MEASUREMENT OF PESTICIDES RESIDUES USING SPECTROSCOPY ON AGRICULTURAL PRODUCTS

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ABSTRACT

A new spectroscopic method for pesticide residues detection on agricultural products was developed. The general determination methods are high performance liquid chromatography (HPLC), gas chromatography (GC) or GC-mass spectrometry. They have provided relatively good detection limit and accuracy with complicated and time-consuming (5hrs above) procedures. In addition freshness is very important for evaluating qualities of agricultural products. This requires a simple and fast method for detection of pesticides.

Reflectance, transmittance and fluorescence spectrometry of pesticides were tested using UV range because most of pesticides contain conjugation band in the molecular structures.

Fluorescence spectrometry showed better sensitive to detect pesticide residues than did reflectance and transmittance spectrometry. Intensity and shape of fluorescence spectra showed different patterns with different structures of pesticides. Detection limit for fluorescence spectrometry was 0.1 ppm to 10 ppm depending on the structures of pesticides. Application of fluorescence spectrometry appears to be an easy method for detection of pesticide residues on agricultural products.

Key Word: UV spectroscopy, Pesticide residues, Reflectance spectrometry, Transmittance spectrometry, Fluorescence Spectrometry

INTRODUCTION

Pesticide residues on agricultural products are very harmful for human health if they are consumed above their limitation. According to increasing consumption of agricultural products, application of pesticides to produce more products and to maintain freshness during distribution has been increased. Over-use and abuse of pesticides could damage human beings, animals and environments. Therefore, the development of improved detection technique for pesticide residues on agricultural products urgently demanded.

The general determination methods are high performance liquid chromatography (HPLC), gas chromatography (GC) or GC-mass spectrometry. They have provided relatively good detection limit and accuracy with complicated and time-consuming (5hrs above) procedures. In addition freshness is very important for evaluating qualities of agricultural products. This requires a simple and fast method for detection of pesticides.

Kim et. al. (1998) applied fluorescence spectrometry to detect pesticide residues on agricultural products. This application was based on Physico-chemical properties of pesticides because conjugation band was mostly contained in the pesticide structures.

The main objectives of this study are as follows:

1. Identify transmittance characteristics of pesticides by absorption wavelength used for insecticides and fungicides.
2. Define fluorescence spectra by absorption spectra.
3. Represent possibility of fluorescence spectrometrical application for determination of pesticide residues.

MATERIALS AND METHODS

Test pesticides

Four insecticides and two fungicides, which have been widely used on fruits and vegetables in Korea, were tested. Table 1 shows the characteristics of the pesticides. Fig. 1 shows the chemical structures of the pesticides.

Table 1. Characteristics of pesticides

No	Name of pesticides	Nomenclature(%)	Class	Company
1	Benomyl wettable powder	Benomyl (50)	Fungicide	D company
2	Ripcod emulsifiable concentration	Cypermethrin (5)	Insecticide	J company
3	Nusta wettable powder	Flusilazole (2.5)	Fungicide	D company
4	Konido wettable powder	Imidacloprid (10)	Insecticide	D company
5	Sing-sing emulsifiable concentration	Pirimiphos-methy (25) Cypermethrin(2.5)	Insecticide	Y company
6	Fenari emulsifiable concentration	Fenarimol (12)	Insecticide	DY company

Experimental apparatus and Methods

The experimental apparatus was constructed to measure transmittance and fluorescence spectra of pesticide solutions as shown in Fig. 2. The apparatus consisted of an UV light source, a spectrometer (MS125, Oriel, USA) for transmittance and an UV light source with band-pass filter, a CUV-FL-DA cuvette holder and a spectrometer (S2000FL, Ocean Optics, USA) for fluorescence.

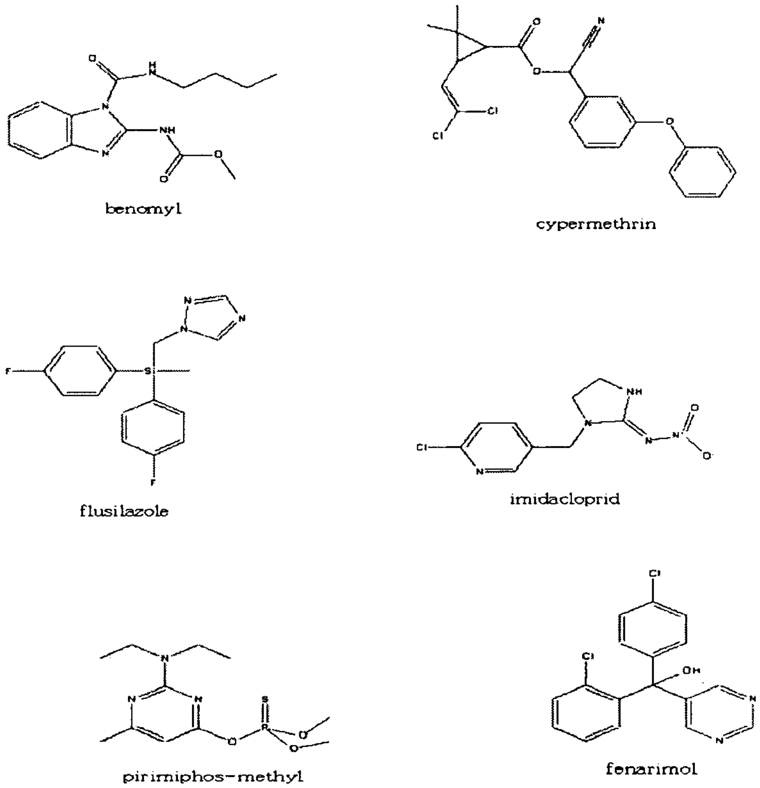

Fig. 1 Chemical Structures of pesticides used

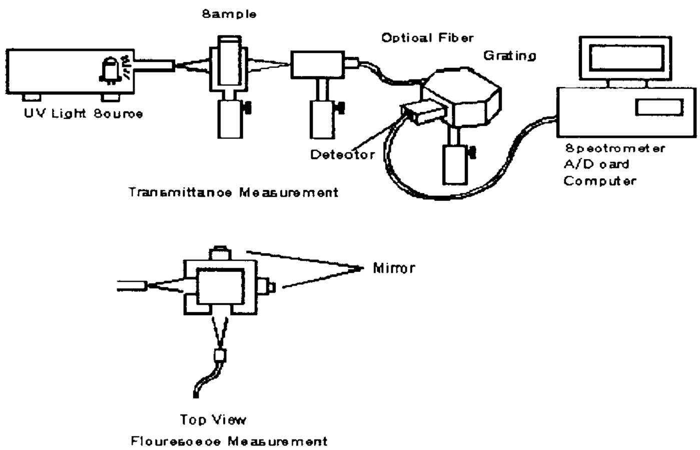

Fig. 2 The schematic diagram of the spectrometer system

The tests were conducted at four levels (10, 100, 500, 1000 ppm) pesticide concentration solutions for transmittance spectrometry and three levels (0.1, 1, 10 ppm) of low concentration for fluorescence spectrometry. Transmittance spectra were obtained and were differentiated by 1st and 2nd derivative to define absorption patterns. The correlation coefficients between transmittance and concentration were calculated. Sample pesticides were sprayed on the surface of apples and on the leaves of sesame. Reflectance spectra were obtained from the surface of apples with and without pesticide. Transmittance spectra were obtained from the solutions extracted with distilled water from the surface of apples. Fluorescence spectra were obtained from those solutions also. For leaves of sesame, fluorescence spectra of pesticide residues were measured with the solutions extracted with ethyl alcohol.

RESULTS AND DISCUSSIONS

Transmittance characteristic of pesticides with different concentrations

Fig. 3 shows the transmittance spectra of Knido at various concentration levels. It shows the transmittance decay as concentration increases. Fig. 4 shows characteristic absorption patterns with different pesticides below 300nm wavelength.

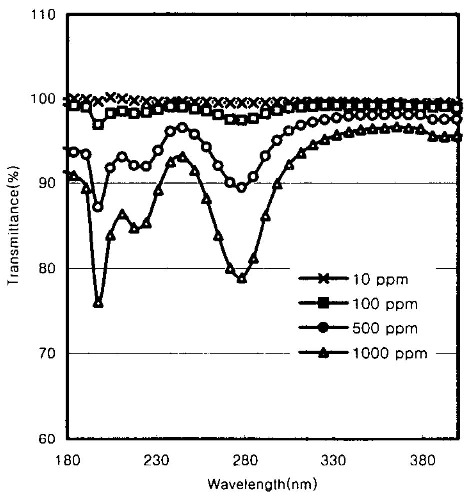

Fig. 3 Transmittance of Konido solution at several concentrations

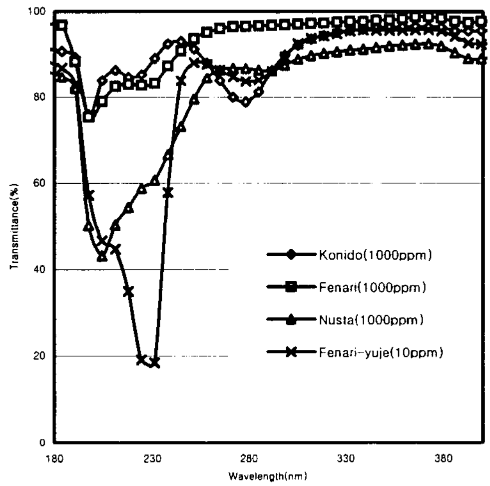

Fig. 4 Transmittance spectra of pesticides solutions

The 2nd derivative spectra in UV range of Konido transmittance spectra are shown in Fig. 5 and four pesticides in Fig. 6. Regression equations are developed by the 2nd derivative spectra and their R^2 is 0.8400~0.9997. Table 2 shows correlations between transmittance and concentration at the absorption wavelength.

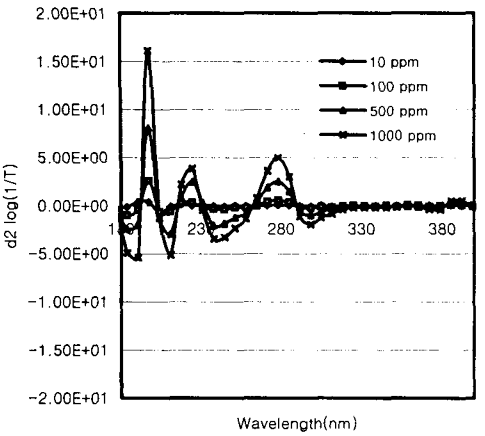

Fig. 5 The 2nd derivatives of Konido transmittance spectra in UV range

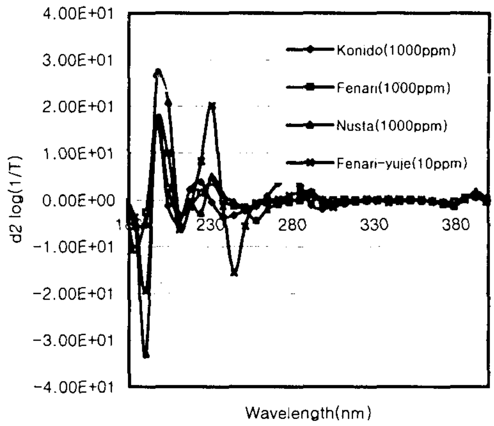

Fig. 6 The 2nd derivatives of pesticides transmittance spectra in UV range

Table 2. Correlation between transmittance and concentration at absorption wavelength

Name of pesticides	Wavelength (nm)	Regression Equations	R^2
Konido wettable powder	220, (276)	Y= -48.1X + 4792.4	0.9997
Fnari wettable powder	(225)	Y= -22.9 X + 2282.1	0.9268
Nusta wettable powder	(287)	Y= -75.1 X + 7492.3	0.9956
Fenari emulsifiable concentration	(227), 282	Y= 14.186 exp(-0.0075 X)	0.8400

*( ) : The values used for regression equations

Fluorescence characteristics of pesticides at several concentrations

Fig. 7 shows the fluorescence spectra of Benomyl solutions at various concentration levels. Intensities of fluorescence spectra were different at various concentration levels specially in the range 300nm~450nm of wavelength. Fig. 8 shows fluorescence spectra at 0.1 ppm concentration of pesticides. Intensities and shapes of fluorescence spectra were different with different pesticides but almost of them could be detected at 0.1 ppm.

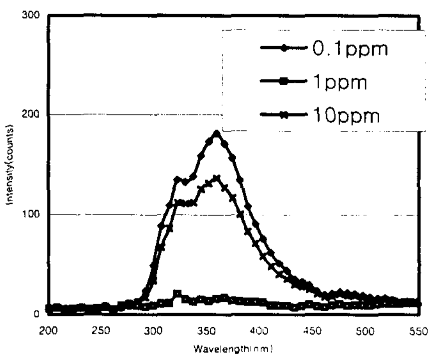

Fig. 7 Fluorescence spectra of Benomyl solution at several concentrations

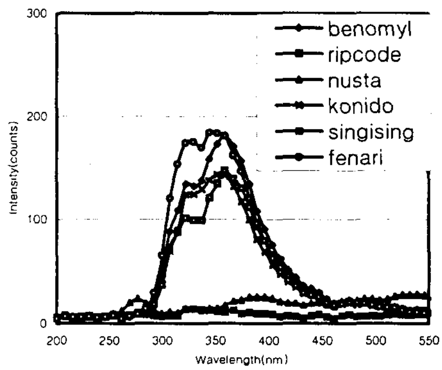

Fig. 8 Fluorescence spectra of pesticides solutions at 0.1 ppm

Determination of pesticide residues

1. Determination of pesticide residues by reflection spectra

Using reflection probe, reflection spectra were obtained from surfaces of apples with and without Konido in Fig. 9. The 2nd derivative spectra of reflectance were shown in Fig. 10. Comparing reflectance spectra, there is no difference between the spectra with and without Konido.

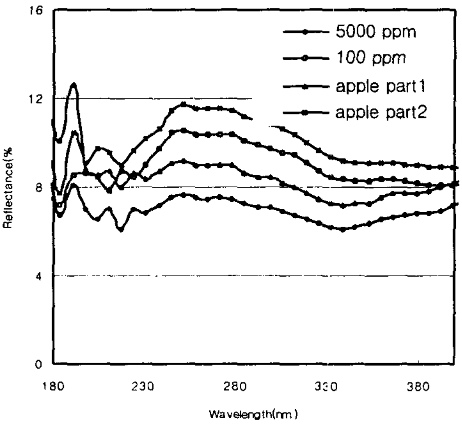

Fig. 9 Reflectance spectra of apple with and Konido application

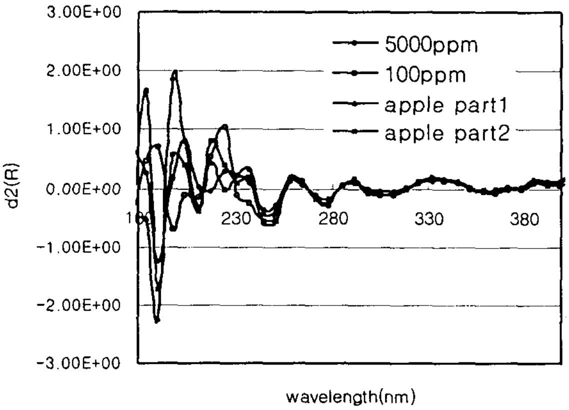

Fig. 10 The 2nd derivatives spectra of apple with and without Konido application

2. Determination of pesticide residues by transmittance spectra

Residual pesticides were extracted from surfaces of apples with and without pesticides by scratching. Transmittance spectra were obtained from the solution containing the scratched pieces. Fig. 11 shows transmittance spectra of Konido residue solutions and Fig. 12 shows the 2nd derivatives of the transmittance spectra of Konid. Comparing transmittance spectra, there is no difference between the spectra with and without Konid.

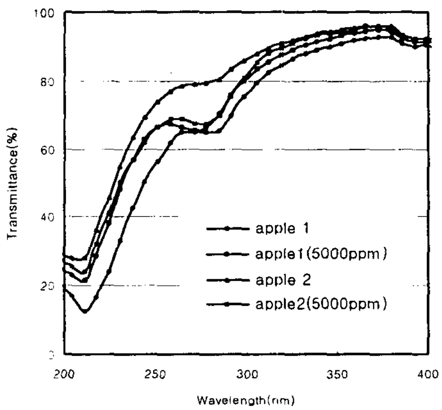

Fig. 11 Transmittance spectra of Konido residue Solution

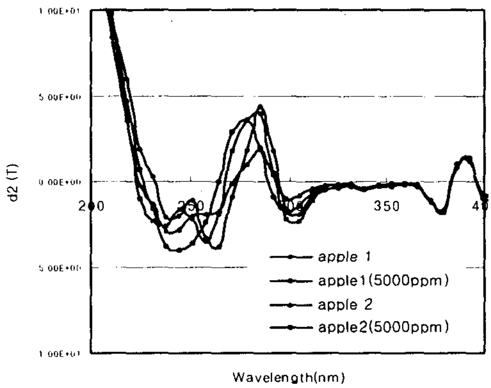

Fig. 12 The 2nd derivative spectra of transmittance of Konido residue

3. Determination of pesticide residues by fluorescence spectra

Pesticide residues were abstracted from leaves of sesame using ethyl alcohol in an ultrasonicator for 2 min. From that solution, fluorescence spectra were obtained. Fluorescence could be detected from the residues of Fenari as shown in Fig. 13. The results show that it is possible to detect pesticide residues using fluorescence spectra (Fig. 14).

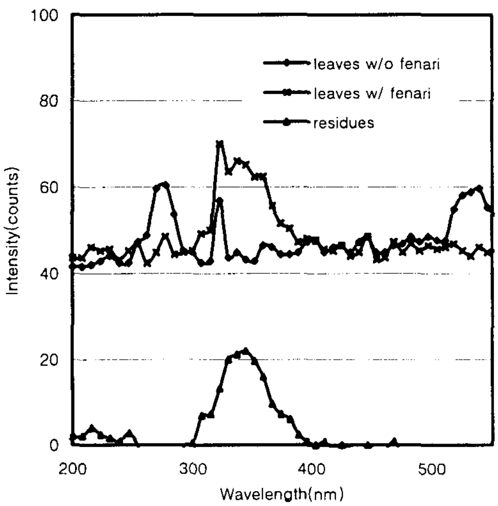

Fig. 13 Fluorescence spectra of Fenari residue solution

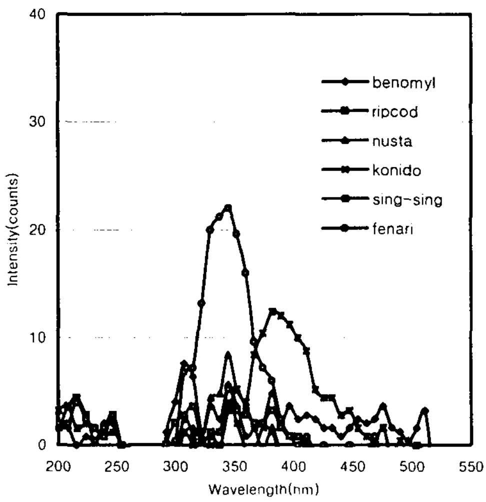

Fig. 14 Fluorescence spectra of pesticides residue solutions

CONCLUSIONS

To detect pesticide residues on agricultural products, reflectance, transmittance and fluorescence spectra were measured.

Pesticides had characteristic absorption patterns in UV region and there was a good correlation between its transmittance and concentration at specific wavelength.

The fluorescence spectra of pesticides had similar wavelength absorption patterns but different shapes and intensities. At 300~450nm fluorescence spectra showed detection limit from 0.1 ppm to 10ppm according to pesticides.

Fluorescence showed more sensitive to detect pesticide residues than did reflectance and transmittance. Fluorescence spectrometry at 300~450nm wavelength appears to be a simple and fast method pesticide residue detection on agricultural products.

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