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Determination of thiophanate-methyl using UV absorption spectra based on multiple linear regression

L. Jiao [a,b], D. Dong [a,b], W. Zheng [a,b], X. Zhao [a,b], S. Zhang [a,b], C. Shen [a,b,*]

[a] Beijing Research Center of Intelligent Equipment for Agriculture, Beijing Academy of Agriculture and Forestry Sciences, China
[b] Beijing Key and Open Laboratory of Information Technology in Agriculture, No. 11, Shuguang Huayuan Middle Road, Haidian District, Beijing 100097, China

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ABSTRACT

As one worldwide used agent for fungi control in the fruit and vegetable field, thiophanate-methyl has been constituted a significant health risk. To determinate thiophanate-methyl, the method using UV absorption spectra based on multiple liner regression is used. Principal absorption wavelengths related closely with thiophanate-methyl ethanol solution are confirmed through analyzing the absorption spectra of thiophanate-methyl. Utilizing multiple linear regression, mathematical model between absorbance obtained from fourteen absorption wavelengths and thiophanate-methyl concentration is established. The result shows concentrations between the predicted values and measured values are well coincident and the related coefficient is 0.9853 over the concentration range 2–35 ppm.

1. Introduction

Pesticides are used in farming on fruit and vegetable to increase yields and product quality. Benzimidazole fungicides as systemic pesticides are widely used in agriculture, floriculture, and fruit farming for the control of a wide range pathogens [1]. As one worldwide used agent for fungi control, thiophanate-methyl is one component of the benzimidazolic family. The use of thiophanate-methyl has constituted a significant health risk [2,3]. Therefore, the determination of thiophanate-methyl residue is of great importance. Thiophanate-methyl can be analyzed by different detection technologies, such as gas chromatography, gas chromatography tandem mass spectrometry, high performance liquid chromatography and so on [4–6]. However, the apparatus used in these technologies are very expensive, and in addition, the apparatus operation and analysis process are complicated. So it is necessary to attempt to explore an inexpensive and simple determination method of the thiophanate-methyl.

The component and quantity of matter can be determinated through the UV spectra caused by the absorption of molecular or ion of the matter. Multivariate statistical methods are frequently used in exploratory data analysis to obtain environmental knowledge. Spectroscopic method based on multivariate statistical methods is most widely used for matter determination due to the excellent limit of detection. Therefore, the technique combining spectroscopy and multiple liner regression was used widely by researchers in the latest years [7,8].

In the present work UV absorption spectra based on multiple liner regression for determination of thiophanate-methyl in ethanol solution is explored. Thiophanate-methyl is detected through analyzing UV absorption spectra.

2. Materials and methods

2.1. Apparatus

The experimental instrument setups used for measuring absorbance of thiophanate-methyl ethanol solution are shown schematically in Fig. 1. UV absorbance spectra were recorded with an AvaSpec-2408-USB2 fiber optic spectrometer. This is a single channel instrument capable of acquiring spectra from 200 to 1100 nm at a resolution of 2.4 nm. The power and spectra data transmission to AvaSoft Basic software can be implemented by a high speed USB interface cable connected to PC. In addition, the spectrometer has a standard SMA fiber optic entrance connector to connect with the fiber. The Integration time and Average of AvaSoft Basic software is setup 30 ms and 100 respectively. A deuterium arc lamp (Avalight-DHS) in the UV range (consistent in the 215–400 nm region) is used. The fiber used in the experiment bundles with core diameters of 200 μm and has a standard SMA905 interface connected with the light source and spectrometer. The variable pathlength holder with variable path length is designed by the

* Corresponding author at: Beijing Research Center of Intelligent Equipment for Agriculture, Beijing Academy of Agriculture and Forestry Sciences, China. Tel.: +86 010 51503654; fax: +86 010 51503626.
E-mail address: 76721256@qq.com (C. Shen).

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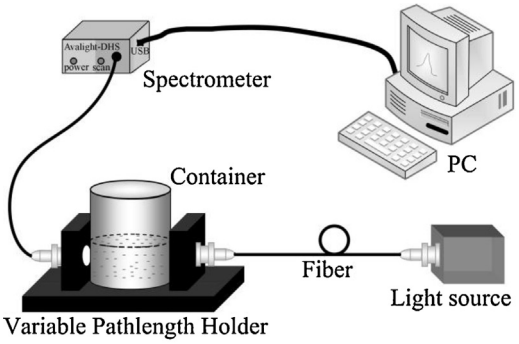

Fig. 1. Experimental instrumental setups for UV absorption spectra measurement of the thiophanate-methyl sample solutions.

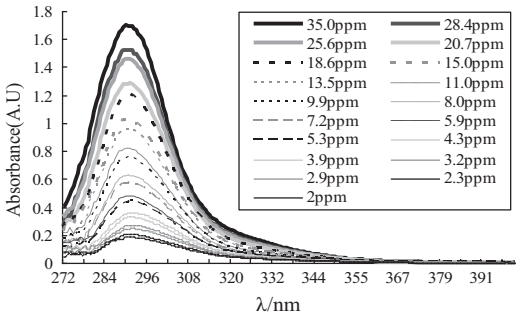

Fig. 2. Nineteen samples absorption spectra selected according to statistical analysis method at the different concentrations for establishing model.

Avantes for low absorption measurements. The variable pathlength holder comes with a base plate and is standard equipped with 2 COL-UV/VIS lenses for applications in the 200–2500 nm range. In the present experiment, the path length is set to 9 mm.

2.2. Solution samples

Thiophanate-methyl wettable powder (Nippon Soda Co., Ltd.) including 70% effective component is bought in the market. Analytical-reagent grade ethanol as solvent is used for preparing all solutions and diluting them. Thiophanate-methyl standard solution: a stock solution (35 ppm) was prepared by dissolving 5 mg of thiophanate-methyl wettable powder in 100 mL ethanol. The samples with varying concentrations of thiophanate-methyl are prepared by diluting a stock solution accurately.

2.3. Methodology

To establish the mathematic model a multivariate data matrix containing concentration data of nineteen thiophanate-methyl samples occupying two-thirds of the total samples and absorbance data at fourteen wavelengths corresponding to every kind of sample is used. Concentration and absorbance data of other nine thiophanate-methyl samples are used for mathematics model verification. The broadband absorption spectrum for each thiophanate-methyl sample is smoothed with the use of four-point moving average algorithm to improve the signal-to-noise ration. All broadband absorption spectra are preprocessed by baseline correction before using for mathematics model.

3. Results

3.1. Model establishment

In order to obtain the absorbance data with varying concentrations of thiophanate-methyl sample, a prepared stock solution (35 ppm) is diluted accurately. In the present experiment, twenty-eight absorption spectra corresponding to each kind of concentration obtained through diluting gradually are recorded by the AvaSoft Basic software with 30 ms Integration time and 100 Average. These twenty-eigth spectra are divided into two groups. One group including nineteen absorption spectra selected according to statistical analysis method is used for establishing multiple linear regression model, the other is used for model verification, the other is used for model verification. Fig. 2 illustrates nineteen absorption spectra at different concentrations of thiophanate-methyl. The absorbance as shown in Fig. 2 tends to be linear change in the wavelength range of 280–300 nm. This phenomenon implied the absorbance is proportional to the concentration of substance to be determined when path length and molar absorption coefficient at different wavelengths are confirmed, such as described by Lambert–Beer law [9,10].

The absorbance at fourteen wavelengths which thiophanate-methyl has the strongest absorption relative to other wavelengths is selected for establishing model in the nineteen absorption spectra as shown in Fig. 2. The mathematic model between the thiophanate-methyl concentrations and absorbance is established through analyzing these data by making use of multiple linear regression method and the correlation coefficient of the established model reaches up to 0.9998.

3.2. Model verification

Absorbance corresponding to other nine concentrations for model verification is shown in Table 1. The data in the first row beginning with second column are fourteen wavelengths which have been selected. The data in the first column beginning with second row are nine concentrations of thiophanate-methyl (measured values). Others are absorbance and will be substituted into the established mathematic model for obtaining the predicted values.

Through substituting these verification absorbance data into the established multiple linear regression model, six predicted concentration values are obtained. The correlation between predicted values and measured values is shown in Fig. 3. It shows that the correlation coefficient is 0.9853 and the slope of correlation line is close to 1.0. It is realized that the predicted values obtained from the established multiple linear regression model show good agreement with measured values in the range of 2–35 ppm. Therefore, it is possible to measure the concentration of thiophanate-methyl effectively through the present method.

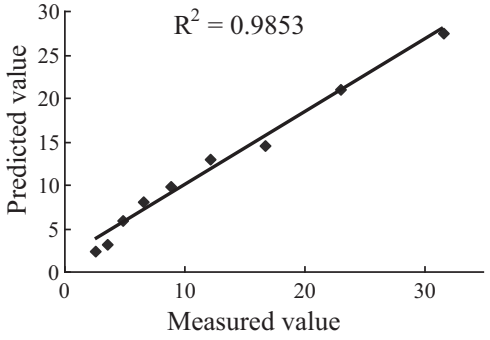

Fig. 3. The correlation between the predicted value and measured value of the thiophanate-methyl samples obtained from the established multiple linear regression model.