The 50 Commonly Used Pesticide Residue of Peppers in Jiangjin Area by GC-MSMS Method for Screening Based on Textual Data Analysis

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Abstract. the detection of pesticide residues in agricultural products is an important issue related to food safety. In recent years, gc-msms technology, as an efficient method for the detection of pesticide residues in agricultural products, has become a hot research topic at home and abroad. In this paper, gc-msms was used to screen 50 kinds of pesticide residues in Zanthoxylum bungeanum in Jiangjin area. In this paper, 50 kinds of common pesticides in Zanthoxylum bungeanum in Jiangjin area were tested. In this paper, the first step is to grind and soak the prickly ash to extract the detection solution, then purify the detection solution, and then test the detection solution. Through the results of this study, gc-msms method has high sensitivity, which can be accurate to 4.00ng/ml, and 5.6min can detect 50 pesticide residues at the same time. Through the experimental data, we can analyze the impact of pesticide residues on the organic matter in prickly ash.

Keywords: Gc-Msms Method, Pesticide Residue, Zanthoxylum, Organic Matter

1. Introduction
Zanthoxylum bungeanum is a kind of shrub in Rutaceae. Its fruit is reddish brown. It is light brown after drying, with prominent gland spots on its surface. Chinese prickly ash is cultivated in most areas of China. It is also called Sichuan prickly ash, big prickly ash, Qin prickly ash, Shu prickly ash, tea prickly ash, etc. according to different producing areas and main uses [1-2]. Pepper has a strong aroma, so it is often used as a seasoning for cooking [3-4]. Zanthoxylum bungeanum is also a kind of high-value traditional Chinese medicine. It is mainly used to treat chronic gastroenteritis, stomachache, chronic arthritis, muscle spasm and other diseases. The plant extracts or volatile oil of Zanthoxylum bungeanum have significant effects on antibiotics, pathogens and microorganisms [5].

There are 582 varieties of pesticides in China, and the total number of agricultural products is more than 9700 [6-7]. Due to the unreasonable use of pesticides by many farmers in the production process, pesticide pollution occurs from time to time in China, and pesticide residues are far beyond the standard [8]. Pesticide residues in agricultural products have become an important issue for China's agricultural products to enter the international market. It is urgent to establish a pesticide residue monitoring system as soon as possible. As an efficient and fast detection method, gc-msms method has
been widely used in agricultural product pesticide detection. Based on this, this paper studies the screening of 50 commonly used pesticide residues in Pepper in Jiangjin area by gc-msms method [9-10].

In this paper, GC-MS quantitative analysis method is summarized firstly, and then combined with the factors that affect the gc-msms detection, the experiment is designed to detect 50 kinds of pesticide residues commonly used in Zanthoxylum bungeanum in Jiangjin area, so as to analyze the advantages of gc-msms in pesticide residues, and analyze the influence of pesticide residues on the organic matter of Zanthoxylum bungeanum through the experimental data.

2. Proposed Method

2.1 Gc-Ms Data Processing and Qualitative and Quantitative Analysis

(1) GC-MS data processing

The data collection method used in this paper collects a large amount of data and rich data content. Therefore, it is easy to lead to improper information processing, which further leads to the loss of data resources needed in this paper.

(2) Qualitative analysis of GC-MS

Qualitative analysis can not only rely on mass spectrometry library. The mass spectrum which can not be separated well is not reliable, not only the reliability of retrieval matching rate is low, but also the mass spectrum analysis is very difficult. The retention time of chromatography and a series of information related to samples are important basis for qualitative analysis. The quantitative analysis used in this paper is to check the experimental samples designed by us in groups, and the materials allocated in each group are calculated. No matter what kind of instrument is used in the experiment, the content of the target compound is calculated according to the functional relationship between the response coefficient of the detector and the content of the compound to be measured under specific conditions.

In addition to the GC / MS quantitative methods mentioned in this paper, there are also some common methods which are the same as chromatography, including the standardized method, external standard method and internal standard method. But each method is different, improper use will inevitably lead to big mistakes.

1) Standardization method

The total content of each component in the sample is taken as 100, and the formula is:

$$w_i = \frac{f_i A_i}{\sum f_i A_i} \times 100\%$$

In this formula, the dependent variable $w_i$ represents the amount of I allocated to this group, $A_i$ represents the peak height of I allocated to this group, and $f_i$ is the mass correction coefficient.

2) External standard method

The external standard method is simply the control variable method. For example, under the same environmental conditions of the experimental samples in this paper, measure the peak area or peak height of the experimental samples to obtain the response coefficient

$$f_i = \frac{w_i}{A_i}$$

In this formula, the dependent variable $w_i$ represents the content of the assigned standard sample, and $A_i$ represents the peak height of the assigned standard sample.

3) Internal standard method

The internal standard method is to overcome the measurement error, select the appropriate reference material to add to the standard sample and the sample to be tested, and calculate the ratio of the response value of the compound to be tested and the internal standard compound:
\[ \frac{i}{S} = \frac{w_i}{w_s} \cdot \frac{A_i}{A_s} \] 

In the formula, \( w_i \) represents the content of the assigned standard sample, \( A_i \) represents the peak height of the assigned standard sample, \( w_s \) is the content of the internal standard compound, and \( w_a \) is the peak height of the internal standard compound.

2.2 Factors Affecting Gc-Msms Detection

(1) Extraction and purification
The extraction and purification of sample is the pre-treatment part of the sample, and it is also the most important part of the sample treatment, in order to reduce the content of matrix components in the sample and facilitate the detection.

(2) Matrix effect
Due to the nature of hardware and software, concentration and type of matrix, concentration of analyte, chemical structure and property, type of purification material and other factors, the measurement value of target analyte may not be accurate enough.

(3) Scanning speed
Scanning speed is the key factor of gc-msms results. When the scanning speed is fast, the efficiency of the collected data points will increase, otherwise, the noise will increase and the reproducibility will decrease.

(4) Ion source
Generally, in the process of gc-msms analysis, ion source is the most frequently used method, which is suitable for heterogeneous substances such as nitrogen, phosphorus, oxygen, sulfur, silicon and special compounds containing halogen.

3. Experiments

3.1 Experimental Materials and Equipment

(1) Instruments and equipment
Gc-msms instrument, vortex mixer, constant speed pressure injection extractor, bench type low-speed centrifuge, electronic balance, fapex tea solid-phase extraction column.

(2) Reagent material
Miananyou, Liangqiao, zhizhapo, liangchongjing, etc

3.2 Experiment Design

(1) Extract
Weigh out 15g ground prickly ash to 50ml centrifuge tube, add 15ml pure water, soak for 30min, add 15ml acetonitrile, 4G anhydrous MgSO4 and 1g NaCl, shake hands for 3min, and centrifuge.

(2) Purification
Add 50mg PSA, 50mg C18 powder and 150mg anhydrous MgSO4 into 2ml centrifuge tube, take out 1ml of extraction solution and add it into centrifuge tube, shake for 1min, then centrifuge, take the supernatant and put it into detection sample bottle for GC-MS / MS detection.

(3) Instrument conditions:
The flow rate of chromatographic column needs to reach 0.3ml/min. The column temperature of chromatographic column needs to reach 40 °C. Injection volume: 5.0 μ L. See Table 1 for mobile phase elution conditions.

4. Discussion

4.1 Lgc-Msms Method to Screen the Residues of 50 Common Pesticides in Zanthoxylum Bungeanum in Jiangjin Area
The results of gc-msms screening of 50 common pesticides residues in Zanthoxylum bungeanum in Jiangjin area were analyzed

(1) Pretreatment key

Check the water injection to make the sample completely immersed in the water, otherwise the test result will be changed. Adding ceramic homoproton can accelerate the mixing speed, which is controlled at 1 drop / second, making it more convenient to collect the target filter later. In order to ensure the accuracy and reliability of experimental results, matrix calibration is used to calibrate the response value and matrix interference of samples. Pesticide residue detection can be completed in 5.6 minutes. Due to the short retention time of some compounds, the peak ion form is replaced. Because the chromatogram is output separately, the shape of the peak is very good, which can be used for quantitative and qualitative judgment.

(2) Linear range measurement and limit calculation

After matrix matching and instrument accurate analysis, the linear equation and correlation coefficient of different experimental compounds in the range of 4.00 ~ 200.00ng/ml are shown in Table 1, and the limit is calculated at the same time.

(3) Laboratory calculation of coefficient of variation and method recovery

Weigh 50 negative samples, add 3 horizontal concentrations (2.0, 6.0, 20.0 μ g / kg), each concentration is parallel for 6 times, see Table 1 for detailed results, ensuring the feasibility and accuracy of the method. Five common pesticides were selected for statistical analysis.

Table 1. 50 statistics of 5 common residues in pesticides

| Pesticide name | Linear equation | Correlation coefficient $R^2$ | Detection limit (μ g / kg) | Recovery range (%) | Variation coefficient range (%) |
|----------------|-----------------|-------------------------------|-----------------------------|-------------------|---------------------------------|
| Pyrimethanil   | $y=153.28x+2600.74$ | 0.9673 | 1.3 | 73.9-84.9 | 91.0-93.8 | 107.1-112.9 | 5.0 | 10.0 | 5.1 |
| Methomyl       | $y=73.99x+1824.52$ | 0.9878 | 4.0 | 31.9-77.2 | 108.9-113.1 | 119.6-122.6 | 7.0 | 9.5 | 2.0 |
| Carbaryl       | $y=579.84x+6132.46$ | 0.9872 | 1.1 | 111.8-129.6 | 110.9-117.2 | 115.4-122.9 | 7.1 | 9.9 | 5.0 |
| Aldicarbl      | $y=154.24x+381.35$ | 0.99987 | 1.2 | 69.9-79.4 | 71.6-76.4 | 91.9-99.6 | 8.2 | 9.9 | 6.0 |
| Carbofuranl    | $y=1241.51x+22543.01$ | 0.9923 | 14.9 | 91.2-100.9 | 104.6-111.0 | 110.4-119.1 | 6.9 | 9.2 | 4.1 |

A GC-MS method for the determination of 50 pesticide residues in Zanthoxylum bungeanum was established. The results show that the method is fast, efficient and environment-friendly, which is more suitable for the rapid analysis of bulk samples.

4.2 Effect of Pesticide Residues on the Content of Organic Matter in Zanthoxylum Bungeanum

According to the analysis of the data collected in this experiment, the influence of pesticide residues on the content of organic matter is shown in Figure 1. Part a of Figure 1 shows the trend of the influence of pesticide residues on Zanthoxylum, Part B shows the influence of pesticide residues on the soluble sugar content of the injured Zanthoxylum, part C shows the influence of pesticide residues on the free amino acid content of the non insect Zanthoxylum, and Part D shows the pesticide residues Effect on the content of free amino acids in Zanthoxylum bungeanum L.
Figure 1. Effect of pesticide residues on the content of organic matter in Zanthoxylum bungeanum

(1) Chemical reaction analysis of agricultural residues on soluble sugar in Zanthoxylum bungeanum

1) The chemical reaction results of agricultural residues on the soluble sugar in Zanthoxylum bungeanum can be seen from Figure 1. The content of soluble sugar in Zanthoxylum bungeanum was higher than that in the control within 1-14 days after application of pesticide. For example, on the first day after the application of pesticide, the control result was 5.026%, the data of the plants sprayed with Omethoate was 8.383%, and the data of the plants using avermectin was 8.261%, which were higher than the control; on the third day after the application of pesticide, the data of the plants applying Omethoate was 9.495%, which was still not the same as that of the conventional results. The data of abamectin showed no significant difference from the control data since the third day; the data of abamectin on the 10th day and the 3rd day after application were basically the same; the data of abamectin on the 14th day after application had no significant difference from the control data. The results showed that the effect of agricultural residues on the content of soluble sugar in Zanthoxylum bungeanum was significant, but the effect was far less than that of boxwood. Chemical pesticide stress was still the main factor affecting the content of soluble sugar in Zanthoxylum bungeanum.

2) The results of chemical reaction analysis of pesticide residues to soluble sugar in pepper can be seen from Figure 1. The content of soluble sugar in pepper is higher than that in the control on the 13th day after application of pesticide. For example, the data of pepper on the first day after application of pesticide is 1.285%, the data of plants spraying Omethoate pesticide on the leaf is 1.405%, and the data of plants spraying avermectin pesticide is 1.350%, which is higher than the control value, the difference is significant, but there is no significant effect of Omethoate and avermectin from three days after white medicine. It can be seen from the experiment that the content of soluble sugar in Zanthoxylum bungeanum decreased significantly after the stress of Omethoate and avermectin, and the influence time was short.

(2) Chemical reaction analysis of free amino acids in pesticide residues

1) Chemical reaction analysis of pesticide residues on the content of free amino acids in Zanthoxylum bungeanum

According to the data in Figure 1, from the first day to the fourteenth day after the application of pesticide, compared with the control plants, the content of free amino acids in the plants sprayed with pesticide decreased. It can be seen from the figure that the degree of reduction is especially significant from the first day to the seventh day. For example, after one day of application, the free amino acid content of the control plant Zanthoxylum bungeanum was 30.94, the free amino acid content of Omethoate was 18.49, the free amino acid content of avermectin was 24.09, the free amino acid...
content of the control plant Zanthoxylum bungeanum was 46.57, the free amino acid content of Omethoate was 39.59 and the free amino acid content of avermectin was 25.51; After 7 days of application, the content of free amino acids in the control plant was 8.422, and there was still significant difference between the control plant and the plant without application; after 14 days of application, only Omethoate was significantly different from the control plant.

2) Effect of pesticide residues on the content of free amino acids in Zanthoxylum bungeanum

According to the data in Figure 1, the content of free amino acids in Zanthoxylum bungeanum is more variable and complex than that in Zanthoxylum bungeanum. As shown in the figure, the content of free amino acids in Omethoate and avermectin was 23.53 and 24.68 respectively one day after application, Compared with the control group, the content of free amino acids is relatively low; the complex situation occurs after 3 days of application, as shown in the figure, the content of free amino acids in plants without application is higher and lower than that in the control group, and the difference is not very significant; however, the content of free amino acids in the control group is significantly increased after 7-14 days of application. Among them, the free amino acid content of Omethoate was the most significant. As shown in the figure, on the 7th and 14th day, the free amino acid content of these two time points was 15.586 and 12.383 respectively.

According to the above experimental data, the soluble sugar content of Zanthoxylum bungeanum under the action of pesticides is on the rise compared with that of Zanthoxylum bungeanum in the control group, which indicates that it is likely to promote the production of Osmoregulation Substances. It can be seen from the figure that the soluble sugar content of prickly ash decreases after the damage of Aphis gossypii, which shows that Aphis gossypii is an important nutrient of hydrocarbons, and soluble sugar is the most basic metabolite of prickly ash. Therefore, under the action of pesticides, the damage of Aphis gossypii will lead to the decrease of soluble sugar content of prickly ash, which will destroy the normal secondary aging metabolism of prickly ash, thus leading to the class of secondary metabolites Type and quantity change.

5. Conclusions

In this paper, gc-msms was used to screen 50 kinds of pesticide residues in Zanthoxylum bungeanum in Jiangjin area. The results showed that gc-msms was simple and efficient. This method was mainly used for the rapid detection of multi batch samples. With the updating and iteration of new high-tech pesticides, the number of tested agricultural products is increasing, and the requirements of modern people for the detection line of agricultural products are also decreasing. The detection of pesticide residues in agricultural products is facing many problems and challenges. Gc-msms technology has gradually become a reliable and rapid method for pesticide residue analysis due to its unique advantages. Combined with the advantages of gc-msms technology, the future development direction will be towards the rapid detection of pesticide residues in agricultural products.

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