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Article

A Correction Method of Mixed Pesticide Content Prediction in Apple by Using Raman Spectra

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Abstract: In the study, a new correction method was applied to reduce error during detection on mixed pesticide residue in apples by using Raman spectra. Combined with self-built pesticide residues detection system by Raman spectroscopy and the application of surface enhancement technology, rapid real-time qualitative and quantitative analysis of deltamethrin and acetamiprid residues in apples can be applied effectively. In quantitative analysis, compared with the intensity value of characteristic peaks of single pesticide with same concentration, the intensity value of characteristic peaks of the two pesticides decreased after mixing the pesticides, which interferes the results severely. By comparing the difference in the intensity of characteristic peaks of single and mixed pesticides, a correction method is proposed to eliminate the influence of pesticides mixture. Characteristic peak intensity values of gradient concentration pesticide from 10^{-1} g·kg^{-1} to 10^{-6} g·kg^{-1} and Lagrangian interpolation are applied in the correction method. And a smooth surface is applied to describe the correction ratio of characteristic peak intensity. Through detecting the characteristic peak intensity values of the mixed pesticide, correction ratio will be obtained. Then real values of the peak intensity of pesticides and the content of each component of the mixed pesticide will be acquired by the correction method. Correlation coefficient of model validation exceeds 0.88 generally and Root Mean Square Error also decreases obviously after correction, which proved the reliability of the method.

Keywords: Raman spectra; mixed pesticides; apple; correction method; rapid; real-time

1. Introduction

Pesticide plays an essential role in crop farming. Application of pesticide in agriculture has created a great deal of grain output and fed many people in the world. But this also caused some problems. Pesticides have chronic and acute impact to human health [1-3]. Pesticide poisoning to human health are either due to processing during agricultural production or living poisoning that is because of consumption of food with high residuals, ingestion, residue and so on [4]. While in the detection of mixed pesticide residue, the interaction between different pesticide components always causes a serious impact on the test results. The phenomenon makes the detection result inaccurate. And it's necessary to find a method to eliminate the interference. Deltamethrin ($C_{22}H_{19}Br_2NO_3$) is a kind of efficient synthetic pyrethroid insecticides created in 1974 with characteristics like wide insecticidal spectrum, significant effect, low residue and so on. And deltamethrin had been widely applied in crops. While deltamethrin is also one of limited used pesticides. Several studies had demonstrated that deltamethrin increased the risk of neurodegenerative disorders like Parkinson, Alzheimer disease, developmental deficits and learning disabilities [5-8]. Thus it's quite necessary to detect deltamethrin for reducing damage to the public safety. In continuous contact to insecticides directly or indirectly may increases potential human health problems. It's necessary to reduce deltamethrin residue on fruits and vegetables to decrease contact. Relevant study on agricultural products had been done by some researchers. And on Oct. 27th 2017, deltamethrin was classified as

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category 3 carcinogens by WHO International Agency for Research on Cancer [9]. Acetamiprid($C_{10}H_{11}ClN_4$) is a synthetic chlorinated nicotimine pesticide against insects that have gained resistance to ganophosphate, carbamate and synthetic pyrethroid. It has been widely used for agricultural pest control in many countries. The long-term intake of high doses of acetamiprid can lead to breast cancer in adult mouse models and rib malformations in fetal mice. Acetamiprid also causes mutagenesis in human peripheral lymphocytes in vitro, and has a synergistic mutagenesis effect with alpha-cypermethrin. Pesticide residue mixture of deltamethrin and acetamiprid residue always exists on crop. In agricultural production, the alternate use or combination of deltamethrin and organophosphorus pesticides, such as non-pyrimid pesticides, is beneficial to slow down the development of pest resistance. While compared with the intensity of characteristic peaks of deltamethrin and acetamiprid, the intensity value of characteristic peaks of the pesticides mixture will reduce in a certain range, which increases the difficulty in Raman detection of the pesticides.

Raman spectroscopy is defined as a spectroscopic and imaging technique that is used to record or observe vibration, rotational or other lower frequency modes in a system [10]. Raman spectroscopy is based on Raman scattering effect or inelastic vibration. Raman technology has been known for its ability to detect chemicals accurately and precisely [11]. Raman spectroscopy possesses strong advantages compared to other analytical techniques [12]. As Raman fingerprint of substance is distinctly unique to each other, Raman technology owns the ability to discern different element in the material [13]. The water molecule contains only a very small single chemical bond. So the Raman scattering signal is very weak [14]. During the Raman detection no samples will be touched by chemical substance, which makes it non-destructive detection. Raman spectroscopy had already been used for pesticide detection. Raman spectroscopy technology had already been used in quality control of pesticide formulations [15]. Tianfeng Xu developed a method to detect chlorpyrifos on apples through Raman spectroscopy technology [16]. And now Raman technology have been a fast, accurate method for non-destructive detection and in several cases in-situ method for detection of various materials is gaining its importance in agricultural application as well [17]. Surface enhanced Raman spectroscopy (SERS) technique, based on Raman scattering effect and combined with surface enhancement mechanism, is an analysis techniques with high sensitivity. It’s one of the important developments of conventional Raman spectroscopy. It can not only detect the detailed structure information of the object, but also provide higher sensitivity with several orders of magnitude than the conventional Raman technology, which improve the detection limit greatly and realize the detection of trace substances.

In Raman spectra detection, it’s obvious that in the case of pesticide samples with same concentration, the characteristic peak intensity of pesticide mixture was lower than the ones of single pesticide. The declining degree of peak intensity changes with the concentration of pesticides. The characteristic peak intensity reflected the content of pesticide. Thus the characteristic peak intensity of pesticide mixture could not reflect the content accurately. This increased the risk of misclassifying excessive pesticide product as qualified product. Thus the phenomenon affected Raman spectra detection on pesticide mixture severely. In the study, acetamiprid and deltamethrin, two pesticides which were commonly used on apples, were the research objects. According to the Raman signal enhancement effect, silver sol was used as surface enhancer. And the exposure time, laser power, enhancement methods, and the number of collection points were optimized to get the best result. In order to find the declining degree and changing rule of peak intensity with pesticide concentration, the characteristic peaks intensity of single pesticide and pesticide mixture with gradient concentration were all detected and compared and the rates were calculated. Then the rates between single pesticide and mixture with concentration from 10^{-1} $g \cdot kg^{-1}$ to 10^{-6} $g \cdot kg^{-1}$ were worked out with Lagrange interpolation method. A correction method was applied in Raman spectroscopy detection of deltamethrin and acetamiprid residue. And a reasonable assessment of model validity was made. The correction method could be used in other Raman spectral detection of pesticide mixture.

2. Materials and Methods

2.1. Experimental Materials

In the experiment, pesticide solution with gradient concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} $g\cdot kg^{-1}$ were made by deionized water and commercially available chlorpyrifos pesticides and acetamiprid pesticide with concentrations of 4.8 $g\cdot kg^{-1}$ and 2.0 $g\cdot kg^{-1}$ respectively. Before the detection, 50 mL of the solution was placed in a small mist spray gun. After washed with deionized water and naturally dried, commercial Fuji apples were sprayed to simulate the spraying process of field pesticides to prepare experimental samples.

60 Fuji apples were bought as samples from the local market with different shape and color. 40 apples were chosen randomly as calibration set and the others formed validation. Experiment samples were prepared with the method of spray simulation as pesticide spraying process in the farmland. Before collecting Raman spectroscopy, 2 μL acetone was dropped on the surface of apple sample with diameter of 2 mm. Then 4μL silver sol treated with centrifuge enrichment was dropped on the acetone drop rapidly with diameter of 3 mm. At last 1 μL nitric acid solution with concentration of 40 $mmol\cdot L^{-1}$ was dropped on the mixture drop. And then Raman spectra signal was collected. In order to get accurate Raman spectra information of apple samples, several detection points were detected from each apple sample. And the detection points were located over the entire surface of the sample. Each detection point was successively applied with acetone, silver sol and nitric acid solution.

After detecting the Raman spectra, the spectra of samples with same concentration were averaged as original spectrum. Raman spectra of single pesticide and pesticide mixture with same concentration were detected from the same apple to reduce interference from apple background.

2.2. Pesticide residue detection system

Pesticide residue detection system developed by the lab was used to collect Raman spectral information in the study. The hardware of the pesticide residue detection system included a laser device, Raman spectrometer, photoelectric charge coupled device, camera, optical fiber, probe, computer and other hardware. The effective detection range of the system was -186.45~2325.72 cm^{-1}. During the study, the excitation light power of the system was 500 mW with a wave length of 785 nm. The pesticide residue detection system was shown in Figure 1.

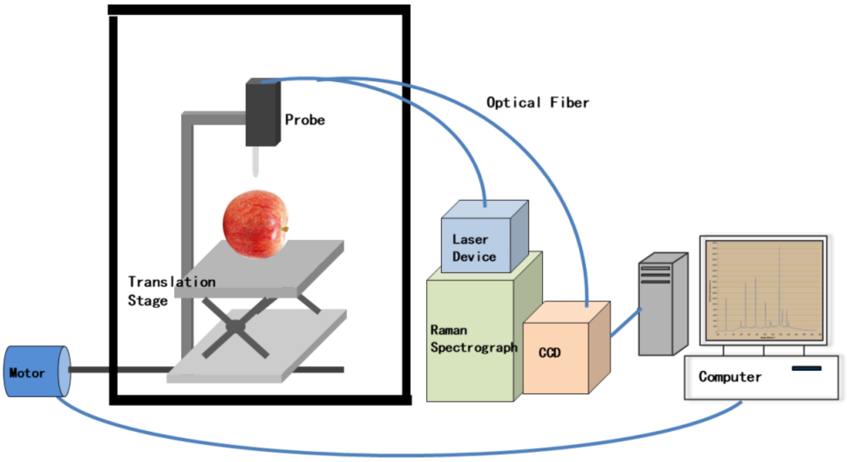

Figure 1. Pesticide residue detection system.

2.3. Preparation of Silver Sol

According to the method made by Nicolae Leopold et al [18], a silver nitrate solution with a concentration of 1.1×10^{-3} $mol\cdot L^{-1}$ was first prepared. And then hydroxylamine hydrochloride and sodium hydroxide were dissolved in 10 mL of deionized water to prepare a mixed solution with concentration of 1.5×10^{-2} $mol\cdot L^{-1}$ and 3.0×10^{-2} $mol\cdot L^{-1}$ respectively. The freshly prepared mixed

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solution was rapidly poured into 90 mL of rapidly stirred silver nitrate solution, and the color of the solution rapidly changed from transparent to gray-brown. And the stirring was continued for 30 min. Then the silver sol was obtained. The obtained silver sol was centrifuged. Then the supernatant was removed. At last the concentrated silver sol was placed in a dark environment at 4°C for use.

2.4. Experiment Method

During the detection, apple sample was placed on a dedicated holding device. The surface of the apple was a curved surface, and the distance from vertex of apple surface to the Raman probe was 7.5 mm. 9 test points were taken in the equator line of apple samples. 9 test points were taken at random and each point was detected 3 times to represent the pesticide residue on the surface of the apple sample. Among them, the relevant parameters of the detection system were: the laser wavelength is 785 nm, and the laser power was 450 mW. Integration time of CCD camera was an important parameter in Raman spectrum detection. The camera integration time was 3s in the study.

3. Results and discussion

3.1. Optimization of exposure time and laser power

Appropriate parameters were essential in the detection process. The main parameters included exposure time and laser power. For samples with high concentration, the signal of characteristic peaks was easy to obtain. However, when the concentration of samples was low, the signal of the characteristic peaks would be weak or disappear if the exposure time was short or the laser power was small. While too long exposure time and too great laser power would lead to signal saturation or samples being burned by laser. Longer exposure time would also lead to time wasting for sample detection. Thus it was necessary to optimize exposure time and laser power before the detection. The spectrum of different exposure time and power were set up for samples with same concentration. It can be seen that when the laser power was certain, the longer the exposure time was, the stronger the characteristic peak signal was. And when the exposure time was short or the laser power was shorter, the signal of the characteristic peak could hardly be observed. Finally when the exposure time was 3s and the laser power was 450 mW, the signal of characteristic peak was the strongest. The maximum power of the laser was 450 mW. Laser of 450 mW would not damage the apple samples. Hence the laser was set at 450 mW. If the exposure time exceeds the threshold, the signal will saturate and the CCD camera may be damaged.

3.2. Data preprocessing and analysis

When Raman spectroscopy was used for sample analyze, signal noise and fluorescence background were important factors which affect the accuracy of the analysis greatly. The noise of the instrument, external environment, etc. leads to signal noise. In this study, the Savitzky-Golay (S-G) 5-point smoothing method [19] was used to remove the spectral noise. This method was proposed by Savitzky and Golay and was widely used in data stream smoothing and noise reduction. And the method was a filtering method based on local polynomial least squares fitting in the time domain. The biggest advantage of the method was that it could ensure the shape and width of the signal while filtering out the noise.

Fluorescence background interference was the most important factor affecting Raman signal analysis especially for organic or biological samples, which made signal of the target analyte submerged. While accurate and effective deduction of fluorescence background was very important in Raman analysis. The principle of adaptive iterative reweighted penalty least squares (airPLS) was to control the fidelity and roughness of the fitting curve by weighting coefficients so as to obtain an ideal fitting curve in this study [20-21]. This method was fast and flexible. The weight of the overall variance between the baseline of the fit and the original signal was changed through iteration. The overall variance weight was acquired from the difference between the baseline and the original signal. The first derivative and second derivative methods could eliminate the interference from the baseline and other backgrounds effectively and improve the resolution and sensitivity. But the

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method may lead to an increase in the signal-noise ratio. Due to the power change of the laser light source and the attenuation of the light intensity, the standard normal variable transformation could eliminate the Raman spectrum noise. However, it could not remove the fluorescence background interference. Baseline calibration deducted the fluorescence background effectively and preserved the original spectral information and eliminates the effects of the instruments. Two baseline calibration methods, the polynomial fitting method of 8 times and the signal minimum maxima, were used in the study. Adaptive scaling was a common calibration method.

3.3. Pesticide mixture signal analysis

SERS signal acquisition was applied to standard solution of acetamiprid and deltamethrin pesticide and mixture of the two pesticides. There were literatures reported that main characteristic peaks of acetamiprid pesticide were located at 634, 1114 and 2164 cm^{-1}, and the characteristic peaks of deltamethrin were located at 574, 735 and 1380 cm^{-1}. Raman spectra signal of single pesticide and pesticide mixture was shown in Figure 2. In the spectrogram, the characteristic peaks of the two pesticides were obvious and the intensity of the characteristic peaks changed with the concentration of pesticides consistently. Thus it was certain that peaks at 634, 1114, 2164 cm^{-1} and 574, 735, 1380 cm^{-1} were characteristic peaks of acetamiprid and deltamethrin pesticide. Overlapping peak didn't exist between acetamiprid and deltamethrin.

In Raman spectra detection, the intensity value of characteristic peaks reflects the content of samples. Thus quantitative analysis could be made from Raman spectra signal. With the decrease of pesticide content, the intensity values of deltamethrin and acetamiprid characteristic peaks reduce linearly. As shown in Figure 2.

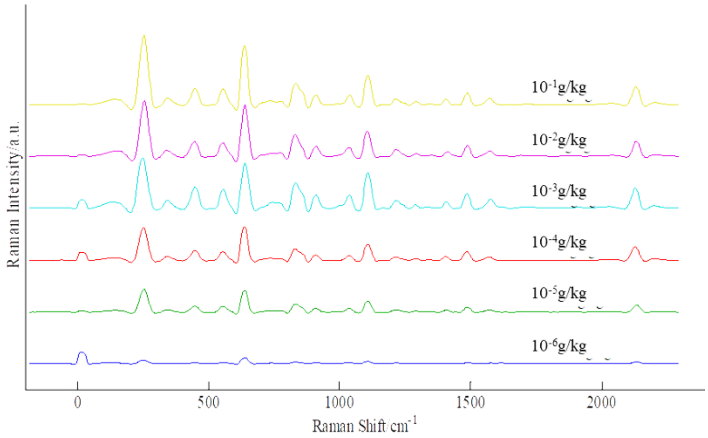

Figure 2. Intensity values of mixture characteristic peaks change with pesticide content.

The location of the Raman vibration peak was only related to the vibration frequency of the chemical bond. Raman spectra peaks in different locations represent different chemical bonds [22]. According to common Raman spectral characteristics of the learning group and comparison of other results analyze, it was possible to acquire the belonging of some characteristic peaks. Characteristic peaks of acetamiprid at 634, 1114 and 2167 cm^{-1} belonged to C-Cl retraction, ring vibration, and ring "breathing" respectively. Characteristic peaks of deltamethrin at 574, 735, 1380 cm^{-1} were caused by C-Br retractable, symmetrical CBr_2 flexing and ring scaling. And apple samples would cause no obvious Raman spectra peaks [23].

As deltamethrin and acetamiprid were always be used in the same agricultural season, it was necessary to detect the mixture of the two pesticides. It could be seen clearly from Figure 3 that intensity of characteristic peaks of deltamethrin and acetamiprid pesticide mixture at 634, 1114 and 2167 cm^{-1} was lower than the ones of single deltamethrin or acetamiprid pesticide solution, which affects the accuracy of detection result severely. It was clear that the intensity of characteristic peaks decreased when the other pesticide was added. Through analyzing original spectra of the two pesticides, it could be found that decrement of the peak intensity was in a certain extent. And the

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extent depended on the concentration of the two pesticides, exposure time of laser and integration time of CCD camera, mainly the concentration of pesticides. Therefore it was necessary to find out the link between the decrement extent of characteristic peaks and concentration of pesticides, and then to get the actual detection result.

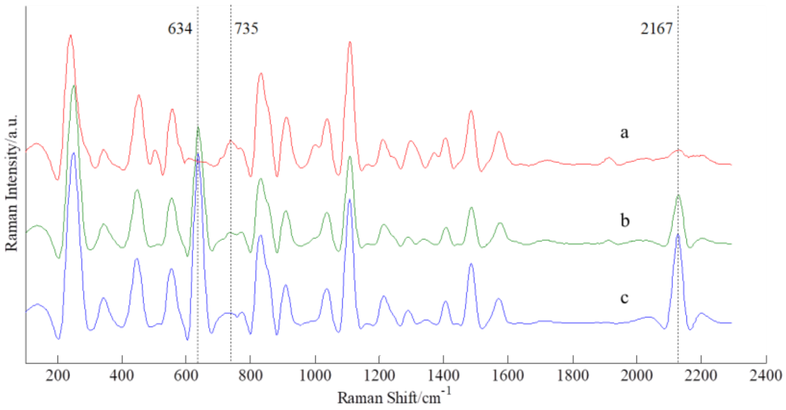


Figure 3. Spectrum of pesticide mixture and single pesticide with concentration of 10^{-1} g·kg^{-1}.

a: spectrum of deltamethrin sample; b: spectrum of deltamethrin and acetamiprid mixture.

c: spectrum of acetamiprid sample.

By comparing a number of Raman spectra, it was clear to find that characteristic peaks intensity value of single pesticide and pesticide mixture were all steady in a range, which means the multiple difference between single pesticide and pesticide mixture was certain. It was possible to find the ratio between characteristic peaks intensity value of single pesticide and the ones of pesticide mixture. Therefore the real peak intensity of one pesticide could be acquired through peak intensity of pesticide mixture and the ratios. The method of ratio would be realiable in Raman spectra detection of deltamethrin and acetamiprid mixture.

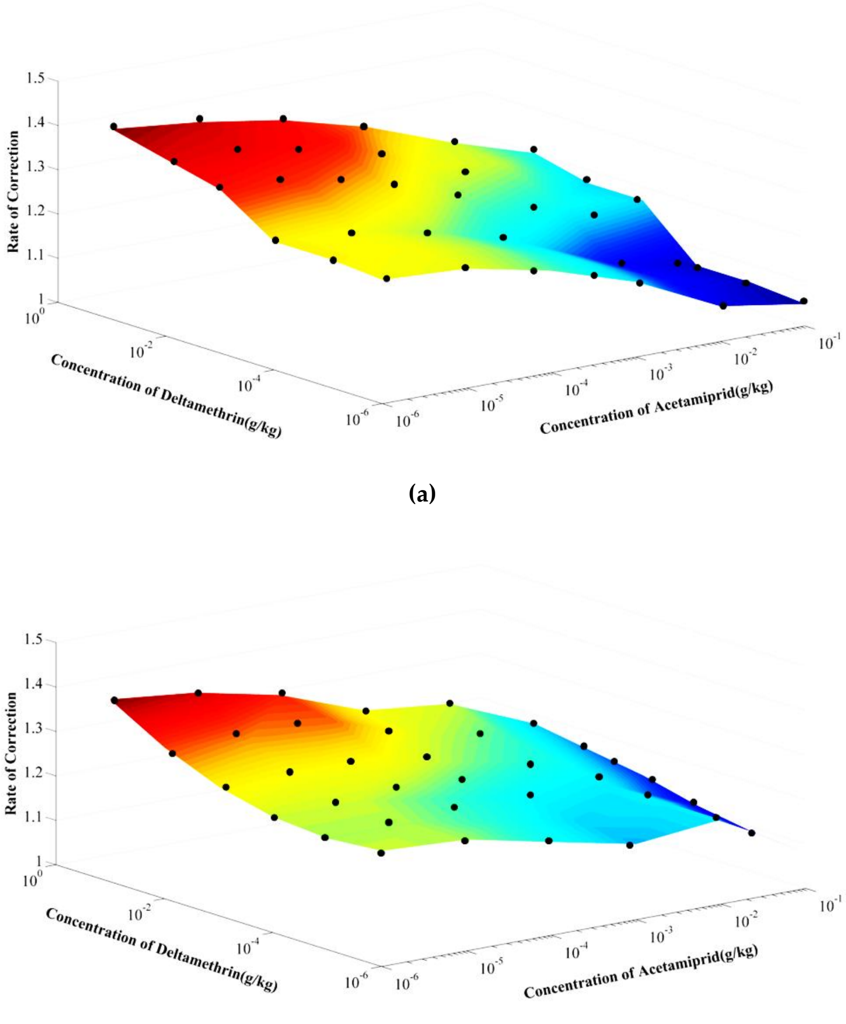
60 Fuji apples were used for detecting Raman spectra signals. 600 sample signals were detected including information of deltamethrin, acetamiprid and the mixture of them. The Raman spectra information of deltamethrin, acetamiprid and the mixture of them with same pesticide content were detected from the similar apple sample to reduce the effect of sample background. Through analyzing massive full-spectrum Raman signal of deltamethrin and acetamiprid it was found that signal of characteristic peaks at 574, 1380 and 2167 cm^{-1} was not strong enough for quantitative analysis. Thus characteristic peaks at 634, 735 and 1114 cm^{-1} were used for data analyze of pesticide mixture.

3.4. Establishment of regression models

The mixture pesticides be detected included the deltamethrin and acetamiprid mixtures with same content and the ones with different concentration. As most pesticide mixture applied in farmland was in low content, detailed analyze of correction ratio change rule was also focused in low content. Deltamethrin, acetamiprid with concentration of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} g·kg^{-1} were mixed as mixture in pairs. And there were 36 mixed mode. At least 15 sample points would be detected for the average as representative concentration in each mixed mode to make sure the representative.

Before correction, the initial characteristic peaks intensity value of each mixed mode would be extracted from the pretreated Raman spectrum at first. While applying initial intensity to quantitative analysis model for pesticide residues would not lead to accurate results. So a correction ratio is necessary to correct the results. The characteristic peaks intensity value would be applied in deltamethrin and acetamiprid quantitative analysis model respectively to get the estimated value of deltamethrin and acetamiprid concentration. And correction ratio would be acquired after applying the estimated values in correction ratio change rule. Finally through multiplying the estimated detection concentration value and correction ratio, the corrected and accurate pesticide concentration would be obtained.

It could be seen from the above that correction ratio change rule was the key to get accurate pesticide concentration. The correction ratio was obtained by dividing the characteristic peak intensity value of a single pesticide by the characteristic peak intensity value of the pesticide mixture at the concentration. As quadratic function relations existed between pesticide content and the correction ratios, two quadratic equations were needed to describe the change rule between content of pesticide mixture and the correction ratios. And the change rule of a characteristic peak was described by a polynomial equation.



(a)

(b)

Figure 4. The change rule fitting surface of characteristic peaks at 634 cm^{-1}(a) and 1114 cm^{-1}(b); between pesticide content and correction ratio.

As shown in Figure 4, the fitting surface of pesticide mixture content and the correction ratios was a smooth and slanted surface. For the characteristic peaks of acetamiprid at 634 cm^{-1} and 1114 cm^{-1}, the correction ratio reduced with not only the increments of acetamiprid content, but also the reduction of deltamethrin content. For the fitting model of peak in 634 cm^{-1}, the sum squared residual (SSE) was 0.0678. Root Mean Square Error (RMSE) and coefficient of correlation were 0.0475 and 0.9328 respectively. And for the fitting model of peak in 1114 cm^{-1}, the sum squared residual (SSE) was 0.0328. Root Mean Square Error (RMSE) and coefficient of correlation were 0.0330 and 0.8883 respectively.

A polynomial regression equation (Equation 1) was acquired from the change rule of characteristic peaks at 634cm^{-1}. In Equation 1, the concentrations of acetamiprid and deltamethrin were all from 10^{-1} g·kg^{-1} to 10^{-6} g·kg^{-1}.

$$\begin{aligned} Z = 1.264 - 0.02345A + 0.01906D + 0.0006864A^2 \\ -0.0001839AD + 1.289 \times 10^{-5}D^2 \end{aligned} \quad (1)$$

Where Z is the correction ratio, *A* is the estimated concentration value of acetamiprid, *D* is the estimated concentration value of deltamethrin.

The polynomial regression equation (Equation 2) of characteristic peaks at 1114 cm^{-1} was also obtained and shown below. In Equation 2, the concentrations of acetamiprid and deltamethrin were all from 10^{-1} g·kg^{-1} to 10^{-6} g·kg^{-1}.

$$\begin{aligned} Z = 1.235 - 0.02271A + 0.01886D + 0.0007016A^2 \\ -0.0001841AD + 1.296 \times 10^{-5}D^2 \end{aligned} \quad (2)$$

Where Z is the correction ratio, *A* is the estimated concentration value of acetamiprid, *D* is the estimated concentration value of deltamethrin.

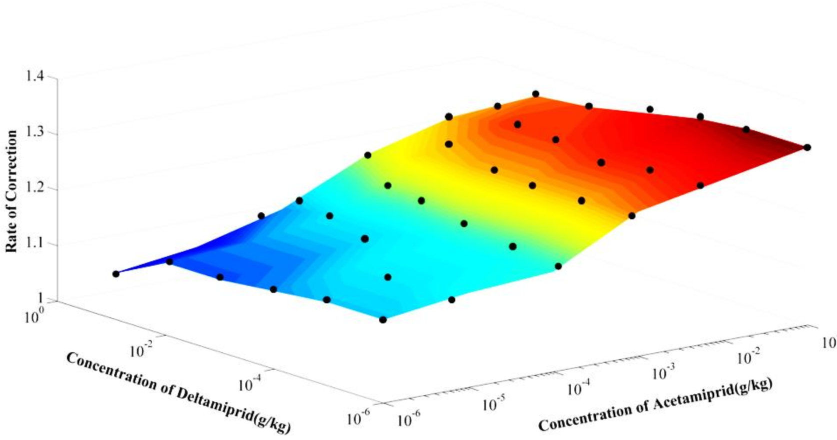


Figure 5. The change rule fitting surface of characteristic peak at 735 cm^{-1} between pesticide content and correction ratio.

The fitting surface of characteristic peak at 735 cm^{-1} was shown in Figure 5. And for the characteristic peaks of deltamethrin at 735 cm^{-1}, the correction ratio increased with the increase of acetamiprid content and the decrease of deltamethrin content. With the increase of acetamiprid content and decrease of deltamethrin content, the correction ratio could be up to 1.32. The SSE of the fitting model was 0.0438. RMSE and coefficient of correlation were 0.0382 and 0.9266 respectively.

The polynomial regression equation (Equation 3) of characteristic peaks at 735 cm^{-1} was acquired and shown below. In Equation 3, the concentrations of acetamiprid and deltamethrin were all from 10^{-1} g·kg^{-1} to 10^{-6} g·kg^{-1}.

$$\begin{aligned} Z = 1.167 + 0.02066A - 0.002236D - 0.0006892A^2 \\ -8.851 \times 10^{-6}AD - 2.88 \times 10^{-6}D^2 \end{aligned} \quad (3)$$

Where Z is the correction ratio, *A* is the estimated concentration value of acetamiprid, *D* is the estimated concentration value of deltamethrin.

3.5. Validation of the correction models

And an experiment had been done to verify the reliability of the regression model. In the verification test of regression model, deltamethrin and acetamiprid residue data of 200 sample signals from 20 Fuji apples was chosen as validation set. The intensity values of the characteristic peaks at 634, 735 and 1114 cm^{-1} were extracted from the Raman spectrum with pretreatment as estimated

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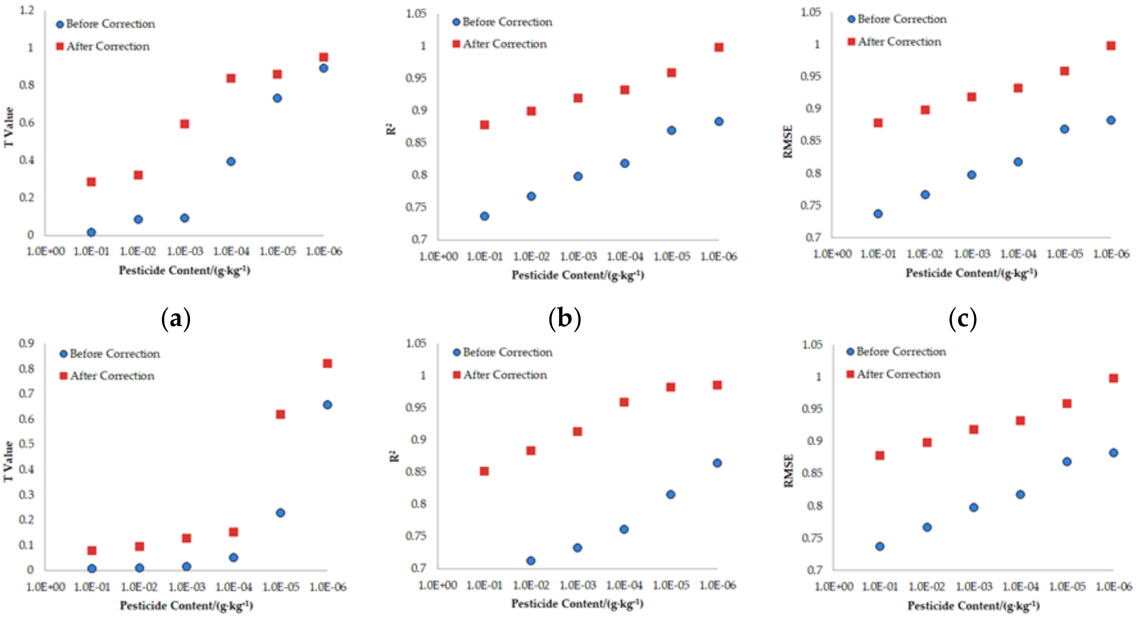
intensity values. Then the intensity values would be substituted the quantitative model to get the estimated pesticide concentration. Correction ratio would be acquired after substituting estimated intensity values into the regression model. Corrected peak intensity would be obtained through multiplying the estimated intensity values and correction ratio. After substituting corrected peak intensity into pesticide residue quantitative model, corrected pesticide concentration would be got. Through comparing the estimated pesticide concentration and corrected pesticide concentration, a series of parameters would be obtained to judge the regression model.

After above steps, Raman signals of validation were processed. T value, correlation coefficient (R^2) and Root Mean Squared Error (RMSE) were applied to judge the regression model. The results were shown in Figure 6. In Figure 6, "●" and "■" stood for the pesticide data before and after correction respectively.



(**a**) (**b**) (**c**)

(**d**) (**e**) (**f**)

Figure 6. Results of regression model between pesticide content and T value, R^2 and RMSE. (a): T value of acetamiprid; (b): R^2 of acetamiprid; (c): RMSE of acetamiprid; (d): T value of deltamethrin; (e): R^2 of deltamethrin; (f): RMSE of deltamethrin.

From the figure it could be seen that with the increase of pesticide content, the parameters improved, which was because when the concentration of the mixed pesticide was high, the signals of the mixture interfered with each other. It could be surmised that when the pesticide content increased, a plurality of pesticides molecules competed for the active sites provided by the silver sol. High concentration of pesticides resulted in a severe reduction in the number of active sites. And the other mixture molecules had fewer active sites and their characteristic peak signals were weaker correspondingly. When the pesticide concentration was relatively low, the number of silver sol active sites occupied by pesticide molecules was small. No obvious competitive relationship existed between pesticides. Therefore, one pesticide characteristic peak signal was not interfered by other pesticides. And all the parameters were improved obviously.

It could be seen from Figure 6 that with the concentration of one pesticide decreasing, the correction ratio of the other pesticide also decreased significantly. It could be deduced that the mutual influence of the functional groups of the two pesticide molecules which weakened each other caused this phenomenon. With the increase of one pesticide concentration, the influence of the other pesticide reduced gradually. Concentration of functional groups of pesticides reflected the intensity of characteristic peaks, in turn reflecting the concentration of pesticides. This phenomenon may exist in other pesticide mixture and correction method would be useful in detecting them accurately.

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4. Conclusions

Interaction between pesticide mixture components made the Raman spectral detection result lower than the results of single pesticide and affected the accuracy severely. In the study, correction regression models toward different characteristic peaks were built to explore the change rule between pesticide content and characteristic peak intensity of deltamethrin and acetamiprid mixture. The compensation result of individual characteristic peak intensity could be used for quantitative calculation to achieve correction of quantitative detection results. And good validation results reflected the accuracy and reliability. The study demonstrates that great potential existed in this correction method and it could be used in other mixed pesticide detection and extended to mixture detection by Raman spectroscopy. The study provided a novel and feasible correction method in detecting pesticide mixture with Raman spectroscopy detection.

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