

Determination of Mancozeb Residues in Vegetables by Head-Space Fourier Transform Infrared Spectroscopy

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Abstract: Near-infrared spectroscopy (NIRS) is used to estimate Mancozeb residues in vegetables. In order to ensure high recognition rate and remove the disturbing factor in chlorophyll, headspace gas method was established to for determining Mancozeb residues. CS₂ gas was generated with acid stannous chloride for 20mins in oven at 95°C. The infra-red absorption peaks of raw spectra at 1520cm⁻¹ match well with each other. So, the wavenumber from 1504cm⁻¹ to 1530cm⁻¹ were selected for subsequent analysis after baseline correction method. Least Squares Support Vector Machines (LS_SVM) was used to establish a model to estimate Mancozeb residues. The results show that in this experiment the accuracy of Mancozeb residues can be believable when the Mancozeb residues content was more than 1.2mg/kg.

1. Introduction

Mancozeb is used widely range of field crops, fruits and vegetables. And it can controls many fungal diseases, such as citrus anthracnose, leaf spot, rust of apple and downy mildew, which can increase yield and protect crops [1, 2]. Nowadays, more and more pesticides were restricted or forbidden in vegetables and fruits, the maximum residue limit (MRL) of Mancozeb getting lower and lower is an inevitable development trend. There is National Standard GB 2763-2012 in china, which includes the MRL of Mancozeb, Mancozeb residues in grains are 1mg/kg, 0.1mg/kg in oil, 0.5-5mg/kg in vegetables and 1-5mg/kg in fruits. European Union provides the highest Mancozeb residues in fruits and vegetables are 0.1-10.0mg/kg. However, conventional techniques, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC), using to determine Mancozeb residues was time consume and expensive. Therefore, Near-infrared spectroscopy (NIRS) is used as a tool to analyse Mancozeb residues.

Green vegetables contain chlorophyll, which bring very big disturbances to the detection result. And it is also difficult to separate chlorophyll from vegetables. In order to ensure high recognition rate and remove the disturbing factor in chlorophyll, a method is provided. Under acidic conditions, Mancozeb can react with stannous chloride, then releases CS₂ as the mixture of Mancozeb and stannous chloride is heated [3, 4]. In this paper, Head-Space Fourier Transform Infrared Spectroscopy was used to determine Mancozeb residues in vegetable, the advantage of this method is effective to eliminate chlorophyll barriers and improve the estimation precision.

2. Materials and Methods

The vegetables from a local farmland were used in this study. These vegetables were washed using water and air-dried in the lab for 4h (at 10°C) before next steps. Apparatus used for analysis and detection included headspace bottles with volume of 20ml (Agilent Technologies), a horizontal rotary shaker (KJ-201BS, Kang Jian Medical Apparatus Corporation, China), a Fourier Transform Infrared Spectrometer (WQF-520A, Beijing Beifen-Ruili Analytical Instrument Co., Ltd., China) and a dry thermostat (DH100-1, Hangzhou ruicheng instruments co., Ltd., China). All chemicals were of analytical reagent grade. The HCl/SnCl₂ mixture was prepared dissolving 1g SnCl₂.2H₂O solution in 25mL of HCl (35-37%) and diluting with water to 50mL. Solution for EDTA-NaOH: 10mL of

0.25mol/L ethylenediamine tetraacetic acid disodium salt (EDTA) mixed with 200mL of 0.45mol/L NaOH [5].

2.1 Test process

About 2.5g vegetables were weighed, then put them into headspace bottles with 4ml EDTA-NaOH and let vibrate for 10minutes. Next, add HCl/SnCl₂ mixture in headspace bottles and mix up the vegetable with HCl/SnCl₂ mixture. Using a medal U tube to connect headspace bottles with durham tube. There were 0.32ml four vinyl chloride in Durham tube. The 180mm length of medal U tube (the outside diameter is 0.5mm and the internal diameter is 0.25mm) used to conduct gases from headspace bottles to durham tube. A mechanical small needle shall be available at durham tube to enable easy balancing, meanwhile the durham tube should be placed in an ice bath. At the same time, the headspace bottle was place in a heater at constant temperature of 95°C for 20 minutes. Then, the gas of CS₂ was collected in durham tube [6], it should stand for about 1 hour to achieve room temperature (20°C) and then collecting the NIR spectrum of the samples.

2.2 Infrared Spectrum of Carbon Disulfide

In bottle B, there is the solution of C₂Cl₄ and CS₂. In order to obtain the concentration of CS₂, we prepare and mix standard solution of C₂Cl₄ and CS₂. The concentration of standard solution are 3ppm, 5ppm, 8ppm, 10ppm, 15ppm, 25ppm 50ppm and 75ppm, respectively. Then, we obtain the spectra of CS₂ using Fourier Transform Infrared Spectrometer. Based on the infra-red absorption peaks of raw spectra, it can be obviously found that a main absorption peaks is at 1520cm⁻¹. So, the wavenumber from 1504cm⁻¹ to 1530cm⁻¹ were selected for subsequent analysis after baseline correction method. From Fig.1, it can be found that the absorbance values of standard solutions increased along with its concentration increasing and the peak is at 1520cm⁻¹.

2.3 Data Analysis and Processing

Based on the curve of CS₂ the wavenumber from 1504cm⁻¹ to 1530cm⁻¹, there are two parameters are extracted. One is the area under curve (AUC) which is calculated based on the concentration-absorption curve. The other parameter is peak value at 1520cm⁻¹. After obtain the two parameters, Least Squares Support Vector Machines (LS_SVM) was used to establish the prediction model. The performance of LS_SVM model depends on the selection of hyper-parameters such as γ and σ^2 . Therefore, the training pairs were used to tune the hyper-parameters using a method of cross-validation and resulting values of $[\gamma, \sigma^2]$ for the concentration of CS₂, and the value of $[\gamma, \sigma^2]$ were [7960.60 19.422]. And the results of standard solution of CS₂, the RMSE was 0.2115 ,and the correlation coefficient was 0.9999.

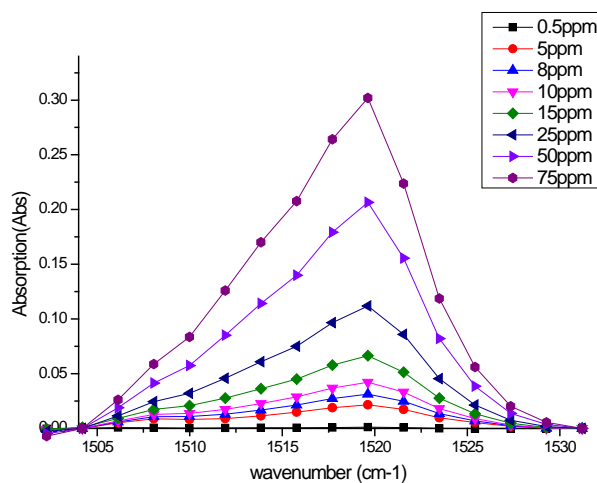


Figure 1. Spectroscopy of standard solution of CS₂

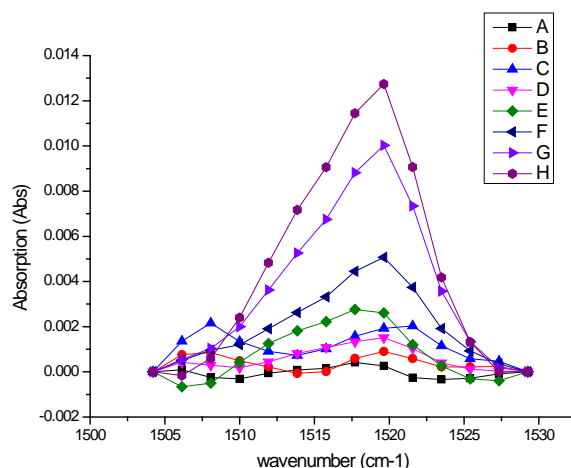


Figure 2. Spectroscopy of vegetable containing Mancozeb

2.4 Spectrum Collection and Processing of Vegetable Samples

Spray the vegetables with different concentration of Mancozeb (the concentration of Mancozeb are 25, 50, 75, 100, 200, 500, 650, 800ppm), and place in lab for 12h to ensure the vegetables dry. There are eight concentration used in this experiment. The eight samples are denoting by A-H, respectively. Then, used the methods mentioned above to extract CS₂.

The baseline calibration is taken to extrude the useful information, and the curves are shown in Fig.2. In Fig.2, the letter A-H is in different color and shape representing different concentration of Mancozeb. In fig.2 one can find that the curve of E, F, G and H have the same change tendency, the peak value does change with concentration of CS₂. However, the solution containing low concentration of CS₂ is different. The tendency was obvious fluctuation, the curve even has double peaks, and the value at 1504cm⁻¹ is cloudy. A total of eight vegetable samples were tested Mancozeb residues according to the standard SN 0157-1992. The results showed in Table 1. Compared the value of Mancozeb residues with the curve of A, B,C, D, E, F, G and H in Fig.2, the concentration less than 1.2mg/kg are not suit for test under this test condition.

Table.1. Mancozeb residues in vegetables using the standard SN 0157-1992

number	Concentration (mg/kg)	number	Concentration (mg/kg)	number	Concentration (mg/kg)
A	0.1	D	0.7	G	1.6
B	0.6	E	1.2	H	4.9
C	0.8	F	1.2		

Using the parameters obtained from curve of E, F, G and H, we can calculate the concentration of CS₂ based on LS_SVM model, the calculation results are 0.841, 1.39, 2.46 and 3.03ppm, respectively. By calculation, the value of Mancozeb residues in E, F, G and H are 0.77mg/kg, 1.23mg/kg, 2.36mg/kg and 2.96mg/kg, respectively.

3. Discuss

Through the practical measurements of Mancozeb residues, some procedures for increasing measurement precision are obtained. (1) In the process of carbon disulfide collection, it is useful to select a small inner diameter metal tube, which makes the flow capacity of gas fell and dissolved in C₂Cl₄. (2) The length of durham tube is 50mm, it is better to choice more length and more internal diameter, this can make all the gas has more time to dissolved in C₂Cl₄. (3) In this experiment, the volume of C₂Cl₄ is 0.32ml, if less C₂Cl₄ is used such as 0.1ml, the detection of Mancozeb residues may reach good effect. (4) The liquid sample cells is thick with the volume of 0.2ml, the less the

volume uses, the better the accuracy is. (5) It is necessary to adopt much thick optical length than 1.5mm used in this experiment. This can be an effective method of determining detection limit.

4. Conclusion

In this paper, NIR was used to determine Mancozeb residues in vegetable. Based on collecting the representative samples with different content of CS₂ combined with LS_SVM, when the Mancozeb residues content was more than 1.2mg/kg, the accuracy of Mancozeb residues can be believable. And the value of Mancozeb residues are 0.77mg/kg in E, 1.23mg/kg in F, 2.36mg/kg in G and 2.96mg/kg in H, respectively.

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