Detection of Profenofos in Chinese Kale, Cabbage, and Chili Spur Pepper Using Fourier Transform Near-Infrared and Fourier Transform Mid-Infrared Spectroscopies

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ABSTRACT: Different types of quantitative technology based on infrared spectroscopy to detect profenofos were compared based on Fourier transform near-infrared (FT-NIR; 12,500−4000 cm⁻¹) and Fourier transform mid-infrared (FT-MIR; 4000−400 cm⁻¹) spectroscopies. Standard solutions in the range of 0.1−100 mg/L combined with the dry-extract system for infrared (DESIR) technique were analyzed. Based on partial least-squares regression (PLSR) to develop a calibration equation, FT-NIR−PLSR produced the best prediction of profenofos residues based on the values for $R^2$ (0.87), standard error of prediction or SEP (11.68 mg/L), root-mean-square error of prediction or RMSEP (11.50 mg/L), bias (−0.81 mg/L), and ratio performance to deviation or RPD (2.81). In addition, FT-MIR−PLSR produced the best prediction of profenofos residues based on the values for $R^2$ (0.83), SEP (13.10 mg/L), RMSEP (13.00 mg/L), bias (1.46 mg/L), and RPD (2.49). Based on the ease of use and appropriate sample preparation, FT-NIR−PLSR combined with DESIR was chosen to detect profenofos in Chinese kale, cabbage, and chili spur pepper at concentrations of 0.53−106.28 mg/kg. The quick, easy, cheap, effective, rugged, and safe technique coupled with gas chromatography−mass spectrometry was used to obtain the actual values. The best FT-NIR−PLSR equation provided good profenofos detection in all vegetables based on values for $R^2$ (0.88−0.97), SEP (5.27−11.97 mg/kg), RMSEP (5.25−11.00 mg/kg), bias (−1.39 to 1.30 mg/kg), and RPD (2.91−5.22). These statistics revealed no significant differences between the FT-NIR predicted values and actual values at a confidence interval of 95%, with agreeable results presented at pesticide residue levels over 30 mg/kg. FT-NIR spectroscopy combined with DESIR and PLSR should be considered as a promising screening method for pesticide detection in vegetables.

1. INTRODUCTION

Common vegetables included in many Thai dishes prepared in household kitchens are Chinese kale (Brassica oleracea var. acephala), cabbage (Brassica oleracea var. capitata Linn), and chili spur pepper (Capsicum annuum Linn. var. acuminatum Fingerh.). Head cabbage is rich in nutrients, very low in calories, and fat free and is a good source of potassium, quercetin, beta carotene, vitamins K, C, A, and E, as well as phytochemicals, particularly sinapic acid which is the most abundant phenolic acid. Chinese kale is an excellent source of glucosinolates and phenolic antioxidants, while chili peppers provide a good range of vitamins, minerals, phytochemicals, and dietary fiber. These vegetables are well known as being consumed universally, and their nutritional components may play a role in decreasing human micronutrient deficiencies. The Thai Department of Agriculture has recognized there is overuse of pesticides and has attempted to reduce usage by launching mitigation campaigns including organic farming.
integrated pesticide management, good agricultural practice, and promoting the use of biopesticides. Even though these policies are implemented with limited support from legislation or infrastructure, many farmers still believe that pesticide application is necessary and believe that the level of protection derived from pesticides is proportional to the amount applied. Consequently, continued use of large amounts of pesticides is likely. Organophosphate (OP) residue has been reported above the limit of Thai maximum residue limits (MRL) in many kinds of vegetables. MRL is the highest concentration (mg/kg) of pesticide residues in fruits and vegetables and is used to define the maximum intake legally permitted by regulations introduced by different countries; however, MRL may vary depending upon the regulations of each country.

Profenofos (O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate, C\textsubscript{11}H\textsubscript{15}BrClO\textsubscript{3}PS), one of the widely used OP pesticides, is normally applied for pest control in cotton, fruit, chili, and vegetable cultivation. It has been classified as a moderately hazardous pesticide (toxicity class II) by the World Health Organization. Despite the requirements for alternative pest management, profenofos is allowed for use in Chinese kale, cabbage, and chili cultivation in Thailand. The imported quantities of profenofos in 2018 and 2019 were 387 and 463 tons, but in 2020, the import of this chemical increased to 653 tonnes (valued at USD 4.4 million), indicating its popularity in agricultural cultivation, perhaps to replace banned chemicals, especially chlorpyrifos. To date, profenofos is listed in the top-10 imported hazardous chemicals according to The Office of Agricultural Economics of Thailand. Profenofos can be used in vegetable production, particularly in Chinese kale, cabbage, and chili at the Thai-MRL of 0.5, 1, and 3 mg/kg, respectively. Frequently, contamination of profenofos in Thai vegetables exceeds the Thai-MRL, with evidence-based risk assessment of profenofos being found in Thai people also being reported. Agricultural chemicals, particularly pesticides, are becoming more and more of a concern to consumers, and an effective routine method for quantifying pesticide residues in vegetables is needed.

Monitoring of pesticide residues and enforcing the MRL are challenging tasks for the responsible agencies, particularly when they must rely on the use of nonquantitative, rapid colorimetric assay kits. Several limitations must be addressed particularly...
when using the enzyme cholinesterase inhibition-based colorimetric technique (ChE) to monitor OP and carbamate pesticides. Thus, the use of ChE may not be able to detect the presence of such chemicals in some samples, potentially creating false negative results. Furthermore, the majority of the currently enforced MRL are at or below the minimum level of detection of the test kit, making the test results somewhat unreliable. Usually gas chromatography (GC) and high-performance liquid chromatography (HPLC) are the standard methods used to determine the concentrations of pesticide residues; however, their application is limited due to time, cost, and labor factors in the analysis. Thus, procedures based on spectroscopy are regarded as having potential to solve the above problems. This method has been widely used in chemical, agricultural, medical, and other applications. This technology achieved safe, fast, reliable, less complex, and low-cost testing and analysis compared to other methods for the determination of pesticide residues. Among the spectroscopic methods, near-infrared (NIR) and mid-infrared (MIR) spectroscopies are the most popular, and they have been widely used in food processing and for on-line quality control due to their heavy-duty, rugged design, and offering high performance and flexibility. Instead of being tested in the laboratory, sample-associated production status is analyzed conveniently on-line and in real-time.

Infrared (IR) spectroscopy is a technique based upon the vibrations of the molecule when passing IR (NIR and MIR) radiation through a tested sample. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of vibration of a part of the sample molecule. The NIR region (800–2500 nm or 12,500–4000 cm⁻¹) is the first spectral region exhibiting absorption bands related to molecule vibration. This region is characterized by overtone and combination bands and is widely used for composition analyses of food products, while the MIR region (2500–25,000 nm or 4000–400 cm⁻¹) is the main region of fundamental vibration. This region retains information, allowing the organic molecule to be identified and the structure and confirmation of molecules to be characterized. In the NIR and MIR regions, various molecular vibrations, including those from C–H, O–H, N–H, C≡O, and other functional groups, can be detected. NIR spectroscopy has been successfully applied to determine pesticide residues in fruit. It could segregate the accepted and rejected products and enhance the wholesomeness of these produce. MIR spectroscopy was also able to determine pesticides in vegetables and herbal medicine. However, the pesticides contaminated in leafy vegetables such as Chinese kale, cabbage, and chili pepper have been less investigated.

The objectives of this work are (1) to compare the ability of Fourier transform-NIR (FT-NIR) and Fourier transform-MIR (FT-MIR) spectroscopy techniques to determine profenofos residues and (2) to use the optimized method for screening detection of profenofos residues in fresh vegetables, particularly Chinese kale, cabbage, and chili pepper. The performance of the FT-NIR—partial least-squares regression (PLSR) optimized equations was validated using statistics following the industrial guidelines ISO 12099 (2017).

### 2. RESULTS AND DISCUSSION

#### 2.1. Comparison of the Ability of FT-NIR and FT-MIR Spectroscopies Combined with the DESIR Technique to Detect Profenofos Standard Solution

Data Analysis and Calibration Equation Development.

The original spectra of profenofos standard solution (0.1–100 mg/L) from dry-extract system for infrared (DESIR) samples based on FT-NIR and FT-MIR are presented in Figure 1A,B, respectively. The complexity of FT-NIR or FT-MIR spectra caused many peaks of interest overlapped by one or more interfering peaks, it has poor peak resolution (Figure 1A,B) resulting in the challenging of the accurate assignments of specific peaks. Therefore, data preprocessing methods such as derivative and standard normal variate (SNV) and their combinations were applied on the FT-NIR and FT-MIR spectra of profenofos prior to the computation of the regression method in order to correct the baseline drift and the scattering effect.

The best calibration equation for predicting profenofos residues was obtained from the FT-NIR—PLSR equation with the first derivative preprocessed FT-NIR in the spectral range 5454–4242 cm⁻¹. This equation provided an accurate prediction with good values of R², standard error of prediction (SEP), root-mean-square error of prediction value (RMSEP), bias, and ratio of performance to deviation (RPD), particularly R² and RPD at 0.87 and 2.81, respectively. Good prediction performance on profenofos detection was also observed from the FT-MIR—PLSR equation (SNV preprocessed FT-MIR in the spectral range 3280–1120 cm⁻¹) with values of R² and RPD at 0.83 and 2.49, respectively (Table 1). According to Williams and Norris on guidelines for interpretation of R² and RPD values, R² at 0.83–0.87 is useable with caution for most applications, including research. The RPD values in the range 2.49–2.81 were possibly due to the very rough screening analysis.

The scatter plots of profenofos established from calibration sample sets from the FT-NIR—PLSR and FT-MIR—PLSR are shown in Figure 1C,D, respectively, while Figure 1E,F show the scatter plots of predicted profenofos concentrations and the actual concentrations of validation sample sets from the NIR—PLSR and MIR—PLSR calibration equations, respectively. Both the FT-NIR—PLSR and FT-MIR—PLSR calibration equations obtained from the DESIR spectra provided good correlation of the predicted values and actual values with R² values in the range 0.83–0.87. The scatter plot of the DESIR samples for

### Table 1. PLSR Calibration Results for Detection of Profenofos (Standard) Residues from DESIR Samples

| measurement | pre-processing method | number of factors | wavenumber region (cm⁻¹) | calibration set | validation set |
|-------------|-----------------------|-------------------|---------------------------|-----------------|---------------|
| FT-NIR      | first derivative       | 6                 | 5454–4242                 | 0.87 10.86      | 0.87 11.68     |
| FT-MIR      | SNV                   | 5                 | 3280–2920 2560–2200 1480–1120 | 0.88 11.52      | 0.83 13.10     |

R²: coefficient of multiple determination; SEC: standard error of calibration; SEP: standard error of prediction; RMSEP: root-mean-square error of prediction; bias: average of differences between reference values and NIR values; RPD: ratio of performance to deviation. Unit: mg/L. SNV: standard normal variate.
the studied range of profenofos concentrations over 30 mg/L indicated that the predicted values were agreeable with the actual values.

The regression coefficient plots of the FT-NIR–PLSR and FT-MIR–PLSR calibration equations for predicting profenofos are presented in Figure 1G, H, respectively. The regression coefficient plots were primarily used to consider the importance wavenumber (X-variable) from the optimized equations, which was described or correlated with the reference value (Y-variable). The wavenumber at a peak with high regression coefficient values indicates that the variable is highly correlated with the reference value.33 Figure 1G shows the regression coefficient at 5345 cm⁻¹ correlated with the organophosphorus group.34 The moderate regression coefficients among variables located at 4767, 4659, 4554, 4451, 4404, 4397, and 4296 cm⁻¹ could have been due to CH in the aromatic ring, as well as the CH group in the profenofos’s chemical structure.33–38 The highest regression coefficient appeared at 4906 cm⁻¹ which was attributed to the C=O (carbonyl) stretching second overtone.39 This C=O may have been due to the small amount of acetone solvent remaining in some DESIR samples.

Figure 1H presents the highest regression coefficient of FT-MIR–PLSR at 1479 cm⁻¹ which refers to the C=C–C bond in the aromatic ring,40,41 as well as at 1468 and 1452 cm⁻¹.40,42 The important variables appeared at 2344 and 1336 cm⁻¹ referring to P=O stretching vibration in the phosphorus acid and ester compound, respectively.41,42 The moderate regression coefficients presented at 3124 and 3088 referred to the C=H in the aromatic ring and 2980, 2500, and 1232 cm⁻¹ referred to the C=H stretching vibration in CH₃ and CH₂.18,42,43 and C=O stretching vibration.43 All mentioned variables could be associated with the profenofos chemical structure; the band assignments of the major peaks of profenofos acquired from the FT-NIR–PLSR and FT-MIR–PLSR calibration equations are summarized in Table 2.

2.1.2. Performance Measurement Statistics. The performance measurement statistics for the equations were bias, SEP, and slope following ISO 12099 (2017);6 these are presented in Table 3. The results of the FT-NIR–PLSR calibration equation study provided the best calibration equation for detecting profenofos residues which was far from the criterion set by ISO 12099 (2017). The bias value of −0.81 was less than the T_sub_b value (4.21). Therefore, the performance of this equation was acceptable. The t_sub_obs value for the slope was 1.96, and the f_(1−α/2) value was 2.04. As t_sub_obs ≥ f_(1−α/2), the slope value here was not significantly different from 1 at the probability level of 95% confidence. The SEP and Tₚₚ value at 11.68 and 14.12 also indicated that the calibration equation was acceptable as a precise routine NIR measurement. The FT-MIR–PLSR equation for predicting profenofos residues was acceptable for routine measurement method as well, with all parameters (bias, SEP, and slope) following ISO 12099 (2017).

The results in Table 1 indicate that the profenofos residues predicted using the FT-NIR–PLSR calibration equation provided good prediction as well as using FT-MIR–PLSR. The main difference between the FT-NIR and FT-MIR analyses was due to the difference in wavenumbers or the energy of the beam, which caused the molecules to respond differently. The MIR spectrum consisted of clear and strong signals, while the NIR spectrum produced more complex signals, some of which were weak and overlapping. However, the advantage of NIR is that the bands are 10–100 times less intense than their corresponding MIR bands;41 thus, the NIR application is able to directly analyze samples with a less or nondestructive method.

The feasibility of using NIR and MIR spectroscopies for pesticide determination has been mentioned in various reports. NIR and MIR spectroscopy techniques were compared for measurement of metribuzin (herbicide) in a concentration range of 1.03–4.02 mg/kg by Khanmohammadi et al.25 They reported that both techniques were able to measure the metribuzin concentrations (RSD of 0.03 and 0.3%, respectively). However, NIR determined the samples at a frequency of 120 h⁻¹ which was higher than for MIR and the reference method of HPLC (60 and 10 h⁻¹, respectively). Similarly, the detection of pesticide residues in fresh produce based on vapor phase-liquid phase microextraction-infrared (VP-LPME-IR) spectroscopy showed good potential for mancozeb detection.26 The VP-LPME-MIR and headspace GC–MS methods were in good agreement, with detected levels of 3.47 and 3.79 mg/kg for lettuce, 2.39 and 2.64 mg/kg for strawberries, and 1.44 and 1.29 mg/kg for corn, respectively.26 Fruit peels could be successfully classified using FT-MIR with a principle component analysis (PCA) technique, resulting in a correct classification score of 90%.45 NIR and MIR coupled with PLSR

### Table 2. Band Assignments of Major Peaks of Profenofos (Standard) Acquired from FT-NIR–PLSR and FT-MIR–PLSR Calibration Equations

| measurement | wavenumber (cm⁻¹) | functional group assignment | references |
|-------------|-------------------|----------------------------|------------|
| FT-NIR      | 5345              | organophosphorus group      | 34         |
|             | 4906              | C=O stretching second overtone | 39     |
|             | 4767, 4659, 4554, | CH=CH₂, CH in aromatic ring and CH group | 35, 37, 38 |
|             | 4451, 4404,     |                            |            |
|             | 4397 and 4296    |                            |            |
| FT-MIR      | 3124, 3088       | C=H in aromatic ring        | 40         |
|             | 2980              | C=H stretching vibration in CH₃ and CH₂ | 42, 43 |
|             | 2500              | C=H                         | 18         |
|             | 2344 and 1336     | P=O stretching vibration and phosphorus acid and ester compound | 41, 42 |
|             | 1479, 1468 and 1452 | C=C–C bond in aromatic ring | 40, 41 |
|             | 1232              | C=O stretching vibration    | 43         |

“Number in references relate to numbered reference list in this paper.

### Table 3. Performance Measurement Statistics of FT-NIR–PLSR and FT-MIR–PLSR Calibration Equations for Detecting Profenofos (Standard) Residues Validated Following ISO 12099 (2017)

| measurement | parameter | calculated value | criterion | results |
|-------------|-----------|------------------|-----------|---------|
| FT-NIR      | bias      | −0.81 mg/L       | T_b = ±4.21 | accepted |
|             | SEP       | 11.68 mg/L       | TUE = 14.12 | accepted |
|             | t_obs     | 0.19             | t_(1−α/2) = 2.04 | accepted |
| FT-MIR      | bias      | 1.46 mg/L        | T_b = ±6.44 | accepted |
|             | SEP       | 13.10 mg/L       | TUE = 14.93 | accepted |
|             | t_obs     | 0.19             | t_(1−α/2) = 2.04 | accepted |

SEP: standard error of prediction; T_b: bias confidence limits; TUE: unexplained error confidence limits value; f_(1−α/2): t-value obtained from table of t-distribution for a probability of α = 0.05; t_obs: observed t-value for slope testing. Criterion values were calculated following ISO 12099 (2017).
were used to detect cartap, thiocyclam, and tebufenozide in Chinese herbal medicines (Radix Angelicae Dahuricae and Liquorices) in the concentration range 0−40 mg/kg. The satisfactory average recoveries obtained from these models were 99.0 and 100.2%, respectively. NIR and MIR spectroscopies showed promising potential to determine low amounts of chemical of interest in agriculture and food commodities.

Nevertheless, a limitation of these two techniques results from the low signal at low concentration, resulting in these techniques being unable to differentiate between the different compounds. A study involving apple orchard trials used FT-MIR spectroscopy (5000−500 cm$^{-1}$) to estimate the drift of the pesticides (impulse and bogiron) while spraying apple at 0.1% concentration. Although the signatures of impulse (two peaks in the range 2800−3000 cm$^{-1}$) and bogiron (three peaks in the range 2800−3000 cm$^{-1}$) were visible, it was not possible to separate the compounds. Similarly, the results from using FT-MIR photoacoustic spectroscopy to determine tricyclazole pesticides (with different principal components of PC1, PC2 and PC3) on rice leaves and husk samples showed that the total variance of the leaves and husks accounted for 86−88%. There were differences in the spectral information.

A major advantage of NIR over MIR is that NIR light can penetrate much further into a sample than MIR radiation. NIR allows the use of a long path length in the spectral acquisition of samples in various packaging materials such as glass, plastic, films, and others that are transparent to NIR light; therefore, it could be applied in a packed product or an intact sample without destruction using the so-called nondestructive method. NIR light can penetrate further through the sample thickness and allows direct measurement of samples that makes NIR spectroscopy ideally suited for rapid online measurements.

Table 4. FT-NIR-PLSR Calibration and Validation Results for Profenofos Residues (mg/kg) in Vegetable Samples

| Vegetables | Preprocessing method | Number of Factors | Wavenumber Region (cm$^{-1}$) | Calibration Set | Validation Set |
|------------|----------------------|-------------------|-------------------------------|----------------|---------------|
| Chinese kale | First derivative + SNV | 4 | 7506−4242 | 0.95 | 6.93 | 0.97 | 5.27 | 5.25 | -0.81 | 4.67 |
| Cabbage | First derivative | 6 | 7506−4242 | 0.87 | 12.13 | 0.88 | 11.07 | 11.00 | 1.30 | 2.91 |
| Chili spur pepper | SNV | 7 | 7506−6094, 5454−4597 | 0.96 | 6.11 | 0.96 | 6.54 | 6.59 | -1.39 | 5.22 |

$R^2$: coefficient of multiple determination; SEC: standard error of calibration; SEP: standard error of prediction, RMSEP: root-mean-square error of prediction; bias: average of differences between reference values and NIR values; RPD: ratio of performance to deviation. Unit: mg/kg. SNV: standard normal variate.

Figure 2. Scatter plots of validation sample sets and regression coefficient plots of FT-NIR−PLSR calibration equations for predicting profenofos residues in Chinese kale (A,B), cabbage (C,D), and green chili spur pepper (E,F) samples.
The scatter plots based on FT-NIR–PLSR (Figure 2A,C,E) demonstrated good correlation between predicted values and actual values of profenofos in Chinese kale, cabbage, and green chili spur pepper, which were in good agreement with the actual values. The regression coefficient plots are shown in Figure 2B,D,F, with Figure 2B showing the regression coefficient plot for predicting profenofos in Chinese kale. The highest regression coefficient was at 4358 cm⁻¹, which referred to C–H in the aromatic ring. The high regression coefficient at around 4458 cm⁻¹ referred to the C–H group. Some moderate regression coefficients at around 5893 and 5700 cm⁻¹ were associated with C–H in the aromatic ring. Some interesting regression coefficients at around 7305, 6749, 5338, 4960, and 4690 cm⁻¹ could be attributed to the C–H group in aliphatic compounds, the phosphate group, and C=O and CC + CH in the aromatic group, respectively.

Figure 2D,F shows the main regression coefficients for predicting profenofos residues in cabbage or green chili spur pepper at around 7127, 7058, 6942, 6827, 6441, 5893, 5700, 5338, 5129, 4937, and 4690 cm⁻¹ that could be related to the O–H in phenolics, the CH group in aromatic compounds, the CH, CH₂, and CH₃ groups in aliphatic hydrocarbon compounds, N–H from protein, P–OH, and the C=O and C–Cl bonds in chlorinated hydrocarbons. Notably, almost all variables from the best FT-NIR–PLSR equations were associated with the profenofos chemical structure. Table 5 shows the results of FT-NIR–PLSR calibration and validation to predict profenofos residues in vegetables (Chinese kale, cabbage, and chili spur pepper) based on the FT-NIR–PLSR calibration equations.

However, the results in this work found that the FT-NIR–PLSR equations for detection of profenofos in vegetables showed better performance than the FT-NIR–PLSR equations for profenofos standard solution. Since major food components generally consisted of complex molecules resulting from the polymerization of monomers, these monomers exhibit specific chemical groups. As each chemical group in vegetables may absorb in the NIR region, this could assist to increase the NIR absorption of the pesticide residues (profenofos).

NIR and MIR spectroscopies are efficient techniques having many applications in both quantitative and qualitative analyses of foods and food products such as grains, seeds, fruits, and vegetables. NIR spectroscopy has clearly poor performance for quantitative detection at low concentrations (<100 mg/kg) in pesticide or food extract solution samples.
spectroscopy has low signal sensitivity at concentrations below 0.1%, making it hard to detect at the parts per million (mg/kg) level of analytes. However, it can be enhanced by using the DESIR technique, and this is often used in the quantitative analysis of trace quantities such as pesticide residues analysis as this technique helps to increase the concentrations of analytes.

In the current study, DESIR improved the sensitivity of FT-NIR spectroscopy, enabling the detection of pesticide residues in the three studied vegetables to the mg/kg level, specifically ≥30 mg/kg.

The results from NIR combined with the DESIR technique enhanced the sensitivity of the spectroscopy method in agreement with other reports and supported that this combined approach is an ideal solution for the detection and analysis of pesticide authenticity and adulteration.

Some studies have reported on the sensitivity of NIR spectroscopy for detecting mg/kg levels of pesticides residues in fruits and vegetables. When DESIR with NIR spectroscopy was applied to detect 95 tomato samples spiked with ethephon (fungicide at 2–90 mg/kg of the active ingredient), the results had a satisfactory SEP of 7.89 mg/kg. Similarly, Wu et al. used NIR-PLSR spectroscopy to detect chlorpyrifos residue (0.1–4 mg/kg) in spinach juice, with their method performing well for the prediction of chlorpyrifos residues with $R^2$ of 0.9986 and RMSEP of 0.0485 mg/kg, respectively. However, in this case, quite low sample numbers and a single juice matrix were used; thus, the robustness of the prediction equation was questionable.

Detection of chlorpyrifos residues in minced white radish (0.007–5.15 mg/kg) using NIR spectroscopy was able to achieve an RMSEP of 0.1 mg/kg but only on a single set of white radish fruit, with random locations on samples. Thus, the robustness of the calibration equation was questionable. The current study used higher sample numbers ($n = 61–63$) with three food sample matrices to investigate the sensitivity of the NIR spectroscopy technique.

Models developed using NIR combined with DESIR and PLSR-discriminant analysis (PLSR-DA) have been used to successfully classify samples by the presence/absence of five pesticide classes of OP pesticides in pepper in the range 0.01–0.1. However, the highest percentages of correctly classified samples were by 75 and 82% for pesticide-free and pesticide-containing samples (intact peppers), respectively. Similarly, classification of diuron herbicide in intact olives using NIR–PLSR-DA had the highest percentage of correctly classified at 85.9% of samples above and below the MRL (0.2 mg/kg). However, the SEP and $R^2$ were poor (1.70 mg/kg and 0.45, respectively) for the external validation set. The low signal associated with a low concentration in the tested samples was still a limitation of this method.

Likewise, the quality detection of diazinon residues (0–32 mg/kg) in cucumber using a visible NIR–PLSR-DA method was successful at classifying cucumbers with contents of diazinon below and above the MRL (0.1 mg/kg) as safe and unsafe samples, respectively. The percentages of correctly classified samples in the calibration and prediction sets were 97.5 and 92.32%, respectively, but the segregation into the unsafe group and safe group was 100 and 60% correct, respectively. Overall, these above reports indicated that NIR spectroscopy techniques have not been successful in the quantification of pesticide residues in fresh produce at low mg/kg levels (<1 mg/kg) which is near the MRL setting for most pesticides.

NIR spectroscopy coupled with the DESIR technique was used to classify chlorpyrifos, cypermethrin, and profenofos residues on mango fruit (at 0.01–10 times the recommended rate with active ingredients of 210,000, 50,000, and 50,000 mg/kg, respectively). PCA and DA were performed to develop an equation, with the best PCA–DA equation correctly classifying 92.5 and 60% for chlorpyrifos, 75 and 60% for cypermethrin, and 85% for profenofos for the calibration and validation sets, respectively.

Likewise, when spiked samples with heavy concentrations of chlorpyrifos solution (0.1–0.5% of active ingredient 50 w/w) were used on mango, apple, and tomatoes, cross validation accurately predicted results with ranges for SEP of 5.20–6.75 and for RMSECV of 20,000–30,000 mg/kg using the calibration equation dataset. Similarly, the detection of dichlorvos residues on the surface of oranges (at 800 and 1000 mg/kg) was accurately predicted using an NIR–PLSR equation with values for $R_{cv}$ of 0.82–0.95 and for RMSECV of 20,000–30,000 mg/kg using the calibration equation dataset. However, all tests were conducted based on very large amount of residues which may not be practical in a real-world situation.

The MRL limits of individual pesticide residues in individual food items are determined by each country, with these values generally limited for pesticide residues in the range 0.01–3 mg/kg. Pesticide residue detection is a form of trace detection and so is very difficult to detect theoretically. Notably, the results discussed above for all related research works demonstrated that the NIR spectroscopy technique may not be able to quantify pesticide residues in food at low residue levels of ≤100 mg/kg. Consequently, the NIR spectroscopy technique cannot replace GC–MS as the analytical method. Nonetheless, these studies should continue on quantitative detection technology for pesticide residues in vegetables based on NIR spectroscopy.

### Table 6. Performance Measurement Statistics of FT-NIR–PLSR Calibration Equations for Detecting Profenofos Residues in Vegetable Samples Validated Following ISO 12099 (2017)$^a$

| Vegetables                  | Parameter | Calculated Value | Criterion | Results |
|-----------------------------|-----------|------------------|-----------|---------|
| Chinese kale                | Bias      | $-0.81$ mg/kg    | $T_b = \pm 1.81$ | accepted |
|                             | SEP       | $5.27$ mg/kg     | $T_{UB} = 8.85$ | accepted |
|                             | $t_{bu}$  | 0.10             | $t_{(1-\alpha/2)} = 2.04$ | accepted |
| Cabbage                     | Bias      | $1.30$ mg/kg     | $T_b = \pm 6.75$ | accepted |
|                             | SEP       | $11.07$ mg/kg    | $T_{UB} = 15.50$ | accepted |
|                             | $t_{bu}$  | 0.07             | $t_{(1-\alpha/2)} = 2.03$ | accepted |
| Chili spur pepper           | Bias      | $-1.39$ mg/kg    | $T_b = \pm 5.20$ | accepted |
|                             | SEP       | $6.54$ mg/kg     | $T_{UB} = 7.87$ | accepted |
|                             | $t_{bu}$  | 0.12             | $t_{(1-\alpha/2)} = 2.04$ | accepted |

$^a$SEP: standard error of prediction; $T_b$: bias confidence limits; $T_{UB}$: unexplained error confidence limits value; $t_{(1-\alpha/2)}$: t-value obtained from table of t-distribution for a probability of $\alpha = 0.05$; $t_{bu}$: observed t-value for slope testing. $^b$criterion values were calculated following ISO 12099 (2017).
since NIR spectroscopy has some advantages such as being rapid, low cost, and using no or less harmful chemicals and it is environmentally friendly; thus, it could be of value for high-throughput screening before subjecting samples to GC–MS analysis. Consequently, this technique could be useful for monitoring pesticide residues during application to crops in the field. It could enhance food safety by screening for remaining pesticides or other agricultural chemicals before harvesting and marketing.

2.2.2. Performance Measurement Statistics. The statistics used to appraise the best equations (bias, SEP, and slope) were verified following ISO 12099 (2017), as shown in Table 6. All statistics obtained from the best equations for predicting profenofos residues in three types of vegetables (Chinese kale, cabbage, and green chili spur pepper) were at acceptable levels based on these criteria. The bias was lower than $T_{95}$ obtained from calculations, confirming the bias was not significantly different from zero. The SEP index was lower than $T_{95}$ indicating that the SEP was low enough to make it acceptable in a practical sense. In addition, the $t_{\text{obs}}$ calculated from the equation for the slope test was lower than $t_{1(1-\alpha/2)}$ which was determined based on the value from the $t$-distribution with a probability of $\alpha = 0.05$. The results also indicated that the slope was not significantly different from 1.

The precision of the calibration equation should be checked for accuracy to confirm the implementation of the NIR method. The calibration equations developed in the current work showed that this method could be useful to predict the concentrations of profenofos residues in three vegetables (Chinese kale, cabbage, and green chili spur pepper) at levels greater than 30 mg/kg since there were no significant differences between the FT-NIR-predicted values and actual values (from GC–MS) at a confidence interval of 95%. All statistics indicated that the calibration equations were acceptable for good performance in FT-NIR measurement.

3. CONCLUSIONS

Both FT-NIR and FT-MIR spectroscopies combined with the DESIR technique generated consistent PLSR calibration equations with good predictive abilities for profenofos pesticide. However, FT-NIR spectroscopy involved easier sample preparation and greater robustness under the tested parameter settings. FT-NIR combined with the DESIR and PLSR techniques could be useful for screening detection of profenofos residues in fresh vegetables at concentrations over 30 mg/kg. Since the FT-NIR spectroscopy technique has the advantages of being simple, rapid, low cost, and using no or less-harmful chemicals in the analysis, it could be used as a screening test rather than an immunoassay-based test or other more costly methods such as HPLC or GC–MS. Consequently, this method will be useful to monitor pesticide residues during crop cultivation and to inspect raw vegetables before harvesting and marketing. This would also help to assure product quality and increase the safety of vegetable consumption. Moreover, further analysis should be carried out in order to standardize the FT-NIR method for detecting profenofos in each vegetable type by increasing the varieties of vegetables and the number of samples to get better accuracy of measurement.

4. MATERIALS AND METHODS

4.1. Comparison of the Ability of FT-NIR and FT-MIR Spectroscopies to Detect Profenofos Residues.

4.1.1. Standard Solution Preparation. Freshly prepared profenofos standard solutions were used by dissolving profenofos (standard grade, Dr. Ehrenstorfer, DE) in acetone (analytical grade, Merck, DE) to achieve different concentrations of 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100 mg/L. The DESIR technique with a glass microfiber filter paper (model GF/A, Whatman, UK) was performed. A sample of 2 mL of the tested solution was dropped on a filter paper and then dried in a vacuum-drying oven (model VD 23, BINDER GmbH, DE) at 35 ± 2 °C for 10 min. The DESIR samples were kept in a desiccator at 25 ± 2 °C for 30 min before the FT-NIR and FT-MIR measurements.

4.1.2. FT-NIR and FT-MIR Measurements and Spectral Collection. Each DESIR sample was placed using clean forceps on the measuring window, covered with the reflector (stainless steel, diameter 8.00 cm) and scanned using the FT-NIR spectrometer (model multi-purpose analyzer, Bruker Optic, DE) at a wavenumber range of 12,500–4000 cm$^{-1}$ in the transfectance mode at a resolution of 16 cm$^{-1}$. The average from 32 scans and the reference spectrum were measured for every sample (25 ± 2 °C). Subsequently, the same DESIR sample was directly scanned using an FT-MIR spectrometer (model Spectrum Two, PerkinElmer, USA) at a wavenumber range of 4000–400 cm$^{-1}$ using the same conditions of spectral collection as for the FT-NIR measurement. To prevent cross-contamination of pesticides on samples, the reflector and the measuring window were cleaned thoroughly between consecutive measurements using 99% acetone.

4.1.3. Data Analysis and Calibration Equation Development. Preprocessing and chemometric methods were performed to develop the FT-NIR and FT-MIR spectroscopy calibration equation for predicting the amounts of profenofos residues. Mathematical treatments (derivative, SNV, and their combination) were applied to correct the baseline drift and instrumental changes. PLSR was performed using the OPUS software (version 6.5, Bruker Optics, DE). Samples were randomly divided into two sets, calibration and validation sets, using an independent test set with a 2:1 ratio: (1) the calibration sample set ($n = 66$ samples) and (2) the validation sample set ($n = 33$ samples). Herein, samples with minimum and maximum of profenofos residues were collected into the calibration sets in order to ensure that the range covered the content for samples in the validation set. The average and standard deviation of the content in the calibration set should be similar to the ones in the validation set. The calibration equations were developed from the calibration sample set, and the accuracy of the equation was tested against values in the validation sample set.

The optimization procedures and the number of optimum components were selected based on the minimum RMSEP. The predictive capability of the calibration equation was assessed using the coefficient of determination ($R^2$), SEP, bias, and RPD.

4.1.4. Performance Measurement Statistics. The accuracy and performance of the optimized calibration equation were evaluated using the validation set according to the procedure described in ISO 12099 (2017).

4.1.4.1. Bias. The significance of bias was checked based on a pair $t$-test to compare the obtained data from the experiment with the predicted data from the FT-NIR and FT-MIR equations. The performance of the equation was based on comparing the bias values (obtained from the FT-NIR and FT-MIR equations) and the bias confidence limits or $T_{95}$ that were
used to determine the limits for accepting or rejecting equation performance, as defined in eq 1

$$T_b = \frac{t((1-\alpha)/2) \cdot \text{SEP}}{\sqrt{n}}$$  \hspace{1cm} (1)$$

where $\alpha$ is the probability of making a type I error, $t$ is the appropriate Student’s $t$-value for a two-tailed test with the degrees of freedom associated with the SEP and the selected probability of type I error, and $n$ is the number of independent samples. A bias value less than the $T_b$ value indicates via the $t$-test that there is no significant difference and the performance of the equation is acceptable.

4.1.4.2. SEP. The SEP was used to express the accuracy of the routine NIR results corrected for the mean difference between the routine NIR and reference methods. The SEP can be verified using the unexplained error confidence limit ($T_{UE}$) value, which expresses the accuracy of the routine NIR results, as defined in eq 2

$$T_{UE} = \text{SEC} \cdot \sqrt{F(\alpha, n, M)}$$  \hspace{1cm} (2)$$

where SEC is the standard error of calibration, $\alpha$ is the probability of making a type I error, $v = n - 1$ is the numerator degree of freedom associated with the SEP test set, $n$ is the number of samples in the validation process, and $M = n_c - p - 1$ is the denominator degree of freedom associated with the SEC, in which $n_c$ is the number of calibration samples and $p$ is the number of terms or PLSR factors in the model. A SEP value less than $T_{UE}$ indicates that the SEP is acceptable.

4.1.4.3. Slope. A $t$-test was used to verify the hypothesis that the slope $b = 1$. The $t_{obs}$ value was considered as different from 1 when $t_{obs} \leq t_{(1-\alpha/2)}$, where $t_{obs}$ is the observed $t$-value, as defined in eq 3

$$t_{obs} = |b - 1| \cdot \sqrt{\frac{s_{\hat{y}}^2 (n-1)}{s_{res}^2}}$$  \hspace{1cm} (3)$$

where $n$ is the number of independent samples, $s_{\hat{y}}^2$ is the variance of the $n$ predicted values, and $s_{res}^2$ is the residual standard deviation as defined in eq 4

$$s_{res} = \sqrt{\frac{\sum_{i=1}^{n}\left(\hat{y}_i - (a + b\hat{x}_i)\right)^2}{n-2}}$$  \hspace{1cm} (4)$$

where $a$ is the intercept equation, $a = \bar{y} - \hat{b}\bar{x}$, $\bar{y}$ is the mean of the reference values, $b$ is the slope, $\hat{y}$ is the mean of the predicted values, and $\hat{y}_i$ is the $i$th predicted value obtained when applying the multivariate NIR model. The slope, $b$, is considered as different from 1 when $t_{obs} \leq t_{(1-\alpha/2)}$, where $t_{obs}$ is the observed $t$-value, calculated according to eq 3, and $t_{(1-\alpha/2)}$ is the $t$-value obtained from the table $t$-distribution for a probability of $\alpha = 0.05$.

4.2. Detection of Profenofos Residues in Vegetables Using FT-NIR Spectroscopy. 4.2.1. Sample Preparation. Chinese kale, cabbage, and green chilli spur pepper samples (pesticide residue free vegetables) were purchased from a supermarket in Bangkok, Thailand. These vegetable samples confirmed that no profenofos traces were found according to the test by using the reference method (GC–MS) prior spiking. The Chinese kale leaves were trimmed using a sharp knife into square shapes (20 cm × 20 cm), with a weight of 20 ± 2 g per sample. The white inner cabbage leaves with the stem were trimmed into square shapes (12 cm × 12 cm), with a weight of 20 ± 2 g per sample. Two green chilli spur peppers 10–12 cm in length and 10 ± 2 g per fruit were chosen. The placenta with the seed was removed using a knife as only the fruit with the skin was used in the model. All vegetables were individually spiked on the surface with drops of profenofos (solutions of standard grade, Dr. Ehrenstorfer, DE) to obtain profenofos at different concentrations of 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100 mg/kg. Then, each sample was dried at 25 ± 2 °C for 2 h before each sample (20 ± 2 g) was blended separately in a food blender, followed by pesticide analysis. Each blended sample was divided into two: (1) a 10 g sample for FT-NIR analysis and (2) a 10 g sample for GC–MS analysis as the reference method. The numbers of samples and the concentrations of profenofos in the vegetable samples are described in Table 7.

4.2.2. Sample Preparation and FT-NIR Spectra Collection. Spiked samples (10 g) were extracted using 10 mL of acetonitrile (analytical grade, Merck, DE) in a glass vial. Then, each sample was shaken for 1 min using a vortex mixer (model 232, Fisher Scientific, UK), kept at 25 ± 2 °C for 30 min before the NIR measurement. Then, each sample was dried at 25 ± 2 °C for 2 h before each sample (20 ± 2 g) was blended separately in a food blender, followed by pesticide analysis. Each blended sample was divided into two: (1) a 10 g sample for FT-NIR analysis and (2) a 10 g sample for GC–MS analysis as the reference method. The numbers of samples and the concentrations of profenofos in the vegetable samples are described in Table 7.

4.2.3. Reference Method. QuEChERS (quick, easy, cheap, effective, rugged and safe) with GC–MS technique was used as the reference method for the profenofos residue analysis. The homogenized sample (10 g) was placed in a 40 mL Teflon centrifuge tube, and 10 mL of acetonitrile (analytical

| Parameter                  | Chinese kale calibration set | validation set | cabbage calibration set | validation set | chilli spur pepper calibration set | validation set |
|----------------------------|-------------------------------|----------------|-------------------------|---------------|------------------------------------|----------------|
| Number of samples          | 63                            | 35             | 63                      | 36            | 61                                 | 34             |
| Maximum (mg/kg)            | 106.28                        | 99.39          | 105.36                  | 99.60         | 102.29                             | 100.31         |
| Minimum (mg/kg)            | 0.60                          | 0.60           | 0.53                    | 0.54          | 0.53                               | 0.55           |
| Average (mg/kg)            | 31.70                         | 30.43          | 32.81                   | 31.80         | 32.01                              | 32.46          |
| Standard deviation (mg/kg) | 32.34                         | 31.65          | 33.67                   | 32.17         | 33.41                              | 34.13          |

*Recovery (%) ± relative standard deviation (%) from spiked vegetable samples (Chinese kale, cabbage, and chilli spur pepper) containing two levels of profenofos residues at 0.50 and 5.00 mg/kg using the QuEChERS and GC–MS method were 95 ± 6 to 110 ± 3%, respectively.*

Table 7. Data of Calibration and Validation Sample Sets on Profenofos in Vegetable Samples Obtained From the GC–MS Method

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grade, Fisher Scientific, UK) was added before capping tightly and then shaking vigorously for 1 min using a vortex mixer (model 232, Fisher Scientific, UK). Then, 4 g of anhydrous magnesium sulfate (MgSO4, AppliChem GmbH—an ITW company, DE) and 1 g of sodium chloride (NaCl, Merk KGaA, DE) were added and mixed immediately for 1 min, before the extract was centrifuged (model S804R, Eppendorf, DE) at 5000 rpm and 25 ± 2 °C for 5 min. A 1 mL aliquot of the upper acetonitrile layer was transferred into a 1.5 mL microcentrifuge vial containing 25 mg of primary secondary amine sorbent (Agilent Technology, USA) and 150 mg of anhydrous MgSO4 capped tightly, and shaken in the vortex mixer for 30 s. Following centrifugation for 1 min at 6000 rpm (mini centrifuge model D1008, Scilogex, USA), 0.5 mL of extract was transferred into a sample vial. The extract samples were dried in a vacuum-drying oven (model VD 23, BINDER GmbH, DE) and then redissolved by mixing with ethyl acetate/cyclohexane (1:1, v/v; pesticide analysis grade, Fisher Scientific, UK) for GC/MS.35

The analysis was performed in an isocratic system using GC–MS (model QP2010, Shimadzu, JP) fitted with a capillary column (liquid phase, TC1701, GL Sciences, DE). The injection mode was splitless and used 1 μL with helium gas as the mobile phase. The system was composed of a 2.0 μL sample at 220 °C and 97.9 kPa with a gas flow rate of 1.5 μL/min.

4.2.4. Data Analysis and Calibration Equation Development. The calibration equations for predicting profenofos residues in vegetable samples were established using a method similar to that described in Section 4.1.3 above. The optimum wavelength range and the preprocessing method of the best calibration equation were selected. The accuracy and performance of the optimized calibration equation were evaluated following the procedure described in ISO 12099 (2017), according to the method in Section 4.1.4 above.

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Notes
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■ REFERENCES

(1) Adelanwa, E.; Medugu, J. Variation in the nutrient composition of red and green cabbage (Brassica oleracea) with respect to age at harvest. J. Appl. Agric. Res. 2015, 7, 183–189.
(2) Liang, Y.; Li, Y.; Zhang, L.; Liu, X. Pheromone and antioxidant activity in four varieties of head cabbages commonly consumed in China. Food Prod. Process. Nutr. 2019, 1, 3.
(3) Wang, Y.-Q.; Hu, L.-P.; Liu, G.-M.; Zhang, D.-S.; He, H.-J. Evaluation of the nutritional quality of Chinese kale (Brassica alboglabra Bailey) using UHPLC-Quadrupole-Orbitrap MS/MS-based metabolomics. Molecules 2017, 22, 1262.
(4) Olatunj, T. L.; Afelayan, A. J. The suitability of chili pepper (Capsicum annuum L) for alleviating human micronutrient dietary deficiencies: A review. Food Sci. Nutr. 2018, 6, 2239–2251.
(5) Laohaudomchok, W.; Nankongnab, N.; Siributananupruk, S.; Klaimgaew, P.; Lianchamroon, W.; Ousap, P.; Jatiket, M.; Kajitvichyanukul, P.; Kitana, N.; Siriwong, W.; Hemachudah, T.; Satayavivad, J.; Robson, M.; Jaacks, L.; Barr, D. B.; Kongsip, P.; Woskie, S. Pesticide use in Thailand: Current situation, health risks, and gaps in research and policy. Hum. Ecol. Risk Assess. 2021, 27, 1147–1169.
(6) Panuwat, W.; Sireerong, S.; Pramaporn, T.; Ryan, B. P.; Fidler, N.; Robson, M. G.; Barr, D. B. Agricultural pesticide management in Thailand: Status and population health risk. Environ. Sci. Pol. 2012, 17, 72–81.
(7) Sapbamrer, R.; Hongphongsong, S. Organophosphorus pesticide residues in vegetables from farms, markets, and a supermarket around Kwan Phayao lake of Northern Thailand. Arch. Environ. Contam. Toxicol. 2014, 67, 60–67.
(8) Wanwimolruk, S.; Kanchanamayoon, O.; Phopin, K.; Prachayasitkul, V. Food safety in Thailand 2: Pesticide residues found in Chinese kale (Brassica oleracea), a commonly consumed vegetable in Asian countries. Sci. Total Environ. 2015, 532, 447–455.
(9) Wanwimolruk, S.; Phopin, K.; Boonpanyrak, S.; Prachayasitkul, V. Food safety in Thailand 4: Comparison of pesticide residues found in three commonly consumed vegetables purchased from local markets and supermarkets in Thailand. PeerJ 2016, 4, No. e2432.
(10) Klonjapo, J.; Therdkiattikul, N.; Siripattanakul-Ratpukdi, S. Profenofos pesticide biodegradation under presence of natural organic carbon. Eng. Appl. Sci. Res. 2016, 43, 314–316.
(11) Office of Agricultural Economics of Thailand. Quantity and value of pesticides imports to Thailand. Available online. https://www.doa.go.th/ard/?page_id=386 (accessed on 16 May 2021).
(12) National Bureau of Agricultural Commodity and Food Standards of Thailand. Pesticide residues-maximum residue limits. Available online. https://www.acfs.go.th/standard/download/MAXIMUM-RESIDUE-LIMITS.pdf (accessed on 15 May 2021).
(13) Silipunyo, T.; Hongubitsong, S.; Phalaraksh, C.; Laoyang, S.; Kerdnoi, T.; Patarasiriwong, V.; Prapamontol, T. Determination of organophosphate pesticides residues in fruits, vegetables and health risk assessment among consumers in Chiang Mai province, Northern Thailand. Res. J. Environ. Toxicol. 2016, 11, 20–27.

(14) Suntudrob, J.; Jongmewasna, W.; Payanan, T.; Srikote, R.; Wittayanon, W. Monitoring of pesticide residues in domestic vegetables in Thailand during 2015. Asia Pac. J. Sci. Technol. 2018, 23, 1–8.

(15) Omaruk, S.; Siriwong, W.; Siripattanarak, S.; Robson, M. Risk assessment of organophosphate pesticides for chili consumption from chili farm area, Ubon Ratchathani province, Thailand. J. Health. Res. Thailand. 2011, 25, 141–146.

(16) Leuprasert, L.; Taneeapanchuskul, S.; Monmora, S.; Puangtapa, S.; Jifan, S.; Siriwong, W.; Chapman, R. Pesticide use and pesticide-related symptom prevalence in Chinese kale farmers in Northeast Thailand. J. Health. Res. Thailand. 2014, 28, 255–262.

(17) Saranwong, S.; Kawan, S. Rapid determination of fungicide contaminated on tomato surfaces using the DESIR-NIR: A system for ppm-order concentration. J. Near Infrared Spectrosc. 2005, 13, 169–175.

(18) Sun, D. W. Infrared Spectroscopy for Food Quality Analysis and Control, 1st ed.; Elsevier Inc.: USA, 2009; pp 1–144.

(19) Lv, G.; Du, C.; Ma, F.; Shen, Y.; Zhou, J. Rapid and nondestructive detection of pesticide residues by depth-profiling Fourier transform infrared photoacoustic spectroscopy. ACS Omega 2018, 3, 3548.

(20) Stuart, B. Biological Applications of Infrared Spectroscopy; John Wiley and Sons: U.K., 1997; p 212.

(21) Sánchez, M. T.; Flores-Rojas, K.; Guerrero, J. E.; Garrido-Varo, A.; Pérez-Marín, D. Measurement of pesticide residues in peppers by near-infrared reflectance spectroscopy. Pest Manag. Sci. 2010, 66, 580–586.

(22) Xue, L.; Cai, J.; Li, J.; Liu, M. Application of particle swarm optimization (PSO) algorithm to determine dichlorvos residue on the surface of Navel orange with Vis-NIR spectroscopy. Procedia Eng. 2012, 29, 4124–4128.

(23) Salguero-Chaparro, L.; Gaitán-Jurado, A. J.; Ortiz-Somovilla, V.; Peña-Rodriguez, F. Feasibility of using NIR spectroscopy to detect herbicide residues in intact olives. Food Contr. 2013, 30, 504–509.

(24) Jamshidi, B.; Mohajerani, E.; Jamshidi, J.; Mineai, S.; Sharifi, A. Non-destructive detection of pesticide residues in cucumber using visible/near-infrared spectroscopy. Food Addit. Contam., Part A 2015, 32, 857–863.

(25) Khamnohmadi, M.; Armenta, S.; Garrigues, S.; De la Guardia, M. Mid-and near-infrared determination of metribuzin in agrochemicals. Vib. Spectrosc. 2008, 46, 82–88.

(26) González, A.; Garrigues, S.; Armenta, S.; De la Guardia, M. Determination at low ppm levels of dithiocarbamate residues in foodstuff by vapour phase liquid phase microextraction-infrared spectroscopy. Anal. Chim. Acta 2011, 688, 191–196.

(27) Yang, T.; Zhou, R.; Jiang, D.; Fu, H.; Su, R.; Liu, Y.; Su, H. Rapid detection of pesticide residues in Chinese herbal medicines by Fourier transform infrared spectroscopy coupled with partial least squares regression. J. Spectrosc. 2016, 2016, 9492030.

(28) International Standard. Statistics for performance measurement. ISO 12099:2017(E): Animal Feeding Stuffs, Cereals and Milled cereal products—Guidelines for application of near infrared spectrometer, Switzerland, 2017; pp 5–12.

(29) Clavaud, M.; Roggo, Y.; Dégardin, K.; Sacré, P.-Y.; Hubert, P.; Ziemons, E. Global regression model for moisture content determination using near-infrared spectroscopy. Eur. J. Pharm. Biopharm. 2017, 119, 343–352.

(30) Okami, Y.; McClure, W. F.; Christy, A. A. Near-Infrared Spectroscopy in Food Science and Technology; John Wiley and Sons, Inc.: USA, 2004; pp 145–169.

(31) Williams, P.; Norris, K. Near-Infrared Analysis Technology in The Agricultural and Food Industry, 2nd ed.; American Association of Cereal Chemists, Inc: USA, 2004; pp 145–169.

(32) Nicolai, B. M.; Beullens, K.; Bobelyn, E.; Peirs, A.; Saeyes, W.; Theron, K. I.; Lammertyn, J. Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review. Postharvest Biol. Technol. 2007, 46, 99–118.

(33) Magwaza, L. S.; Opara, U. I.; Terry, L. A.; Landahl, S.; Cronje, P. J.; Nieuwoudt, H.; Mouazen, A. M.; Saeyes, W.; Nicolai, B. M. Prediction of “Nules Clementine” mandarin susceptibility to ring breakdown disorder using Vis/NIR spectroscopy. Postharvest Biol. Technol. 2012, 74, 1–10.

(34) Wang, S.; Xiang, B.; Su, Y.; Tang, Q. Direct determination of dichlorvos in water by partial least square-discriminant analysis. Environ. Chem. Lett. 2012, 10, 383–387.

(35) Saranwong, S.; Kawan, S.; Amari, C. M.; Yoshida, M. The reliability of pesticide determinations using near infrared spectroscopy and the dry-extract system for infrared (DESIIR) technique. J. Near Infrared Spectrosc. 2007, 15, 227–236.

(36) Gowen, A. A.; Tsuchisaka, Y.; O’Donnell, C.; Tsenkova, K. Investigation of the potential of near infrared spectroscopy for the detection and quantification of pesticides in aqueous solution. Am. J. Anal. Chem. 2011, 02, 53–62.

(37) Arias, N.; Arazuri, S.; Jarén, C. Ability of NIRS technology to determine pesticides in liquid samples at maximum residue levels. Pest Manag. Sci. 2013, 69, 471–477.

(38) Workman, J. J.; Weyer, L. Practical Guide and Spectral Atlas for Interpreting Near-Infrared Spectroscopy, 2nd ed.; CRC Press, Taylor and Francis Group: USA, 2012; p 326.

(39) Moros, J.; Armenta, S.; Garrigues, S.; De la Guardia, M. Univariate near infrared methods for determination of pesticides in agrochemicals. Anal. Chim. Acta 2006, 579, 17–24.

(40) Coates, J. Interpretation of Infrared Spectra, A Practical Approach. In Encyclopedia of Analytical Chemistry; Meyers, R. A., Ed.; John Wiley and Sons Ltd: USA, 2000; pp 10815–10837.

(41) Stuart, B. Infrared Spectroscopy: Fundamentals and Applications; John Wiley and Sons: Ltd: U.K., 2004; Vol 15, pp 71–78.

(42) Sahil, K.; Prashant, B.; Akanksha, M.; Premjeet, S.; Devashish, R. Interpretation of infrared spectra. Int. J. Pharm. Chem. Sci. 2012, 1, 174–200.

(43) Xiao, G.; Dong, D.; Liao, T.; Li, Y.; Zheng, L.; Zhang, D.; Zhao, C. Detection of pesticide (chlorpyrifos) residues on fruit peels through spectra of volatiles by FTIR. Food Anal. Methods. 2015, 8, 1341–1346.

(44) Kira, O.; Linker, R.; Dubowski, Y. Estimating drift of airborne pesticides during orchard spraying using active open path FTIR. Atmos. Environ. 2016, 142, 264–270.

(45) Tang, G.; Tian, K.; Song, X.; Xiong, Y.; Min, S. Comparison of several supervised pattern recognition techniques for detecting additive methamidophos in rotenone preparation by near-infrared spectroscopy. Spectrochim. Acta, Part A 2014, 121, 678–684.

(46) Zhang, Y.; Xiang, B.; Dong, Y.; Xu, J. Rapid determination of prochioraz in orange juice by near-infrared spectroscopy. Anal. Lett. 2013, 46, 2739–2751.

(47) Xie, Y.-J.; Wang, Z.; Hu, W.-P.; Xu, S. Fast determination of trace dimethyl fumarate in milk with near infrared spectroscopy following fluidized bed enrichment. Anal. Bioanal. Chem. 2012, 404, 3189–3194.

(48) Chen, J.; Peng, Y.; Li, Y.; Wang, W.; Wu, J. A method for determining organophosphorus pesticide concentration based on near-infrared spectroscopy. Trans. ASABE 2011, 54, 1025–1030.

(49) Beseos, J. M. E.; Yaptenco, K. F.; Yaptenco, K. F.; Esguerra, E. B.; Peralta, E. K. Evaluation of dry extract system involving NIR spectroscopy (DESIR) for pesticide residues detection on fresh Carabao mango (Mangifera indica L. ‘Carabao’) fruit. J. Adv. Agric. Technol. 2018, 24, 30–40.

(50) Wu, J.; Liu, C.; Chen, Y.; Chen, Y.; Xu, Y. Study on detection technology of pesticide residues in vegetables based on NIR. Proceedings of International Conference on Computer and Computing Technologies in Agriculture II, Beijing, China, October 18–20, 2008; pp 2217–2222.

(51) Zhou, Y.; Xiang, B.; Wang, Z.; Chen, C. Determination of chlorpyrifos residue by near-infrared spectroscopy in white radish
based on interval partial least square (iPLS) model. *Anal. Lett.* **2009**, *42*, 1518−1526.

(52) Acharya, U. K.; Subedi, P. P.; Walsh, K. B. Evaluation of a dry extract system involving NIR spectroscopy (DESIR) for rapid assessment of pesticide contamination of fruit surfaces. *Am. J. Anal. Chem.* **2012**, *03*, 524−533.

(53) Pochanagone, S.; Rittiron, R. Rapid detection of infrared inactive sodium chloride content in frozen tuna fish for determining commercial value using short wavelengths. *J. Near Infrared Spectrosc.* **2019**, *27*, 424−431.

(54) Bantadjian, Y.; Rittiron, R.; Malithong, K.; Narongwongwattana, S. Rapid starch evaluation in fresh cassava root using a developed portable visible and near-infrared spectrometer. *ACS Omega* **2020**, *5*, 11210.

(55) Anastassiades, M.; Lehotay, S. J.; Štajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce. *J. AOAC Int.* **2003**, *86*, 412−431.