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of Detection and Quantitative method Research of Cypermethrin, Fenvalerate and Deltamethrin Residues in Sediment by Gas Chromatography

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Abstract. A gas chromatography method was developed for the quantification and identification of cypermethrin, fenvalerate, and deltamethrin residues in sediment with electron capture detector (ECD). Homogenized samples were extracted by N-hexane/dichloromethane (1/1), desulfurization with copper powder. The samples were cleaned up by silica solid phase extraction (SPE) cartridge. There were many isomers in cypermethrin and fenvalerate, but the proportions of different isomers were different in different concentrations, so it was more accurate to quantify by the total quantity. The analytes were quantified by the standard materials dissolved in matrix solution. Under optimal experimental conditions, good linearity was observed in the range of 20~2000 ng/mL for cypermethrin, fenvalerate and 2~200 for deltamethrin, the correlation coefficients were 0.9984~0.9991. The results showed that the limit of quantitation (LOQ) was $0.4 \sim 4 \mu \text{ g/kg}$. The recovery and RSDs of three-level spiked samples were in the ranges of $83.2\% \sim 92.1\%$ and $3.2\% \sim 8.5\%$. This method is highly effective to reduce time for pretreatment of sample, and the result showed that was accurate to detect the cypermethrin, fenvalerate, and deltamethrin residues in sediment.

1. Introduction

Pyrethroids are the third most applied group of insecticides worldwide and are extensively used in agricultural and non-agricultural applications. Pyrethroids are hydrophobic and readily bind to sediment including sediments suspended in water ^[1-3]. And pyrethroids can migrate with water flow or colloid, so they could also be detected in sediments of rivers and lakes where that was not used [4-5]. Research showed that pyrethroids exhibit low toxicity to mammalian and avian, but have extremely high toxicity to fish and non-target invertebrates ^[5]. But another studies had shown that it was associated with the brain tumors in children ^[6]. At the same time, it may raise the level of estrogen in the body, and promote the occurrence of breast cancer. Their high hydrophobicity, along with pseudopersistence due to continuous input, indicates that pyrethroids will accumulate in sediment, pose longterm exposure concerns to benthic invertebrates and ultimately cause significant risk to benthic communities and aquatic ecosystems^[5].

The pollution of pyrethroid pesticides had attracted worldwide attention. Although numerous papers have been presented on multi-residue methods for analysis of pesticides in food ^[7-9], a few studies are available that detailed methods to detect pyrethroids in sediments. Some studies ^[10] are purified by

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self-filling column but low stability. Others ^[11] used rapid solvent extraction to extract, which requires special equipment. Therefore, a simple and effective method is needed to research.

Compared with food and water samples, the interaction between the analytes and the matrix is much stronger in sediment. To obtain comparable results, a more exhaustive extraction procedure is required to liberate the bound residues from the matrix. In contrast, the more extensive the extraction procedure used, the more co-extracted interference can be expected. Accurate quantification of pyrethroids has been problematic due to their matrix effect and potential for isomerization during the extraction and quantification process. Few publications have addressed the problem of analysis of pyrethroids in sediments. Therefore, analytical methods to detect pyrethroids in sediment are still under development. In this paper, the pre-treatment method and data analysis method by gas chromatography in sediment was systematically studied to avoid quantification errors during analysis caused by the matrix effect and isomerization. This method was convenient, efficient and the quantitative method is accurate.

2. Materials and method

2.1. Materials and instrument

The GC system consisted of an Agilent 7890A GC (Agilent Technologies, Shanghai, China), equipped with an electron capture detector (ECD). The GC was fitted with a HP-5MS fused silica capillary column (5% phenyl polysiloxane as non-polar stationary phase, 30 m, 0.25 mm i.d. and 0.25 μ m film thickness) from Agilent (J&W Scientific, Folson, CA, USA).

Cypermethrin, fenvalerate and deltamethrin standards were purchased from Dr.Ehrenstorfer GmbH and had purities >98%. Stock solutions were prepared for all standard substances were different based on analytical instrument sensitivities. Cypermethrin and fenvalerate were individually dissolved in n-hexane at 100 μ g/mL, and deltamethrin was 10 μ g/mL. Spiking mixtures was obtained by mixing appropriate amounts of each individual pyrethroids stored at -20°C.

N-hexane and dichloromethane were purchased from J.T.Baker (Avantor Performance Materials, Inc.) and all solvents were HPLC grade. Copper powder was purchased from sinopharm chemical reagent Co.,Ltd. Silica SPE cartridges (500mg/6mL) were purchased from Agela Technologies.

2.2. Sample collection and handling

The sediment used in the present study was collected from Tai lake across the jiangsu province and zhejiang province in China. Sediment samples were placed in amber glass bottles on ice after collection and were held at 4 °C in the laboratory. Sediments were air dried, homogenized, sieved to less than 1 mm, and stored in amber glass bottles at 4 °C until extracted.

2.3. Sediment extraction and cleanup

Five grams of prepared sediment were weighed into a 50 mL centrifuge tube. The samples were added 30 mL aliquots of extraction solvent mixture of n-hexane/dichloromethane (1/1, v/v) and soaking for 15 min. Then they were ultrasonically extracted at room temperature for 20 min. The each mixture was centrifuged at 8000 r/min for 8 min. The extraction procedure was repeated twice and the extracts from each time were combined into a pear-shaped bottle and evaporated in a rotary evaporator to dry at a low temperature and weak vacuum. The residue was dissolved by 20 mL n-hexane twice and then the dissolved solution was subjected to clean up.

The dissolved solution was added five grams copper and shocked for 5 min, then centrifuged at 8000 r/min for 5 min. The supernatant was normally passed through a Silica SPE cartridge conditioning with 5 mL n-hexane / acetone (6/1, v/v) and 5 mL n-hexane without pressure. The effluent was given up and another 3mL n-hexane was used to rinse the cartridge. Then the mixed solvent of 5 mL n-hexane / acetone (6/1, v/v) was used to elute the analytes. The collected elute solvent was dried by a rotary evaporator. The residue was reconstituted with 1 mL n-hexane and mixed in a vortex stirrer.

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2.4. Instrumental analysis

The final samples were detected on an Agilent 7890A GC, coupled to an electron capture detector (ECD). Nitrogen with a purity of 99.999% was used as the carrier gas. The column temperature program was as below: 150° C hold for 1 min, ramp at 25° C/min to 230° C, hold for 2 min; ramp at 20° C /min to 240° C, hold for 1 min; ramp at 20° C/min to 260° C, and hold for 5 min; ramp at 3° C/min to 280° C, and hold for 5 min; ramp at 2° C/min to 285° C, and hold for 10 min. The carrier gas (nitrogen) flow rate was 2.5 mL/min, injection port temperature was 240° C, and injection volume was 1 µL. The injection was made in the splitless mode with purge on after 0.75 min.

2.5. Standard curve

Standard solutions at various concentration levels were obtained by mixing blank sediment matrix solution and appropriate amounts of each individual pyrethroids. The concentrations of deltamethrin were 2, 5, 10, 25, 50, 100, 200 ng/mL, and the concentrations of cypermethrin and fenvalerate were 20, 50, 100, 250, 500, 1000, 2000 ng/mL. The calibration curves were obtained by performing a linear regression analysis using the standard area against analytes concentrations.

3. Results and Discussion

3.1. Extraction method

Soxhlet extraction has historically been the standard sediment extraction method, but requires a long extraction time (6–24 h) and large volumes of organic solvents. Ultrasonic extraction (USE) has been widely employed due to its shorter extraction time, equipment simplicity, and procedural simplicity. Ultrasonic extraction of pyrethroids in sediment can achieve similar recovery with Soxhlet extraction [¹²], and takes less time. The ultrasonic time is the key factor to impact the extraction effect. If the ultrasonic time is too long that will make the extracted pyrethroids adsorbed on the container wall and affect the recovery ^[13]. In this study, the result showed that the recovery of ultrasound for 10 minutes was less than 70%, and the recoveries of ultrasound for 20 min and 30 min were all up to 85%. So ultrasound for 20 min was used.

3.2. Sulfide removal method

Sulphide in sediment is an important interference in pesticide detection in sediment, and addition of copper to extracts is a common method removing interfering materials ^[14]. In this study, it was found that 10 minutes incubation with room temperature oscillation could completely remove sulphide interference, which was ten times shorter than the previous report ^[15]. A research^[16] showed no significant difference between the recoveries of target analytes during using the two different levels (2 g and 5 g) of copper, but 2 g copper was found to be inadequate to remove sulphide interference for some sediment samples. Therefore, 5 g copper was chosen for this research. It is found that it can completely remove the interference of sulphide no matter when to add copper powder, before or after sample extraction. In order to remove sulphide more thoroughly, the experimental steps of desulphurization after extraction was chosen.

3.3. Purification method

Silica SPE cartridge was selected for purification experiment. N-hexane/acetone at different volume ratio of 3/1, 4/1, 5/1, 6/1, 7/1, 8/1, 9/1 and 10/1 was chosen as eluent to experiment. The recovery rate was low and there were impurity interference when the proportion of acetone was large. With the decrease of the proportions of acetone, the recovery rate increased gradually, and the impurity peaks also decreased. The recovery rate reached the maximum when the eluent was n-hexane/acetone (6/1, v/v). The recovery rate was relatively stable when the eluent was n-hexane/acetone (8/1, v/v). Then the recovery rate decreased along with the acetone volume content decreased. The purification effect was better and the recovery rate was more than 85% with n-hexane/acetone (6/1, v/v) as eluent to purify sediment sample. So the silica SPE cartridge was selected as the purification method.

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3.4. Matrix influence

Matrix enhancement effect was found in detecting pyrethroids in sediments by gas chromatography ^[17]. The first reason for this phenomenon maybe that the matrix components could inhibit pyrethroid isomerization ^[18]. The second reason was probably that matrix components closed the silanol group and metal active sites at the instrument inlet, thus more analytes entered the chromatographic column. The matrix enhancement effect caused by pyrethroid isomerization inhibition can be effectively reduced by adding 0.1% acetic acid into n-hexane ^[18], but that could not eliminate the effect caused by the second reason. It was not appropriate to increase the purification steps to reduce the influence of matrix effect, because it was not only increase the time and labour costs, but also increase the uncertainty caused by loss of targets ^[19]. It was practically impossible to use extensive clean-up steps to remove all matrix components. Therefore, quantification by matrix standard solution was an effective method to eliminate the influence of matrix effect and improve quantitative accuracy.

3.5. Quantitative analysis

The chemical structure of pyrethroids is complex that there are optical isomers or cis-trans stereoisomers. So each substance had multiple peaks in capillary column separation, as shown in Figure 1. Cypermethrin had 4 peaks (peaks 1, 2, 3, and 4), fenvalerate had two peaks (peak 5 and 6).



Figure 1. Chromatograms of pyrethroid insecticides matrix standard (A) (1. cypermethrin 1, 2.cypermethrin 2, 3.cypermethrin 3, 4.cypermethrin 4, 5.fenvalerate 1, 6.fenvalerate 2, 7.deltamethrin)

The proportion of the four peaks of cypermethrin and the two peaks of fenvalerate in the total peak area varied in the matrix standard solution with different concentrations. When the concentration reached a certain level, the proportion of different peaks tended to be stable. The variation regularity was shown in Figure 2 and Figure 3. The result showed that the proportion of each isomer in the total amount was different under different total concentration, so the concentration of each isomer varied and it was inaccurate to quantify the single isomer. Therefore the quantitative method of calculating the total concentration by the total peak area was more accurate.



Figure 2. Variation trend of percentage of cypermethrin isomers in total cypermethrin at different concentrations



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3.6. Method performance

The calibration curves and correlation coefficients were showed in the table 1. Good linearity was obtained for all analytes. The limit of quantification (LOQ), defined as the concentration which yield an S/N equal to 10, ranged from 0.4μ g/kg to 4.0μ g/kg (Table 1). The analytes recovery of this procedure was evaluated by spiking 4.0, 20 and 50 μ g/kg for cypermethrin and fenvalerate and 0.4, 2.0 and 5.0 μ g/kg for deltamethrin in replicates of six. The results were listed in Tables 2. The average recoveries of each compound ranged from 83.2% to 92.1%. The reproducibility of this method was represented by percent relative standard deviation (R.S.D.) at each level for each compound and these values are also summarized in Table 2. The results show that the method's precision was within 10%, which is meet the requirement.

Table 1. Regression equations, linear ranges, correlation coefficient(r), and the limit of quantification (LOQs) for pyrethroids.

Analyte	Regression equation	Linear range $\rho/(ng/mL)$	Correlation c oefficient (r)	LOQ (µg/kg)
Cypermethrin	Y=35.155X-302.46	20-2000	0.9985	4.0
Fenvalerate	Y=36.719X-572.86	20-2000	0.9992	4.0
Deltamethrin	Y= 360.19X-1319.6	2-200	0.9987	0.4

Table 2. Recoveries of pyrethroids in sediment $n= 6$.											
Analyte	4.0 or 0.4 μg/kg			20 or 2.0 μg/kg			50 or 5.0 μg/kg				
	Average concentrati on μg/kg	Recover y %	RS D %	Average Concentrat ion μg/kg	Recover y %	RS D %	Average Concentrat ion μg/kg	Recover y %	RS D %		
Cypermethr in	3.33	83.2	5.5	17.5	87.5	4.8	44.9	89.8	8.5		
Fenvalerate	3.57	89.2	4.9	17.9	89.5	4.7	45.6	91.3	5.0		
Deltamethri n	0.363	90.7	3.2	1.84	92.1	4.0	4.48	89.6	5.9		

4. Conclusion

In this study, a comprehensive analytical method was developed for simultaneous extraction and determination of cypermethrin, fenvalerate, and deltamethrin in sediment. It was effective to remove the sulphide by copper powder and to purify with silica SPE cartridge. The matrix effect was eliminated by using matrix standard curve to quantitative analysis. The quantitative method was more accurate to analysis of the total isomers. The method clearly demonstrated good linearity, accuracy, and precision.

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