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Rapid Determination of Cypermethrin and Permethrin in Crucian by Matrix Solid-Phase Dispersion Coupled with Gas Chromatography

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A simple pretreatment and analytical method was developed and validated for the quantitative determination of cypermethrin and permethrin in crucian samples. The proposed methodology is based on matrix solid-phase dispersion (MSPD), using neutral alumina oxide as dispersant material and diatomite as clean-up absorbent, eluted by *n*-hexane-dichloromethane (1:1, v/v) and followed by gas chromatography electron capture detection (GC-ECD) on an DB-5 capillary column. Good linearity was observed in a range of 0.0005-0.50 μg/mL and 0.008-4.00 μg/mL for permethrin and cypermethrin, respectively. The average recovery of cypermethrin and permethrin at three levels of spiked samples were ranged from 72.5 % to 106.6 % with RSD ≤ 6.7 %. The limits of detection based on signal to noise of 3 were 0.004 mg/kg for permethrin and 0.032 mg/kg for cypermethrin. This proposed MSPD-GC-ECD method was satisfactorily applied to different crucian samples.

Key Words: Matrix solid phase dispersion, Gas chromatography, Crucian, Pyrethroids, Cypermethrin.

INTRODUCTION

Cypermethrin and permethrin are two kinds of pyrethroid pesticides, which are widely used to prevent and treat insects and clear crucian pond, trash and kill pests in daily life, agriculture or crucianeries due to their broad spectrum insecticidal capacity and high effectiveness[1]. Although the wide applications of these pesticides provide benefits for the society, their residues in fruits, vegetables, crucian and other products will represent a serious hazard to human health such as cancer, infertility, nerve disorders, immunological and respiratory diseases[2]. Therefore, there is a growing interest in the development of fast and reliable analytical procedure for extraction and determination of these pesticides in food or agriculture productions.

The determination of pesticide residues in food matrices is a formidable challenge mainly due to the trace level of analytes and large amounts of interfering substances which can be co-extracted with analytes and in most cases, adversely affect the results of quantitative analysis[3]. So the sample must initially be cleaned up before the final instrument analysis. At present, a few analytical methods for determination of these pesticides had been reported in the last few years[4]. Generally, a preliminary extraction step followed by liquid-liquid extraction (LLE)[5] or solid-phase extraction (SPE)[6] was employed to clean the sample matrix for further instrument analysis. However, these processes were complicated, time-consuming and needed large amount of organic solvent.

Matrix solid-phase dispersion (MSPD) is one of the most promising techniques for the simultaneous disruption, extraction and clean-up of solid, semi-solid and highly viscous samples[7]. It combines the sampling, extraction and clean-up into a single step, which eliminates most of the complications of performing classical liquid-liquid extraction and solid-phase extraction of solid and semi-solid samples. Moreover, MSPD could help to reduce considerably the size of sample and the solvent consumption[8]. Until now, MSPD has been successfully applied to the extraction of a wide range of drugs, pesticides, naturally occurring constituents and other compounds from a wide variety of complex samples[9,10]. To our knowledge, this work presents the first attempt for extraction and determination of cpermethrin and permethrin in crucian samples using MSPD method. The proposed MSPD-GC-ECD method revealed high purification for complex crucian matrix and could be potentially applied for the determination of trace pyrethroids in different fish products.

EXPERIMENTAL

Cypermethrin and permethrin were supplied by Yangnong Chemical Co. Ltd. (Yangzhou, China). Neutral alumina oxide (100-200 mesh), diatomite and anhydrous sodium sulphate

(National Pharmaceutical Group Chemical Reagent Co., Ltd.), were activated after drying at 650 ºC for 4 h before use. Ethyl acetate was obtained from Tianjin Jinfeng Chemical Co. Ltd. Dichloromethane, acetone, *n*-hexane were all analytical grades and purchased from Kermel Chemical Co. Ltd. (Tianjin, China). All the other reagents used in the experiment were of the highest grade commercially available.

The chromatographic analysis was carried out on a Shimadzu GC-2014 system equipped with a split/splitless injector and an ECD detector (Shimadzu, Japan). High-purity nitrogen (99.999 %) was used as carrier gas and a GH-300 high-purity hydrogen generator and GA-2000A air pump (Beijing ZXHL Technology Development Co. Ltd.) were used to supply hydrogen and air at the rate of 40 and 400 mL/min, respectively. The capillary column was DB-5 (30 m × 0.53 mm × 1.0 μm) and its column flow rate was set at 7.45 mL/min with a split ratio of 1:1. An N-2000 data workstation (Zheda Zhineng Co. Ltd., Hangzhou, China) was used as the data acquisition system. The temperature-programmed mode was as follows: the initial oven temperature was set at 250 ºC for 4 min and then ascended to 285 ºC at the rate of 6 ºC/min and held for 10 min. The injection port and detector temperatures were maintained at 285 and 290 ºC, respectively.

Procedure of matrix solid-phase dispersion: 0.25 g homogeneous crucian sample was thoroughly blended with 0.75 g of neutral alumina oxide in a glass mortar to obtain a homogeneous mixture. This mixture was introduced into a cartridge, which containing a frit at the bottom was filled (from bottom to top) with a layer of 1 g of anhydrous sodium sulfate and then another layer of 1 g of diatomite (these materials act as co-column or clean-up phases in the cartridge) and covered with another frit at the top, then slightly compressed with a syringe plunger. The cartridge was eluted with 6 mL *n*-hexane-dichloromethane(1:1, v/v) at the flow rate of 0.5 mL/min, then the eluent was evaporated to dryness under vacuum and the residue was re-dissolved in 200 μL *n*-hexane solution and 1 μL was used for further GC analysis.

RESULTS AND DISCUSSION

Effect of sorbent type: MSPD procedures greatly simplify the sample treatment by proper choosing of the dispersant material and the clean-up absorbent. So extraction and clean-up materials had to be carefully selected to achieve the highest recovery for cypermethrin and permethrin contained in the crucian samples while eliminating most of the interfering matrix components. Varies of dispersant materials and the clean-up absorbents were assessed and the results listed in Table-1. Neutral alumina oxide as dispersant material and diatomite as clean-up absorbent were selected for the following studies owing to their high clean-up degree and satisfactory recovery for cypermethrin and permethrin. Also the use of anhydrous sodium sulphate as clean-up absorbent was shown as a significant factor to improve the ability of both adsorbents to retain the interferences-lipids. So 0.75 g of neutral alumina oxide as dispersant material and clean-up absorbent of diatomite (1 g) and anhydrous sodium sulphate (1 g) were chosen to develop the extraction method.

Ratio of matrix/dispersant: During the blending process, the MSPD sorbents act both as an abrasive and as a bound solvent that break the sample architecture, disperse its components and promote more effective interactions between them and the analytes. Commonly, how much solid support is used depends on the sample type and sample/sorbent ratios typically range from 1:1 to 1:4. A suitable ratio of sample matrix to sorbent could increase the surface area of the analytes and sorbent and allow complete adsorption of the sample components and to facilitate the transfer into the cartridge. Therefore, the ratios of sample to sorbent ranged from 1:1 to 1:4 were evaluated and the results indicated that the best recoveries of analytes were achieved at the ratio of 1:3. Further enhancing the ratio of neutral alumina oxide gave no improvement of recovery.

Elution profile of cypermethrin and permethrin: In general, an appropriate solvent system should allow the elution of analytes free of matrix components. This can be done either by an additional washing step to remove interferences or by leaving the matrix components absorbed on the cartridge. To keep the absorbed matrix components leaving on the cartridge, elution of the two pesticides was carried out with 10 mL of different solvents (*n*-hexane, acetone, ethyl acetate, dichloromethane, *n*-hexane-acetone (1:1, v/v), *n*-hexane-ethyl acetate (1:1, v/v), *n*-hexane- dichloromethane (1:1, v/v)), thus established the best elution procedure. The results (Fig. 1) showed that *n*-hexane-dichloromethane (1:1, v/v) solution could provide the stisfactory recovery of the two analytes. To evaluate the elution volume of *n*-hexane-dichloromethane, various volume (4, 6, 8, 10 and 11 mL) were investigated and the results in Fig. 2 indicated 6 mL of *n*-hexane-dichloromethane as elution solvent provided the satisfied recovery.

Validation of the proposed method: Under the optimized conditions, satisfactory separation was observed (Fig. 3A) and good linearity constructed using the areas of the chromatographic peaks measured at seven increasing spiked concentrations was observed in a range of 0.0005-0.50 and 0.008-4.00 μg/mL for permethrin and cypermethrin, respectively. Intra-assay and inter-assay precision expressed as the RSD of analyzing seven replicates of the control samples at three-concentration levels, extracted on the same day and five different days were less than 6.9 % and 8.0 %. The limits of detections based on S/N=3 were 0.004 mg/kg for permethrin and 0.032 mg/kg for cypermethrin. Good recovery (72.5-106.6 %) for three different levels of spiked samples was observed with

TABLE-1
THE CONDITIONS OF EXTRACTION AND CLEAN-UP MATERIALS

Dispersant materials	Clean-up absorbents	Recovery of cypermethrin (%)	Recovery of permethrin (%)
Neutral alumina oxide	Diatomite	96.3	81.4
Diatomite	Neutral alumina oxide	19.0	16.2
Neutral alumina oxide	Graphite carbon	31.8	71.4
Diatomite	Graphite carbon	10.4	12.9

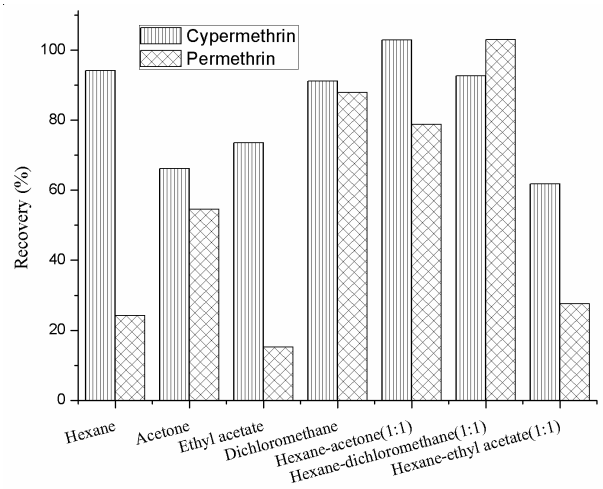

Fig. 1. Effect of elution solvent on recovery

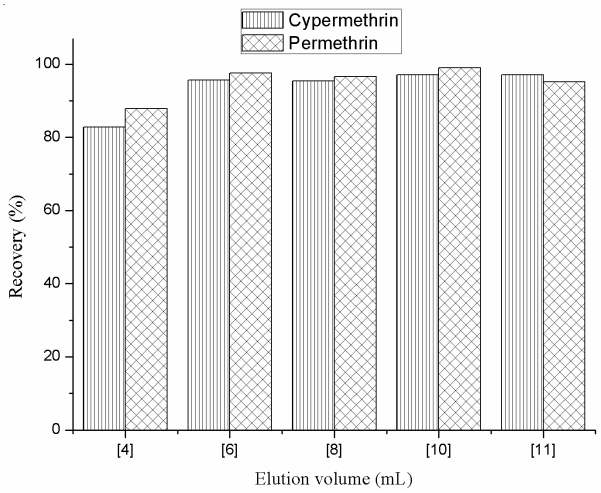

Fig. 2. Effect of elution volume on recovery

RSD ≤ 6.7 % (N = 5) (Table-2). In order to further validate the MSPD-GC-ECD method, five crucian products collected from the local markets of Baoding were deal with the MSPD procedure and analyze by GC-ECD method. One of the samples was observed 0.07 μg/g of permethrin, which indicated that the proposed MSPD-GC-ECD method could meet the trace level of permethrin and cypermethrin analysis (Fig. 3B).

TABLE-2
RESULTS OF CRUCIAN SAMPLES ANALYSIS AND SPIKED RECOVERY

Analytes	Content (μg/g)	Spiked levels (μg/g)	Recovery (%)	RSD (%)
Permethrin	0.07	0.02	80.2	1.3
		0.08	83.8	3.6
		0.40	104.0	3.6
Cypermethrin	Undetected	0.13	72.5	6.1
		0.64	93.2	6.7
		3.20	106.6	2.1

Conclusion

A simple MSPD-GC-ECD method was proposed for the quantitative determination of cypermethrin and permethrin in crucian samples, using neutral alumina oxide as dispersant material, diatomite as clean-up absorbent and *n*-hexane-dichloromethane (1:1, v/v) as elution solution. Good separation were obtained on a DB-5 capillary column with the recovery at three spiked levels were ranged from 72.5-106.6 %. The proposed MSPD-GC-ECD method is a good alternative for routine analysis due to its simplicity, sensitivity and at the same time reliability.

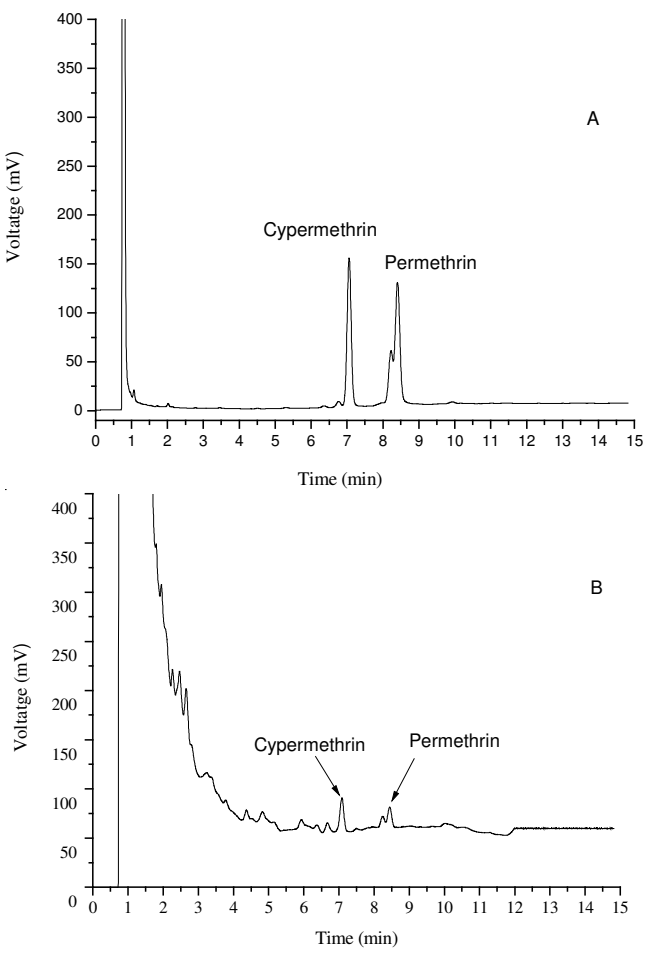

Fig. 3. Chromatogram of the standards and spiked crucian sample. (A: standard solution, B: spiked crucian sample)

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REFERENCES

1. D.M. Soderlund and D.C. Knipple, *Insect Biochem. Mol. Biol.*, **33**, 563 (2003).
2. P.P. Vazquez, A.R. Mughari and M.M. Galera, *Anal. Chim. Acta*, **607**, 74 (2008).
3. A. Wilkowska and M. Biziuk, *Food Chem.*, **125**, 803 (2011).
4. F.A. Esteve-Turrillas, A. Pastor and M. Guardia, *Anal. Bioanal. Chem.*, **384**, 801 (2006).
5. H. Liu and P.K. Dasgupta, *Anal. Chem.*, **68**, 1817 (1996).
6. Q.X. Zhou, Y.J. Ding, J.P. Xiao, G.G. Liu and X.Y. Guo, *J. Chromatogr. A*, **1147**, 10 (2007).
7. B. Shao and H. Han, *J. Chromatogr. B*, **850**, 412 (2007).
8. A.I. Valenzuela, R. Lorenzimi, M.J. Redondo and G. Font, *J. Chromatogr. A*, **839**, 101 (1999).
9. J. Cheng, M. Liu, Y. Yu, X. Wang, H. Zhang, L. Ding and H. Jin, *Meat Sci.*, **82**, 407 (2009).
10. E. Sobhanzadeh, N.K.A. Bakar, M.R.B. Abas and K. Nemati, *J. Hazard. Mater.*, **186**, 1308 (2011).