.3     | 95.0         | 2.3     | 97.8         | 2.1     |
| Aerosol insecticide (1) | Tetramethrin   | 6.717          | 2.31    | 96.8         | 2.0     | 97.1         | 2.8     | 95.3         | 2.5     |
|                         | Permethrin     | 4.174          | 2.92    | 92.3         | 3.1     | 94.5         | 2.4     | 96.2         | 2.7     |
| Aerosol insecticide (2) | Transallethrin | 5.782          | 1.56    | 97.1         | 1.4     | 96.9         | 2.1     | 101.2        | 1.9     |
|                         | Cyphenothrin   | 4.577          | 2.37    | 95.7         | 2.8     | 93.0         | 2.9     | 95.1         | 2.6     |



**Fig. 2.** Chromatogram of the extract of mosquito coil and aerosol products (A is mosquito coils products; B and C are two brands of aerosol products; B was diluted seven times by acetone; IS2 is iso-octyl phthalate ester).

matrix effect due to endogenous substances in the sample matrices. No interfering peaks from the product matrix were observed at the retention time of compounds of interest, which demonstrates the good selectivity of the present method.

#### 3.4. Assay of pyrethroids in different real samples

To examine the applicability of the method for pyrethroid determination in different products, three mosquito coils and aerosol insecticide products from different manufacturers were collected from local market. Typical chromatograms are shown in Fig. 2. The results shown in Table 2 indicate that the content of pyrethroids in the mosquito coils and aerosol products is by 5–10% higher than that marked by the manufacturers. Recoveries were determined to investigate the effect of the actual sample matrix by spiking three different levels of analytes into the actual blank samples. The results in Table 2 show that the means recoveries for all analytes were in a range of 92.3–101.2% with RSD less than 3.1%, which indicated that the method was reliable and can be used for the determination of pyrethroids in mosquito coils and aerosol products.

#### Acknowledgements

The project was supported by National Natural Science Foundation of China (20905019), SRF for ROCS, SEM, Inha University Research Grant (INHA-2009),

#### References

- [1] T. Yoshida, Simultaneous determination of 18 pyrethroids in indoor air by gas chromatography/mass spectrometry, *J. Chromatogr. A* 1216 (2009) 5069–5076.
- [2] M. Narendra, G. Kavitha, A.H. Kiranmai, N.R. Rao, N.C. Varadacharyulu, Chronic exposure to pyrethroid-based allethrin and prallethrin mosquito repellents alters plasma biochemical profile, *Chemosphere* 73 (2008) 360–364.
- [3] M. Kazempour, E. Noroozian, M.S. Tehrani, M. Mahmoudian, A new second-derivative spectrophotometric method for the determination of permethrin in shampoo, *J. Pharm. Biomed. Anal.* 30 (2002) 1379–1384.
- [4] G.A. Bonwick, M. Putman, P.J. Baugh, Immunoassay development for permethrin residues, *Food Agric. Immunol.* 6 (1994) 341–356.
- [5] E.G. Matveeva, G. Shan, I.M. Kennedy, S.J. Gee, D.W. Stoutamire, B.D. Hammock, Homogeneous fluoroimmunoassay of a pyrethroid metabolite in urine, *Anal. Chim. Acta* 444 (2001) 103–117.
- [6] F. Ye, Z. Xie, X. Wu, X. Lin, Determination of pyrethroid pesticide residues in vegetables by pressurized capillary electrochromatography, *Talanta* 69 (2006) 97–102.
- [7] H.P. Li, C.H. Lin, J.F. Jen, Analysis of aqueous pyrethroid residuals by one-step microwave-assisted headspace solid-phase microextraction and gas chromatography with electron capture detection, *Talanta* 79 (2009) 466–471.
- [8] T. Lopez-Lopez, M.D. Gil-Garcia, J.L. Martinez-Vidal, M. Martinez-Galera, Determination of pyrethroids in vegetables by HPLC using continuous on-line post-elution photoirradiation with fluorescence detection, *Anal. Chim. Acta* 447 (2001) 101–111.
- [9] A. Ramesh, P.E. Ravi, Electron ionization gas chromatography–mass spectrometric determination of residues of thirteen pyrethroid insecticides in whole blood, *J. Chromatogr. B* 802 (2004) 371–376.

- [10] E. García, A. García, C. Barbas, Validated HPLC method for quantifying permethrin in pharmaceutical formulations, *J. Pharm. Biomed. Anal.* 24 (2001) 999–1004.
- [11] R.A. Simonaitis, R.S. Call, Gas-liquid chromatographic determination of resmethrin in corn, cornmeal, flour and wheat, *J. Assoc. Off. Anal. Chem.* 58 (1975) 1032–1036.
- [12] P. Chocholous, D. Satinsky, R. Sladkovsky, M. Pospisilová, P. Solich, Determination of pesticides fenoxycarb and permethrin by sequential injection chromatography using miniaturized monolithic column, *Talanta* 77 (2008) 566–570.
- [13] P.P. Vazquez, A.R. Mughari, M.M. Galera, Solid-phase microextraction (SPME) for the determination of pyrethroids in cucumber and watermelon using liquid chromatography combined with post-column photochemically induced fluorimetry derivatization and fluorescence detection, *Anal. Chim. Acta* 607 (2008) 74–82.
- [14] J. Cheng, M. Liu, Y. Yu, X. Wang, H. Zhang, L. Ding, H. Jin, Determination of pyrethroids in porcine tissues by matrix solid-phase dispersion extraction and high-performance liquid chromatography, *Meat Sci.* 82 (2009) 407–412.