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Residue of chlorpyrifos in processed leeks by solid phase extraction and gas chromatography-mass spectrometry

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ABSTRACT

Chlorpyrifos belongs to a kind of organophosphorus pesticide and is widely used in leeks. Chlorpyrifos often degrades during the processing of leeks. The Solid Phase Extraction and GC-MS method for determination of chlorpyrifos is simple, rapid and appropriate for eliminating interference effects of sulfur compounds in leeks. It is a great help to reduce the chlorpyrifo's residues by 53.04% in leeks washed operation with 0.1% detergent solution. The boiling operation also can decrease the content of chlorpyrifos by 16.40%.

KEYWORDS

Chlorpyrifos;
Leeks;
Processing.

INTRODUCTION

Chlorpyrifos [O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate] (Figure1) is an organic phosphorous insecticide[5], used in leafy vegetables and fruits for a variety of pests with chewing and sucking mouthparts and other noxious insects, such as soil insect[6]. It reflects on the nervous system of insects by inhibiting acetylcholinesterase and has no systemic action, protecting the safety of farms and consumers[8].

Preferred by Chinese consumers, leek is often a kind of vegetables for exports. However, different countries have different maximum residue limit of chlorpyrifos in leeks, 0.01mg/kg in Japan and Korea, 0.05mg/kg in Europe, 0.1 mg/kg in China[9,11], which caused serious challenges for the export of leeks.

In the processing with leeks, the most of processing are used to make fillings for dumplings. Operations include washing, cutting, mixing with condiments, making dumplings and boiling. But the relationship of operations and the residue of chlorpyrifos is poorly understood.

Washing is simple and effective means of removing residues of pesticides in food whether in the family or in the factory production[2]. Zohair[12] thought that the soaking measures to eliminate organic phosphorus pesticide were more effective than organic chlorine pesticide. In recent papers, high temperature cooking and frying may reduce the residues of pesticide. Xiaohong Zhang[10] investigated the treatment with electric stove boiled vegetables could eliminate 78% of fenvalerate. The study of K.M Soliman[3] demonstrated that washing with water and/or other solutions as well as the cooking process (blanching and frying) helped to eliminate the most of the pesticides' residues in the potato tubers. The aim of this work was to study the effects of operations in making dumpling on the contents of chlorpyrifos and then to get a better knowledge about the influence of processing on the decrease of chlorpyrifos for human health.

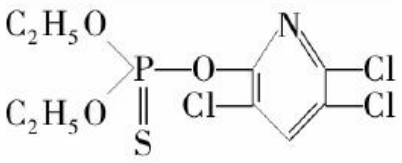

Figure 1: Chemical structure of chlorpyrifos

MATERIALS AND METHODS

Plant materials and experimental design. Leeks (treated by chlorprifos during growing) were harvested from experimental plot in Beijing University of Agriculture.

At the laboratory, clusters were selected to make dumpling. First treatment was performed by immersion 100 g of leeks for 5 min with detergent solution (0.1%). Another 100 g of samples without immersion was served as the control. Following treatment, 100 g of leeks were cut into filling and were mixed with other condiments (1.0 g salt and 2.0mL oil). The dumplings were made by fillings and wrappers. Boiling with induction cookers was made to cook the dumplings at 100 °C for 10min. The samples were taken for analysis of chlorpyrifos before and after washing and mixing and boiling.

Sampled methods. For each sample, about 10g of leek tissues was homogenized in 50 mL of 6g of anhydrous sodium sulfate and 30mL ethyl acetate and then centrifuged at 5000r/min for 5min. The residues were treated with 30mL of ehyl acetate once more. The whole supernatants were condensed to nearly 1 mL by a rotary evaporator (RE52-99 Yarong biochemical instrument factory of Shanghai) in 40 °C water bath. 2 mL of ethyl acetate-n-Hexane (1:1) was added to dissolve the concentrate for SPE cleaning-up[4,7].

SPE cleaning-up

The samples were purified with Active Carbon SPE tube (500mg/6mL) and Florisil SPE tube (1000mg/6mL) (Dikma Technologies), respectively. Firstly, two kinds of tubes were rinsed with the solution of ethyl acetate-n-Hexane (1:1).2mLof samples was transferred into tubes and eluted with 3 mL of ethyl acetate-n-Hexane (1:1). The elutes were collected and condensed at 40°C with rotary evaporator. The concentrate was dissolved with 1.0 mL of ethyl acetate and filtered with 4.5μm of membrane for GC-MS.

Chlorpyrifos determination

Chlorpyrifos standard was obtained from National Pesticide Product Quality Inspection Center (Shen yang, China) with a certified purity of 98.9%. Standard solution: accurately weigh certain amount of Chlorpyrifos standard and dissolve it with a small volume of ethyl acetate. Dilute with Ethyl acetate to make the standard stock solution of 100μg/mL. The solution was stored in a refrigerator at 0°C~4°C. Anhydrous sodium sulfate was ignited at 650°C for 4 h, and then stored in a tightly sealed container[1]. The 200mL solution of ethyl acetate-n-hexane (1:1 *V/V*) was obtained. The instrument of GC-MS (Agilent Technologies) was used to determine the contents of chlorpyrifos . The carrier gas was Helium (puritye—99.999%) delivered at a flow-rate of 1.0 mL/min. Chlorprifos was detected and quantified on a 30 m×0.25mm HP-5 silica capillary column. The quantitation ion (m/z) is 197 and confirmation ions are 258,286,314. Injection of the samples (1μL) was performed using an autosampler.

Statistical analysis

Data for the analytical determinations were subjected to analysis of variance (ANOVA). Mean comparisons were performed using HSD the turkey'test to examine if differences were significant at $p<0.05$. All analyses were performed with the SPSS software package version 11.0 for Windows.

RESULTS AND DISCUSSION

Different concentrations of chlorpyrifos standard solution were determined by gas chromatography-mass spectrometer. There was a good linear relationship between peak area and concentration of chlorpyrifos (Figure 2).

The retention time of chlorpyrifos was 14.01min, as shown in Figure 3. According to the quantitation ion (m/z=197), the peak area of leek samples during every processing operation could be obtained.

As figure 4 shown, the leeks of Batch 1 picked from the experimental plot (control) were 0.125mg·kg^{-1}. After washed these leeks with detergents, the concentration of chlorpyrifos in leeks became 0.065 mg·kg^{-1}. After cut and mixed with salt and oil, the content of residue reduced to 0.063 mg·kg^{-1}. Made dumplings with

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these mentioned fillings and boiled them for 10min. Then the concentration of chlorpyrifos was 0.052 mg·kg^{-1}.

The contents of chlorpyrifos in the leeks of Batch 2 picked after 5 days were determined by the same method. Figure 5 illustrated the similar trend with Figure 4. And it showed that the concentration of chlorpyrifos of Batch 2 was lower after five days of natural degradation.

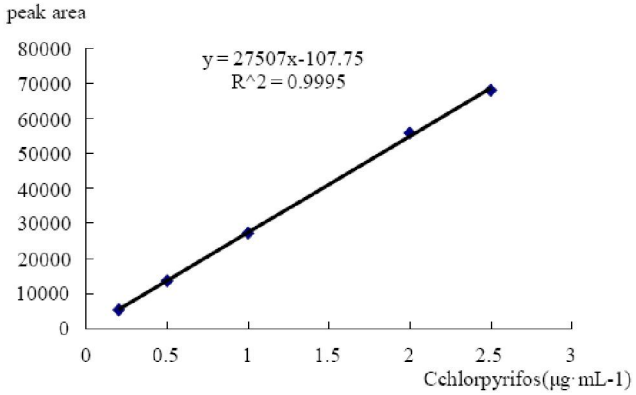
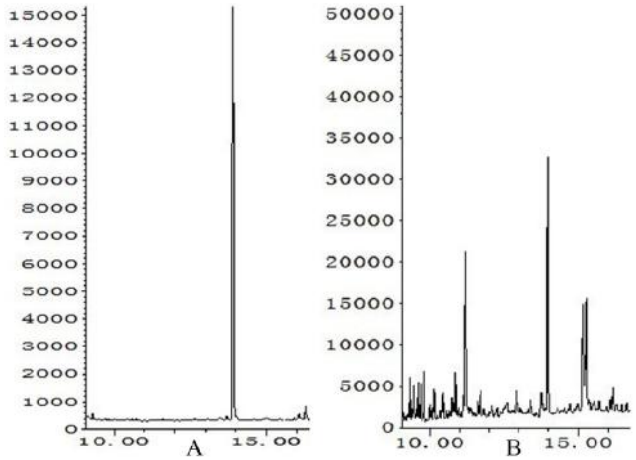


Figure 2 : The standard curve of chlorpyrifos



A: the content of standard chlorpyrifos; B: the content of chlorpyrifos in leeks.

Figure 3 : The chromatogram of standard and a leek sample

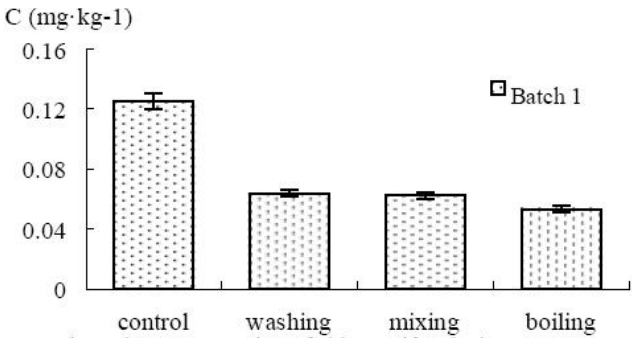


Figure 4 : The concentration of chlorpyrifos during every process sing unit operation of batch 1.

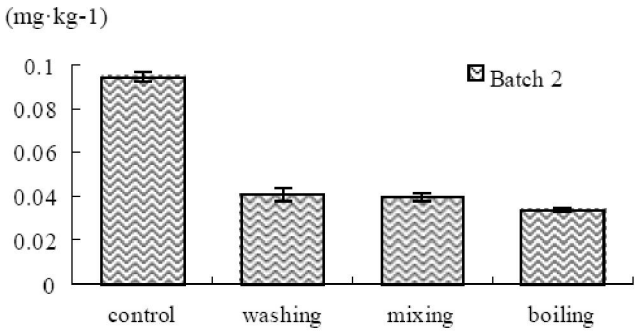


Figure 5 : The concentration of chlorpyrifos during every process sing unit operation of batch 2.

As TABLE 1 suggestedÿthe processing unit operation of washing played an important role to degrade the content of chlorpyrifos residue in leeks by 53.04%. And the heat treatment also could reduce the residue by 16.40%. The data between control and washing of the two batches are significantly different at $P<0.05$ according to the SPSS software. And the data between mixing and boiling are significantly different at $P<0.05$.

TABLE 1 : Reducing rate of every processing unit operation of leeks

Batch	Reducing rate (%)		
	washing	washing to mixing	mixing to boiling
1	49.36±2.44	1.51±0.14	14.61±0.10
2	56.71±0.96	2.52±2.46	15.01±2.13

CONCLUSION

The proposed SPE-GC-MS method for determination of chlorpyrifos in leeks' processing reported in this paper was simple, rapid and thus was very appropriate for eliminating interference effects of sulfur compounds in leeks. The operation of washing with detergents for leeks was a great help to reduce the residues of chlorpyrifos by 53.04%. And the boiling operation also could decrease the content of chlorpyrifos by 16.40%. In a word, washing with detergent solutions as well as the cooking process (boiling) helped to eliminate the most of chlorpyrifos residues in leeks.

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