Qualitative Determination of Pesticide Residues in Purple Cabbage Based on Near Infrared Spectroscopy

Min Li *, Linju Lu, Xiaoying Zhang

School of electronics and materials engineering, Leshan Normal University, Sichuan, Leshan, 614000, China

Corresponding author’s e-mail: cassie_li@163.com

Abstract: A qualitative detection model of pesticide residues based on near infrared spectroscopy and support vector machine (SVM) classification is proposed in this paper. The model was used to identify the pesticide free purple cabbage and pesticide containing purple cabbage. Cypermethrin, matrine and avermectin were selected respectively, and the ratio of pesticide and water was 1:100. The correct rates of classification and identification were 90%, 100% and 100%, respectively. The experimental results show that the model has high accuracy and universality for qualitative analysis of pesticide residues in purple cabbage. This paper presents an effective method for rapid and nondestructive detection of pesticide residues in vegetables.

1. Preface
Purple cabbage is rich in high-quality protein, cellulose, minerals and vitamins, and is loved by the public. In the process of Purple Cabbage Cultivation, there are not many diseases, mainly easy to grow aphids and Pieris rapae. In order to ensure the yield and appearance, vegetable farmers spray pesticides during the planting process. When eating purple cabbage, in order to preserve its rich nutrients, people often choose to eat it cold. If there are pesticide residues on the surface of purple cabbage, it is harmful to human health, so the detection of pesticide residues is particularly important.

The traditional detection methods of pesticide residues in vegetables mainly include gas chromatography, mass spectrometry, and chromatography-mass spectrometry[1,2]. Although these detection methods have high accuracy, the detection process is very complex, and the pretreatment of samples is very complicated. It is often necessary to squeeze vegetables into juice and add some chemical reagents. The sample preparation takes a long time and the detection cost is high, so it is difficult to realize the rapid and non-destructive detection of pesticide residues in vegetables on site [3-5]. In recent years, detection methods based on near infrared spectroscopy technology are widely used in the quality and safety detection of agricultural products. Spectrum nondestructive testing technology has the advantages of no damage, no pollution, high efficiency and so on.

In this paper, a qualitative detection model of pesticide residues based on near infrared spectroscopy and support vector machine (SVM) classification is proposed. The model was used to identify the pesticide free purple cabbage and pesticide containing purple cabbage. Cypermethrin, matrine and avermectin were selected respectively, and the ratio of pesticide and water was 1:100. The correct rates of classification and identification were 90%, 100% and 100%, respectively. The experimental results show that the model has high accuracy and universality for qualitative analysis of pesticide residues in purple cabbage. This paper presents an effective method for rapid and nondestructive detection of pesticide residues in vegetables.
2. Spectral Data Acquisition

2.1. Instruments and Reagents
Agilent Cary 630 FTIR was selected as NIR spectrometer. The ATR attenuated total reflection spectrum acquisition mode was selected, and the spectrometer parameters were set as: background scanning: 64 times; sample scanning: 64 times; resolution: 8cm⁻¹. A computer is needed for spectrum acquisition, and the supporting software microlab PC and resolutions Pro are installed. The experimental apparatus is shown in Fig. 1.

The crystal of spectrometer should be cleaned with anhydrous alcohol in laboratory. Cypermethrin, matrine and avermectin were selected as the research objects. Cypermethrin mainly killed aphids, avermectin mainly killed Pieris rapae, matrine can kill both aphids and Pieris rapae.

2.2. Sample Preparation
In order to ensure the universality of the experiment and ensure that there is no pesticide, purple cabbage ordered by vegetable growers was selected as experimental supplies. Purple cabbage was divided into four groups, the first group was not sprayed with pesticides, and the second group, the third group and the fourth group were used to prepare samples containing moderate pesticide residues. The second group was sprayed with fenpropathrin solution with the ratio of pesticide to water of 1:100; the third group was sprayed with Matrine solution with the ratio of pesticide to water of 1:100; the fourth group was sprayed with avermectin solution with the ratio of sun pesticide and water of 1:100. In order to ensure the uniformity of pesticide spraying, spray method is adopted. After the sample is made, it should be placed in a cool and ventilated place for 24 hours.

2.3. Experimental Description
The prepared purple cabbage samples were made into 40 small samples of about 2mmx2mm in each group, and the near-infrared spectral data were collected respectively. Each spectral data acquisition is carried out in strict accordance with the following steps: first step: clean crystal with absolute alcohol; second step: collect background spectrum; third step: put purple cabbage sample on spectrometer to collect sample spectrum. 40 spectral data were collected from each group of purple cabbage, a total of 160 spectral data were collected, each data dimension was 1942, and the wave number range of near-infrared light was 7800-400cm⁻¹.

3. Classification and Identification Model
This paper mainly studies two kinds of qualitative classification and identification models of spectral data, namely, the classification and identification of samples without pesticide and with one pesticide. The flow chart of spectral data classification and identification is shown in Figure 3. The first step is to divide the spectral data into training set and test set; the second step is to normalize the training set and test set respectively, and the normalization range is [-1,1]; the third step is to create SVM training model, the penalty parameter is 2, the kernel function is linear kernel function, and the classification effect is the best. Step 4: test the test set with SVM.
4. Classification and Result Analysis

In the first experiment, two groups of purple cabbage samples without pesticide and containing cypermethrin were selected for classification and identification. Each group selects the spectral data of the first 30 samples to form the training set, with a total of 60 spectral data. The spectral data of the last 10 samples in each group constitute the test set, with a total of 20 spectral data. The qualitative classification results are shown in Figure 4, and the classification accuracy of test set is 90%.

In the second experiment, two groups of purple cabbage samples without pesticide and with Matrine were selected for classification and identification. The construction of training set and test set is the same as the first experiment. The qualitative classification results are shown in Figure 5, and the classification accuracy of test set is 100%.
In the third experiment, two groups of purple cabbage samples without pesticide and containing avermectin were selected for classification and identification. The construction of training set and test set is the same as the first experiment. The qualitative classification results are shown in Figure 6, and the classification accuracy of test set is 100%.

The experimental results show that the detection model has high accuracy for the qualitative detection of pesticide residues in purple cabbage. The detection method is effective for Cypermethrin, matrine and avermectin.

5. Conclusion
In this paper, a qualitative detection model of pesticide residues on purple cabbage surface was established based on near infrared spectroscopy and support vector machine classification algorithm. The accuracy of the model was 90%, 100% and 100%, respectively. The model is rapid, nondestructive and accurate for the qualitative analysis of pesticide residues in purple cabbage.

Due to the limited number of experimental samples and the types of pesticides, the future research should further increase the number of samples and the types of pesticides, and use multi spectral fusion technology to explore a more accurate and universal rapid and non-destructive detection method for pesticide residues in vegetables, which will have more practical significance.
**Brief introduction of the author**
Li Min (1977 -), female, from Ya'an, Sichuan Province, is a professor and postgraduate student. She is mainly engaged in intelligent computing, spectral analysis and its application in agricultural engineering.

**Acknowledgment**
This work was supported by Key natural science fund project of Sichuan Provincial Education Department (18ZA0231).

**Reference**
[1] Sun Jun et al., detection of pesticide residues in lettuce leaves based on PDWT and hyperspectral analysis [J], Acta agriculturalis Sinica, December 2016 (Vol. 47), PP: 323-329.
[2] Dai Ying et al., research progress on Application of near infrared spectroscopy in detection of pesticide residues in fruits and vegetables [J], Journal of food safety and quality inspection, 2014.03 (volume 05), PP: 659-664.
[3] Liu Wenming et al., identification of pesticide species on the surface of Long Jujube by near infrared hyperspectral technology [J], food research and development, 2014.08 (Volume 35), PP: 81-86.
[4] Zhang lingbiao et al., nondestructive detection of pesticide residues on Tomato surface based on visible / near infrared hyperspectral imaging technology [J], food and machinery, 2014.01 (30 volumes), PP: 82-85.
[5] Deng Haiyan et al., rapid determination of low concentration atrazine pesticide based on near infrared and mid infrared spectral data fusion [J], spectroscopy and spectral analysis, October 2016 (36), PP: 183-184.