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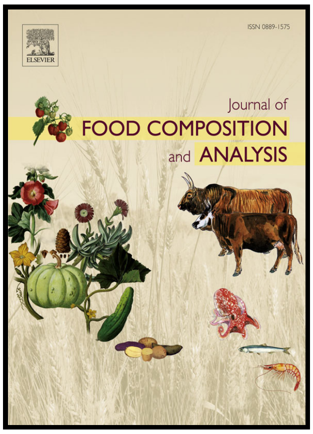

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Monitoring pesticides with portable NIR spectroscopy in different intact fruits

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Abstract

This study aimed to investigate the use of portable NIR spectroscopy with data mining techniques for pesticide quantification in cherry tomatoes and strawberries. For each product, reflectance spectra of 240 samples, composed of three fruits and treated with different concentrations of azoxystrobin, chlorothalonil, chlorpyrifos, difenoconazole, lambda-cyhalothrin, or tetraconazole, were obtained in the wavelength range of 900 - 1700 nm, using the DLP NIRscan and FieldSpec 3 spectrometers. Reference analyses were performed using liquid chromatography. Mathematical pre-processing techniques as well as variable selection were applied to the spectral data. The regression models were developed using Partial Least Squares Regression (PLSR), Orthogonal Projection for Latent Structures (OPLS), Random Forest (RF) and Support Vector Machine (SVM) techniques. The OPLS models with selection of RFE or SFM variables were able to quantify pesticides with R^2p from 0.80 to 0.96, RMSEP from 0.01 to 0.03, RPDP from 2.24 to 4.76, and R^2p from 0.73 to 0.80, RMSEP from 0.06 to 0.12, RPDP from 1.93 to 2.27 in samples of cherry tomatoes and strawberries, respectively. These results show that portable NIR spectroscopy, combined with data mining techniques, holds promise for monitoring pesticide residues in cherry tomatoes and strawberries.

Keywords: Chemical Residues, Machine Learning, Near Infrared, Tomatoes, Strawberries.

1. Introduction

Tomatoes (*Solanum lycopersicum* L.) and strawberries (*Fragaria* × *ananassa*) are among the most consumed vegetables in the world, with varieties that are highly attractive to the national and international market, due to their flavor, nutritional value, concentration of important vitamins for the body, and health benefits, given their anti-inflammatory, anticancer, and antioxidant characteristics (Shahbazi et al., 2020; Mendonça et al., 2021; Dai et al., 2023; Ngouana et al., 2023).

Because they are crops very susceptible to the incidence of pests and diseases, it is common that in conventional production systems there is frequent use of chemical agents to prevent and/or combat these problems. However, the lack of criteria for adequate use of chemical agents has increased the risks of contamination of food and the environment (Guo et al., 2021; Wang et al., 2021; Ouakhssase & Addi, 2023).

The excessive use of pesticides and harvesting before the minimum safety interval are concerns for control agencies and consumers about the presence of chemical residues in products available on the market. For this reason, the production and marketing chain needs to meet the requirements of the various national and international regulatory agencies (Eissa et al., 2024).

In Brazil, country that is one of the largest consumers of pesticides in the world, and where crops have great economic relevance, the control of use is carried out by standards and control programs established by agencies linked to the government, and by international guidelines recommended by the Food and Agriculture Organization of the United Nations (FAO), World Health Organization

(WHO) and CODEX Alimentarius (Berlitz et al., 2023; Moreira et al., 2023; Jardim; Caldas, 2024).

The Program for the Analysis of Pesticide Residues in Food (PARA) of the National Health Surveillance Agency (ANVISA), which is the main means of evaluation in Brazil, demonstrates in different reports that tomatoes and strawberries are among the foods with the highest levels of chemical residues. This information reinforces the importance of complying with the requirements imposed on the production chain, in order to ensure food safety. Therefore, producers need to comply with quality standards in terms of Maximum Residue Limits (MRLs), which must be achieved through constant monitoring of the presence of pesticides in products (Ciarrocchi et al., 2020; Berlitz et al., 2023; Jardim; Caldas, 2024).

Currently, the monitoring of pesticide residues in agricultural products is carried out through highly complex methods, such as liquid or gas chromatography, mass spectrometry, and immunoassays, which are expensive and unfeasible for real-time analysis, as they require sample preparation, sophisticated reagents/equipment, large amounts of solvents, and disposal of other chemical substances into the environment (Zhuang et al., 2022; Dong et al., 2023; Liu et al., 2023).

The near infrared spectroscopy (NIRS) has been widely used to monitor physicochemical quality traits in fruits and vegetables, which could also be an efficient method for monitoring pesticide residues in agricultural products. The NIRS determines quality traits through the interaction between the NIR electromagnetic radiation (780 - 2500 nm) with the chemical and physical traits of the sample. Indeed, benchtop and portable NIR spectrometers have been increasingly used for non-destructive, rapid and sustainable quality control of a wide range of agricultural products. Many portable equipment, in addition to adding lower costs, greater ease of handling, reduced energy consumption, also have performances and sensitivities close to those of the bench, which can simplify the application within quality monitoring processes (Fulgencio et al., 2022; Moraes, Cruz-Tirado, & Barbin, 2022; Ferreira et al., 2023; Funsueb et al., 2023).

NIRS has already been used to analyze pesticide contamination in products such as cucumber (Jamshidi et al., 2016), cabbage (Lu et al., 2021), and cocoa beans (Villanueva et al., 2023). In tomatoes, Saranwong and Kawano (2005) and Acharya et al. (2012) used a NIRS-associated dry extract system (DESIR) for detection of different pesticides, while Nazarloo et al. (2021) and Soltani Nazarloo et al. (2021) evaluated the potential of a Vis-NIR spectrometer to quantify different concentrations of another type of pesticide in fruit. In strawberries, Yazici et al. (2019) investigated the ability of NIR spectroscopy to quantify different concentrations of two types of chemical residues of a commercial pesticide in fruit.

In the context of these analyses, the use of different modeling algorithms, such as some adopted in the present work, from the traditional approach by Partial Least Squares Regression and the extended approach Orthogonal Projection for Latent Structures, or by machine learning, from the approach by Random Forest and Support Vector Machine, are fundamental for the development of models with different forms of processing and consequently different results of prediction (Trygg & would, 2002; Mehmood et al., 2012; Boateng, Otoo, & Abaye, 2020).

Another fact is that while the studies cited looked at the use of NIRS to monitor pesticide residues on fruits, they did not assess the potential of this technology to detect and quantify more than two types of pesticides or the accuracy of low-cost portable spectrometers, compared to benchtop spectrometers. Therefore, this study aimed to investigate the use of portable NIR spectroscopy with data mining techniques to quantify different pesticide concentrations in cherry tomato and strawberry samples.

2. Material and Methods

2.1. Sample preparation

A total of 1440 vegetables, represented by 720 cherry tomatoes (*Solanum lycopersicum* var. cerasiforme) and 720 strawberries (*Fragaria x ananassa Duch.* var. portola), organically grown were purchased in commercial establishments in Juazeiro, Bahia State, Brazil. Organic fruits were used in order to ensure the absence of preexisting residues related to possible other chemical compounds, which enabled the development of robust calibration curves, with control of the concentrations of pesticides used for the experiment. It is an approach already used in other literature, which allows isolating the spectral signals associated with the active ingredients of interest and minimizing other interferences. Wider variability in commercial samples can be added to the models within a further process of external analysis (Soltani Nazarloo et al., 2021; Villanueva et al., 2023).

For both vegetables, 240 samples composed of three fruits were divided equally among four commercial pesticide treatments. Tomato samples were treated with chlorpyrifos, difenoconazole, lambda-cyhalothrin, and tetraconazole. Strawberry samples were treated with azoxystrobin, chlorothalonil, chlorpyrifos and difenoconazole (Figure 1).

These pesticides are commonly recommended for pest and disease control during crop production and have residual recurrences in fruits after harvest. The fruit samples of each treatment were subdivided into the following groups: no pesticide spraying; pesticide spraying in a ratio of 1:1000 in water; pesticide spraying in a ratio of 1:100 in water; and pesticide spraying in a ratio of 1:40 in water.

In order to simulate real commercial conditions, and ensure greater variability in the pesticide residue data, 32 samples of each treatment were analyzed 2 hours after spraying, and 28 samples after the pre-harvest interval established for each pesticide (Table 1). Figure 2 shows the schematic diagram of the experimental system.

2.2. Spectral acquisition

Spectral acquisitions were performed sequentially by two spectrometers: first by portable DLP and then by benchtop FieldSpec 3 for all samples. The order of the samples was kept constant, but the three fruit replicates of each sample were measured in non-sequential order between both spectrometers, for greater randomness in the acquisition. In addition, the analyses in both spectrometers were carried out on the same day, to try to minimize possible temporal and environmental variations that could significantly influence the results.

2.2.1 Portable instrument

Reflectance spectra were obtained on both sides of each fruit using a portable DLP NIRscan Nano EVM spectrometer (Texas Instruments, Dallas, Texas, USA) with 10 nm resolution, 248 digital resolution, 2.88 kHz maximum EVM scan speed, diffraction grating, single element detector, 900 to 1700 nm spectral range, and DLP NIRscan Nano GUI v2.1.0 software. The spectrum of each fruit corresponded to the average of 10 scans performed by the instrument, with values presented in absorbance.

2.2.2 Benchtop instrument

Reflectance spectra were obtained on both sides of each fruit using a FieldSpec 3 benchtop spectrometer (Analytical Spectral Devices, Boulder, Colorado, USA) with a resolution of 3 to 10 nm, a reading time of 100 ms, an accuracy of ± 1 nm, an InGaAs photodiode array detector, a 14.5 W quartz-tungsten-halogen light source, and a spectral range of 350 to 2500 nm.

To increase the quality and homogeneity of the spectral data, the instrument was turned on 30 minutes before the start of spectral acquisition, and a Spectralon® ceramic plate (Labsphere Inc., North Sutton, NH, USA) with approximately 100% reflectance was used as the calibration standard for the spectral acquisitions. To perform the analyses, the spectrometer was housed in a darkroom measuring 100 x 50 x 50 cm.

Before each analysis, the samples were placed on the ceramic plate at a perpendicular distance of 7.0 cm from the optical fiber of the sensor. The spectrum of each fruit corresponded to the average of 30 scans performed by the instrument within the spectral range of 900 to 1700 nm. RS3 and ViewSpec Pro software (Analytical Spectral Devices, Boulder, Colorado, USA) were used to acquire and transform reflectance data into absorbance data (log(1/R)). The results obtained with the data were used as a reference for comparison with the results of the portable NIRscan DLP spectrometer.

2.3 Reference analyses

The adapted QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was used to prepare the samples and extract the pesticides (Anastassiades et al., 2007). Quantifications were performed by liquid chromatograph LC-20 AT (Shimadzu®, Kyoto, Japan) (without pre-column) with autosampler (SIL-20 A) and diode array detector (DAD, SPD-M20A) associated with an LC-Solution® 1.0 data processing station.

Chromatographic separations were performed at 30 °C, with a mobile phase composed of methanol and acidified water (0.1% formic acid), injection volume of 3 µL, flow rate of 0.8 mL $^{min-1}$ and execution time of 30 min. The analytical curves were calibrated using the working standards azoxystrobin (CAS Number: 131860-33-8; 98% purity HPLC grade), chlorothalonil (CAS Number: 1897-45-6; 98% purity HPLC grade), chlorpyrifos (CAS number: 2921-88-2; 98% purity HPLC grade), difenoconazole (CAS number: 119446-68-3; 95% purity HPLC grade), lambda-cyhalothrin (CAS number: 91465-08-6; 95% purity HPLC grade) and tetraconazole (CAS number: 112281-77-3; HPLC grade 98% purity). The distribution frequencies of the different concentrations quantified in the tomato and strawberry samples can be seen in Figure 3.

2.4 Development and performance of the regression models

The raw spectral data were subjected to different types of mathematical pre-processing to remove noise and/or intensify the signal. To smooth the signal and correct the baseline in spectral segments with different window sizes, the Savitzky-Golay filter was applied, and the first and second derivatives with second-order polynomials were applied. Multiplicative signal correction (MSC) and standard normal variation (SNV) were used to correct for the multiplicative and additive effects of the spectra due to light scattering.

The regression models were developed using the following techniques: (1) Partial Least Squares Regression (PLSR); (2) Orthogonal Projection for Latent Structures (OPLS); (3) Random Forest (RF); and (4) Support Vector Machine (SVM).

Raw and pre-processed spectral data were used as independent input variables (X) and pesticide concentration values in tomato or strawberry were used as dependent output variables (y). For each treatment, the sample data set was split in an 80/20 ratio, with 80% allocated to training or calibration and 20% to prediction or external validation. Cross-validation was applied to the entire calibration set.

The spectral datasets responsible for developing the best regression models in cross-validation were subjected to a variable selection process using the methods presented in Scikit-learn (2022): (1) SelectFromModel (SFM); (2) Recursive Feature Elimination (RFE); (3) Recursive Feature Elimination with Cross-Validation (RFECV); and (4) Sequential Feature Selection (SFS). The wavelengths selected for the greatest contribution to the characterization of pesticides were used to reconstruct the models.

The performance of the regression models was evaluated using the following statistical parameters: coefficient of determination (R^2) (Equation 1); Root Mean Squared Error (RMSE) (Equation 2); and Residual Predictive Deviation (RPD) (Equation 3), calculated by the ratio between standard deviation (SD) and RMSE. The best calibration models were chosen based on the coefficient of determination (R^2cv), error (RMSECV) and predictive deviation (RPDCV) in the cross-validation stage and, subsequently, they were evaluated by the coefficient of determination (R^2p), error (RMSEP) and predictive deviation (RPDP) in the prediction stage.

$$\mathrm{R}^2 = \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}(\hat{\mathrm{y}}_\mathrm{i}-\hat{\mathrm{y}})(\mathrm{y}_\mathrm{i}-\bar{\mathrm{y}})^2}{(\mathrm{n}-1)(\sigma_\mathrm{r}\sigma_\mathrm{p})} \tag{1}$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}(\mathrm{y}_\mathrm{i}-\hat{\mathrm{y}}_\mathrm{i})2}{\mathrm{n}}} \tag{2}$$

$$\mathrm{RPD} = \frac{\mathrm{SD}}{\mathrm{RMSE}} \tag{3}$$

Where:

$\hat{y}_i$ - Value predicted by the calibration model (mg/g);

yi - Reference value (mg/g);

$\bar{y}$ - Average of the predicted values (mg/g);

n - Number of calibration or validation samples;

m - Number of predicted samples;

σr - Standard deviation of the reference values (mg/g);

σp - Standard deviation of predicted values (mg/g).

3. Results

The raw average spectra for samples not sprayed or sprayed with the pesticides are shown in Figures 4 and 5. The presence or absence of pesticides affected the intensity of absorption of the spectra by the samples but had no effect on the spectral pattern and the location of the absorption peaks at 970, 1200 and 1450 nm.

OPLS models with variable selection, processed from DLP data, achieved the best performances for pesticide quantification (Tables 2 and 3). Values of R^2cv = 0.97, RMSECV = 0.01, RPDCV = 6.02, R^2cv = 0.97, RMSECV = 0.01, RPDCV = 5.91, R^2cv = 0.97, RMSECV = 0.01, RPDCV = 5.52 and R^2cv = 0.85, RMSECV = 0.04, RPDCV = 2.56 were achieved with models reconstructed from 10 wavelengths (964, 1217, 1220, 1247, 1260, 1276, 1325, 1335, 1480 and 1697 nm), 20 wavelengths (1043, 1047, 1240, 1383, 1443, 1446, 1452, 1456, 1459, 1467, 1471, 1561, 1631, 1651, 1664, 1667, 1670, 1672, 1681 and 1693 nm), five wavelengths (1189, 1240, 1313, 1325 and 1489 nm) and 15 wavelengths (908, 1024, 1322, 1325, 1329, 1339, 1358, 1384, 1543, 1616, 1642, 1661, 1681, 1684 and 1695 nm), selected by the RFE filter, for chlorpyrifos, difenoconazole, lambda-cyhalothrin, and tetraconazole in tomatoes, respectively.

Values of R^2cv = 0.81, RMSECV = 0.05, RPDCV = 2.27, R^2cv = 0.83, RMSECV = 0.05, RPDCV = 2.44, and R^2cv = 0.75, RMSECV = 0.11, RPDCV = 1.98 were achieved with models reconstructed from five wavelengths (1358, 1406, 1421, 1456, and 1564 nm), (1233, 1588, 1602, 1605, and 1697 nm), and 10 wavelengths (1182, 1286, 1456, 1561, 1581, 1590, 1599, 1653, 1659, and 1670 nm), selected by the RFE filter, for azoxystrobin, chlorpyrifos, and difenoconazole in strawberries, respectively. For chlorothalonil, values of R^2cv = 0.80, RMSECV = 0.10, and RPDCV = 2.25 were achieved with models reconstructed from five wavelengths (1377, 1380, 1569, 1599, and 1653 nm) selected by the SFM filter.

Values of R^2p = 0.80, RMSEP = 0.01, RPDP = 2.24, R^2p = 0.96, RMSEP = 0.01, RPDP = 4.76, R^2p = 0.82, RMSEP = 0.02, RPDP = 2.33, and R^2p = 0.81, RPDP = 2.31 and RMSEP = 0.03 were achieved in the prediction of chlorpyrifos, difenoconazole, lambda-cyhalothrin, and tetraconazole in tomatoes, respectively. In contrast, values of R^2p = 0.76, RMSEP = 0.12, RPDP = 2.04, R^2p = 0.80, RMSEP = 0.06, RPDP = 2.25, R^2p = 0.80, RMSEP = 0.09, RPDP = 2.27, and R^2p = 0.73, RMSEP = 0.11, RPDP = 1.93 were achieved in the prediction of azoxystrobin, chlorothalonil, chlorpyrifos, and difenoconazole in strawberries, respectively. Graphs showing the location of selected wavelengths within the spectral range and the dispersion of predicted concentrations versus measured concentrations for the pesticides are shown in Figures 6 and 7.

4. Discussion

Non-pulverized fruits were responsible for the highest absorbances recorded for most of the treatments evaluated (Figures 4, 5A and 5B). This indicated that the peaks observed at 970, 1200, and 1450 nm were due to the vibrations of the stretching of the O-H bond and the combined C-H and N-H bands, which correspond to the water and organic compounds constituting carbohydrates, proteins, polyphenols, and vitamins of fruits, and stood out in relation to the spectral responses of pesticides (Shen et al., 2018; Włodarska et al., 2019; Mancini et al., 2020; Borba et al., 2021; Najjar & Abu-Khalaf, 2021; Égei et al., 2022; Tan et al., 2023; Wold et al., 2024).

The significant contributions of pesticide chemical bonds to the raw spectral uptake of strawberries sprayed with chlorpyrifos and difenoconazole, within the regions of 1400 nm and 900 to 1700 nm (Figures 5C and 5D), respectively, can be explained by the close relationships between the short PHI adopted for post-spray analysis (Table 1), with the dissipation kinetics, and characteristic properties compared to other sprayed pesticides (Song et al., 2020; El-Morsy et al., 2022). All these observations, associated with the results found after data modeling, showed the importance of applying different mining techniques for the process of quantifying pesticides on fruits (Su et al., 2017).

For cherry tomatoes, the highest calibration and cross-validation performances achieved by the OPLS models with selection of RFE variables (R^2c from 0.90 to 0.98; R^2cv of 0.85 to 0.97), were similar to those of previous studies with DESIR (dry extract system associated with NIR spectroscopy) and PLS models with second derivative that presented R^2c of 0.96 and R^2cv of 0.95 to evaluate different concentrations of diclofluanide (1800 - 2500 nm) (Saranwong and Kawano, 2005) and metiram/pyraclostrobin (1850 - 2048 nm) (Acharya et al., 2012) in tomato samples, respectively. However, in these studies, DESIR aimed to remove water to reduce its effects on the NIR spectra of the samples, while in the present study, NIR spectra were obtained non-destructively in intact fresh tomato and strawberry fruits, making this technology faster and more practical for monitoring pesticide residues under commercial conditions.

In the prediction, the R^2p performances (0.80 to 0.96) were superior to those reported by Nazarloo et al. (2021) for the PLS model developed without variable selection ($R^2p = 0.72$) or with dimensionality reduction by Random Frog (RF) ($R^2p = 0.83$). In the aforementioned study, the models were developed with spectra in the Vis-NIR region (460–1050 nm) to evaluate the residue of the pesticide profenofos sprayed on "Queen" tomatoes in the proportion of 2 per 1000 L in water.

For strawberries, the highest cross-validation and prediction performances achieved by the OPLS models with selection of RFE and SFM variables (R^2cv from 0.75 to 0.83) (R^2p from 0.73 to 0.80) were superior to those of the PLSR model associated with different types of mathematical pretreatments ($R^2cv = 0.76$ and $R^2p = 0.69$), presented by Yazici et. al. (2019) in work with NIR spectroscopy (11000 - 4000 cm⁻1) to quantify pyroclostrobin in Albion strawberries treated with eleven different solutions of the pesticide (0-0,1-0.5-1-2-4-6-8-10-15-20 times the prescribed dose).

Selected wavelengths, for example, at 964, 1358, 1406, 1446, 1452, 1456, 1459, 1467, 1471, 1480, 1489, and 1561 nm correspond to vibrations and bonds by first and second harmonic O–H (H_2O), CH3, first N–H overtone (CONHR, CONH2, and -CONH-), and primary NH amides, which are related to different chemical groups of pesticides (Lapcharoensuk et al., 2023).

The selection of wavelengths was crucial for the extraction of specific spectral information related to the characterization and, consequently, quantification of the different concentrations of pesticides in fruits. The increase or maintenance of performance observed after the reconstruction of the models with the selected wavelengths indicates that the selection helped to reduce potential spectral errors 5and redundant variables in the modeling process, and to make the models simpler, without losing the quality of the prediction (Mishra et al., 2021). The best prediction of some pesticides is related to the fact that their molecules absorb more radiation at specific wavelengths that do not overlap with other molecules in the fruit.

Higher values of R^2 and RPD observed for the models developed with data from the portable instrument may be related to the greater sensitivity of the equipment in detecting vibrations related to O-H elongation in the region of wavelengths around 900 to 1000 nm, and/or to the difference between the lengths of the optical paths specified for DLP and FieldSpec (Van Kollenburg et al., 2021).

High R^2ps, low RMSEPs, and RPDPs greater than 2 or greater than 4 show the high reliability of most models for pesticide quantification, and the feasibility of using them satisfactorily for screening or quantitative predictions of fruit samples (Baqueta et al., 2019; Heil; Schmidhalter, 2021; Jiang et al., 2022; Safaie et al., 2023).

5. Conclusions

In this work, portable NIR spectroscopy, combined with different data mining techniques was evaluated as a promising tool to monitor azoxystrobin, chlorothalonil, chlorpyrifos, difenoconazole, lambda cyhalothrin and tetraconazole residues in cherry tomato and strawberry fruits. The OPLS models constructed from data collected by DLP portable spectrometer (900–1700 nm), and wavelengths selected by RFE or SFM filters, demonstrated high predictive capacity to quantify the different pesticide concentrations, from R^2p values between 0.73 and 0.96, and RPDP between 1.93 and 4.76. Therefore, portable NIR spectroscopy combined with different data mining techniques is a promising alternative and/or complementary method for monitoring pesticide residues in cherry tomatoes and strawberries.

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Tables

Table 1. Characteristics of the pesticides sprayed on cherry tomatoes and strawberries.

Pesticide (active ingredient)	Commercial name	Molecular formula	Class	PHI (days)	TC	MRL (mg/kg)
Azoxystrobin	Amistar	$C_{22}H_{17}N_3O_5$	Fungicide	1	IV	0.3
Chlorothalonil	Bravonil	$C_8Cl_4N_2$	Fungicide	(a)	IV	NA
Chlorpyrifos	Klorpan	$C_9H_{11}Cl_3NO_3PS$	Insecticide	(1[b]) (7[c])	I	NA
Difenoconazole	Score	$C_{19}H_{17}Cl_2N_3O_3$	Fungicide	(1[d]) (3[e])	V	0.5
Lambda-cyhalothrin	Karate Zeon	$C_{23}H_{19}ClF_3NO_3$	Insecticide	3	IV	0.05
Tetraconazole	Domark	$C_{13}H_{11}Cl_2F_4N_3O$	Fungicide	7	IV	0.2

PHI - pre-harvest interval that must elapse between the last application of the pesticide and harvest, as defined by Brazil's National Health Surveillance Agency (ANVISA); a - samples belonging to treatments with unauthorized pesticide for strawberries, and analyzed 1 day after spraying, considering this to be the longest safety interval among the pesticides authorized; b and c - samples belonging to treatments with unauthorized pesticide, analyzed 1 and 7 days after spraying, considering this to be the longest safety interval among the pesticides authorized for strawberries and tomatoes, respectively; d and e - samples belonging to treatments with authorized pesticide, analyzed 1 and 3 days after spraying, considering the safety interval for strawberries and tomatoes, respectively; TC - toxicological classification; MRL - Maximum Residue Limit; NA - Not authorized for the crop.

Table 2. Statistical performance of the regression models OPLS developed for the quantification of pesticides in cherry tomatoes using two NIR spectrometers.

R^2c - coefficient of determination in calibration; RMSEC - root mean squared error in calibration; RPDC - residual predictive deviation in calibration; R^2cv - coefficient of determination in cross-validation; RMSECV - root mean squared error in cross-validation; RPDCV - residual predictive deviation in cross-validation; R^2p - coefficient of determination in

Spectrometer (spectral range)	Pesticide (active ingredient)	Spectral set size	R^2_c	RMSEC	RPDC	R^2_{cv}	RMSECV	RPDCV	R^2_p	RMSEP	RPDP
DLP (900 – 1700 nm)	Chlorpyrifos	Full	1.00	0.00	57.47	0.94	0.02	4.28	0.78	0.01	2.15
		RFE (10)	0.98	0.01	6.88	0.97	0.01	6.02	0.80	0.01	2.24
	Difenoconazole	Full	1.00	0.00	58.07	0.96	0.01	4.96	0.92	0.01	3.59
		RFE (20)	0.98	0.01	7.01	0.97	0.01	5.91	0.96	0.01	4.76
	Lambda-cyhalothrin	Full	1.00	0.00	85.79	0.97	0.01	5.40	0.80	0.02	2.24
		RFE (5)	0.97	0.01	6.18	0.97	0.01	5.52	0.82	0.02	2.33
	Tetraconazole	Full	1.00	0.00	22.72	0.74	0.05	1.97	0.60	0.05	1.58
		RFE (15)	0.90	0.03	3.14	0.85	0.04	2.56	0.81	0.03	2.31
FieldSpec (900 – 1700 nm)	Chlorpyrifos	Full	0.99	0.01	11.46	0.91	0.02	3.25	0.69	0.03	1.80
		RFE (10)	0.95	0.01	4.48	0.94	0.02	4.23	0.79	0.03	2.20
	Difenoconazole	Full	0.97	0.01	6.25	0.87	0.02	2.75	0.69	0.03	1.80
		RFE (10)	0.86	0.02	2.72	0.84	0.02	2.48	0.74	0.03	1.96
	Lambda-cyhalothrin	Full	0.96	0.01	5.32	0.82	0.02	2.37	0,62	0.03	1.62
		SFS (10)	0.80	0.02	2.24	0.77	0.02	2.09	0.63	0.03	1.64
	Tetraconazole	Full	0.97	0.02	5.50	0.74	0.04	1.96	0.70	0.06	1.95
		RFE (5)	0.86	0.03	2.72	0.83	0.04	2.46	0.72	0.06	1.83

prediction; RMSEP - root mean squared error in prediction; RPDP - residual predictive deviation in prediction.

Table 3. Statistical performance of the regression models OPLS developed for the quantification of pesticides in strawberries using two NIR spectrometers.

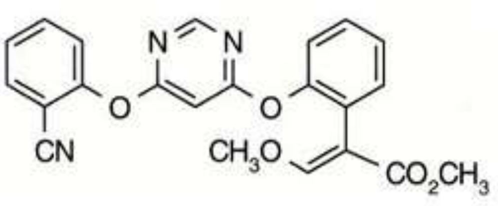
Spectrometer (spectral range)	Pesticide (active ingredient)	Spectral set size	R^2_c	RMSEC	RPDC	R^2_{cv}	RMSECV	RPDCV	R^2_p	RMSEP	RPDP
DLP (900 – 1700 nm)	Azoxystrobin	Full	0.98	0.02	7.32	0.76	0.06	2.05	0.75	0.12	1.99
		RFE (5)	0.85	0.05	2.60	0.82	0.05	2.34	0.76	0.12	2.04
	Chlorothalonil	Full	0.99	0.02	9.13	0.81	0.09	2.31	0.77	0.06	2.07
		SFM (5)	0.83	0.09	2.40	0.80	0.10	2.25	0.80	0.06	2.25
	Chlorpyrifos	Full	0.97	0.02	5.85	0.81	0.05	2.31	0.76	0.09	2.05
		RFE (5)	0.88	0.04	2.84	0.83	0.05	2.44	0.80	0.09	2.27
	Difenoconazole	Full	0.95	0.04	4.67	0.71	0.11	1.84	0.68	0.12	1.78
		RFE (10)	0.78	0.10	2.15	0.75	0.11	1.98	0.73	0.11	1.93
FieldSpec (900 – 1700 nm)	Azoxystrobin	Full	0.75	0.08	2.00	0.56	0.11	1.50	0.54	0.09	1.48
		SFS (10)	0.57	0.11	1.52	0.51	0.12	1.43	0.47	0.09	1.38
	Chlorothalonil	Full	0.85	0.07	2.59	0.66	0.10	1.70	0.54	0.19	1.47
		RFE (5)	0.71	0.09	1.85	0.65	0.10	1.69	0.60	0.18	1.57
	Chlorpyrifos	Full	0.89	0.05	2.96	0.73	0.07	1.94	0,72	0.06	1.90
		SFS (5)	0.77	0.07	2.10	0.73	0.08	1.91	0.69	0.06	1.80
	Difenoconazole	Full	0.80	0.09	2.25	0.66	0.12	1.72	0.59	0.16	1.55
		SFS(5)	0.68	0.11	1.76	0.66	0.12	1.71	0.66	0.14	1.71

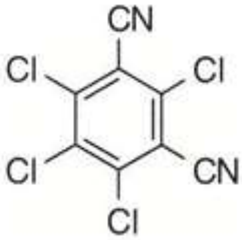
R^2c - coefficient of determination in calibration; RMSEC - root mean squared error in calibration; RPDC - residual predictive deviation in calibration; R^2cv - coefficient of determination in cross-validation; RMSECV - root mean squared error in cross-validation; RPDCV - residual predictive deviation in cross-validation; R^2p - coefficient of determination in prediction; RMSEP - root mean squared error in prediction; RPDP - residual predictive deviation in prediction.

Figures

(A)

(B)





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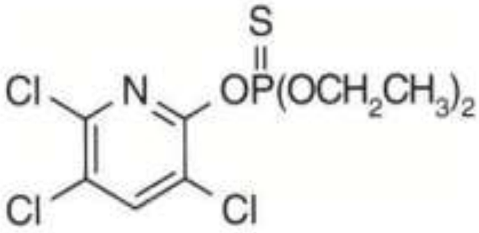

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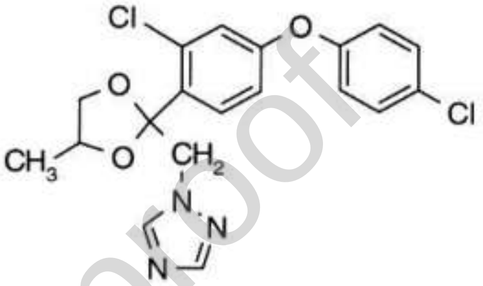

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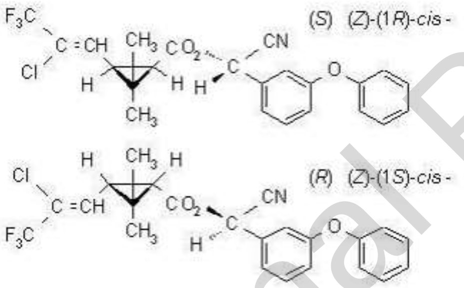

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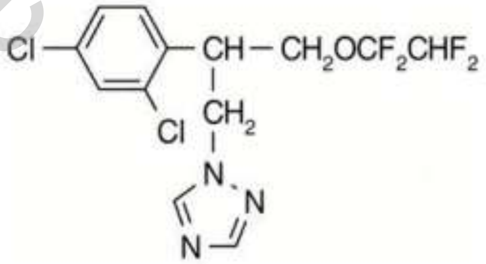


Figure 1. Structural formula for the pesticides azoxystrobin (A), chlorothalonil (B), chlorpyrifos (C), difenoconazole (D), lambda-cyhalothrin (E) and tetraconazole (F).

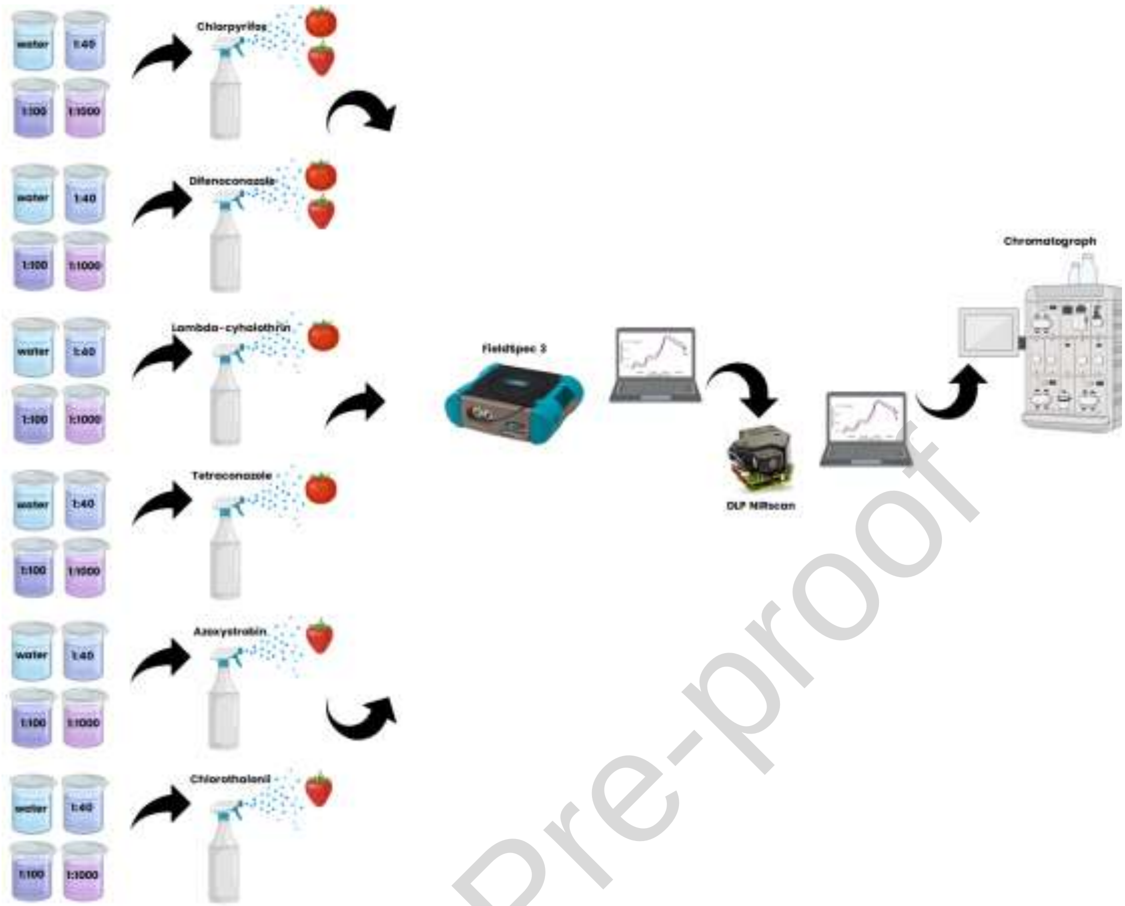
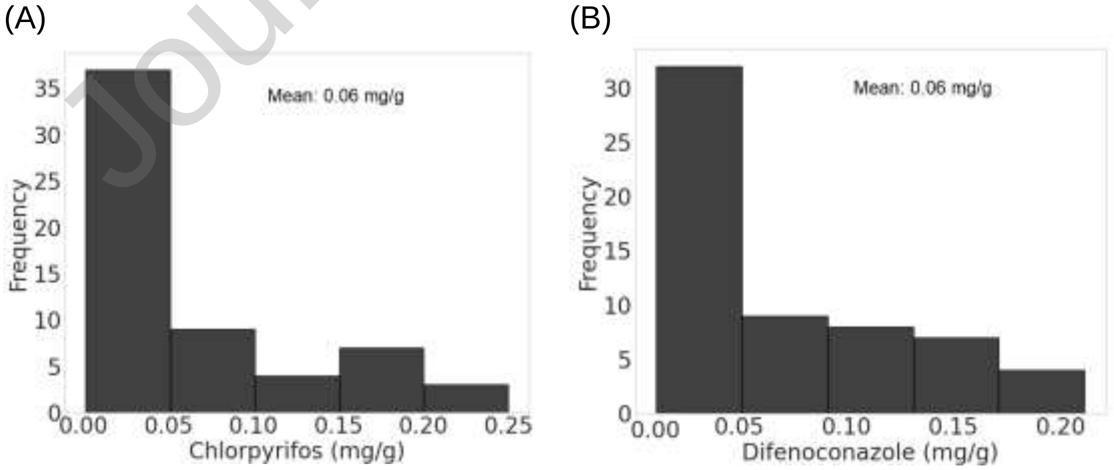


Figure 2. Schematic diagram of the experimental system, illustrating the sample preparation process, spectral acquisition instruments used and reference chromatographic analysis equipment.



(C) (D)

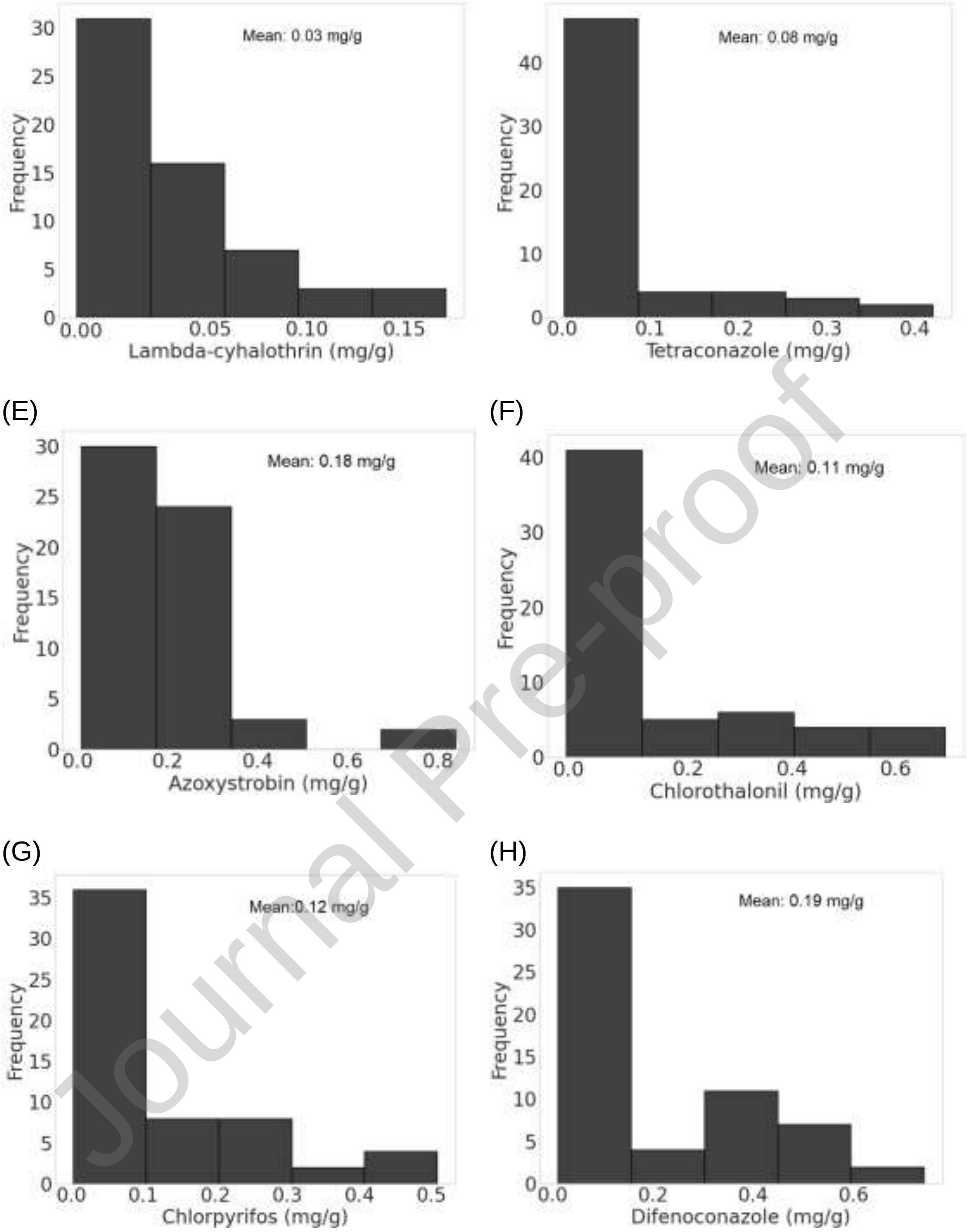


Figure 3. Histogram of concentrations for the pesticides chlorpyrifos (A), difenoconazole (B), lambda cyhalothrin (C), tetraconazole (D) quantified for cherry tomatoes and azoxystrobin (E), chlorothalonil (F), chlorpyriphos (G) and difenoconazole (H) quantified for strawberries.

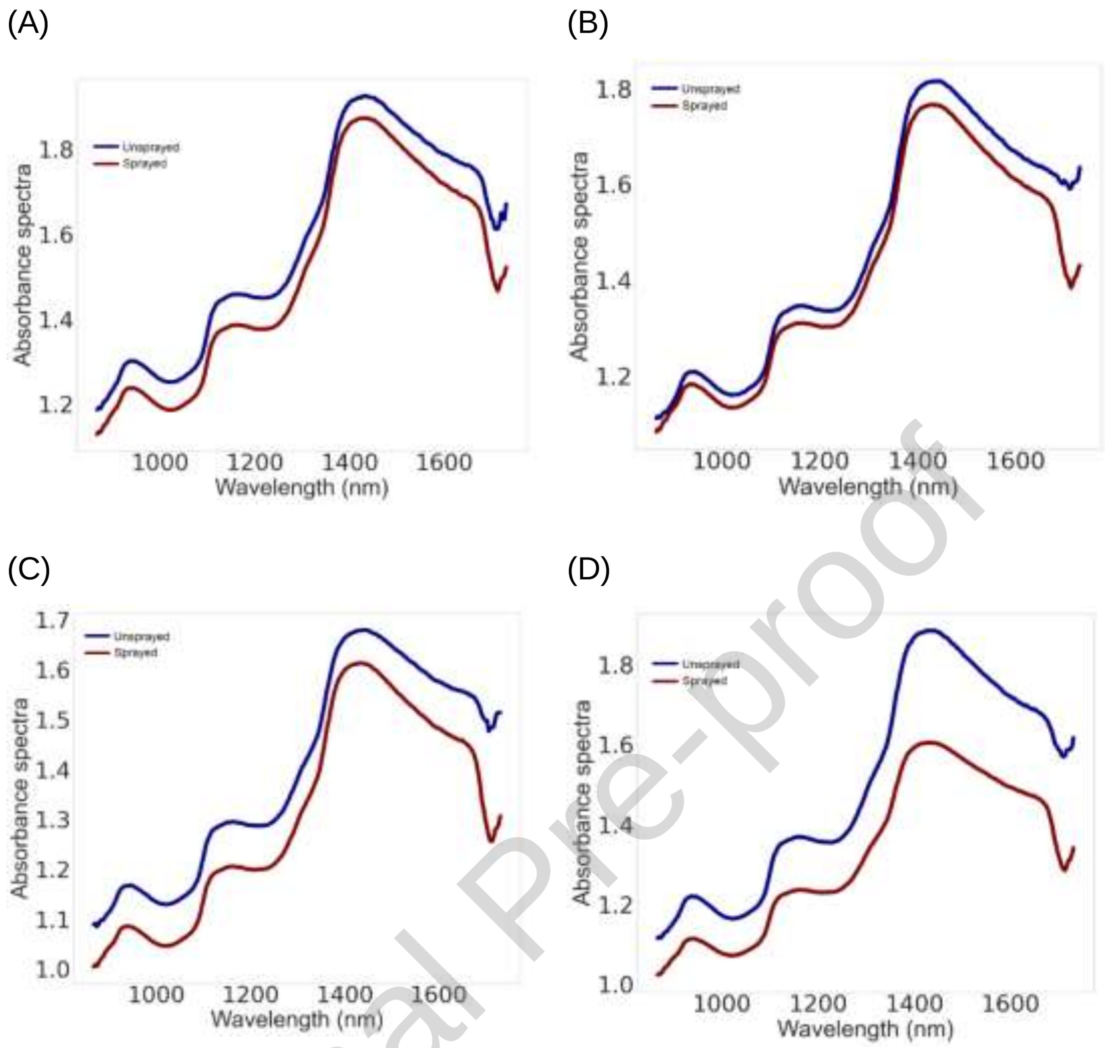
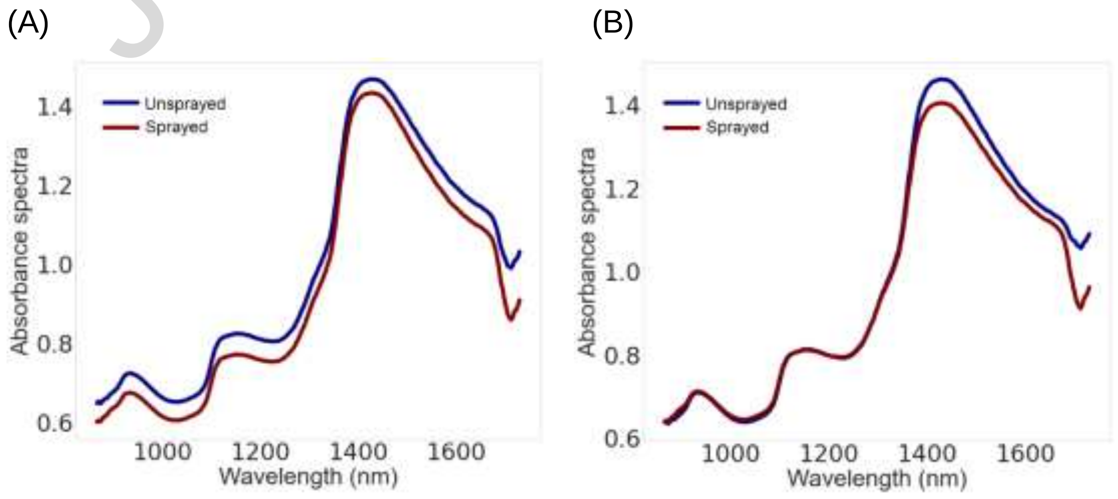


Figure 4. Average raw absorbance spectra for cherry tomatoes unsprayed or sprayed with pesticides chlorpyrifos (A), difenoconazole (B), lambda-cyhalothrin (C) and tetraconazole (D)



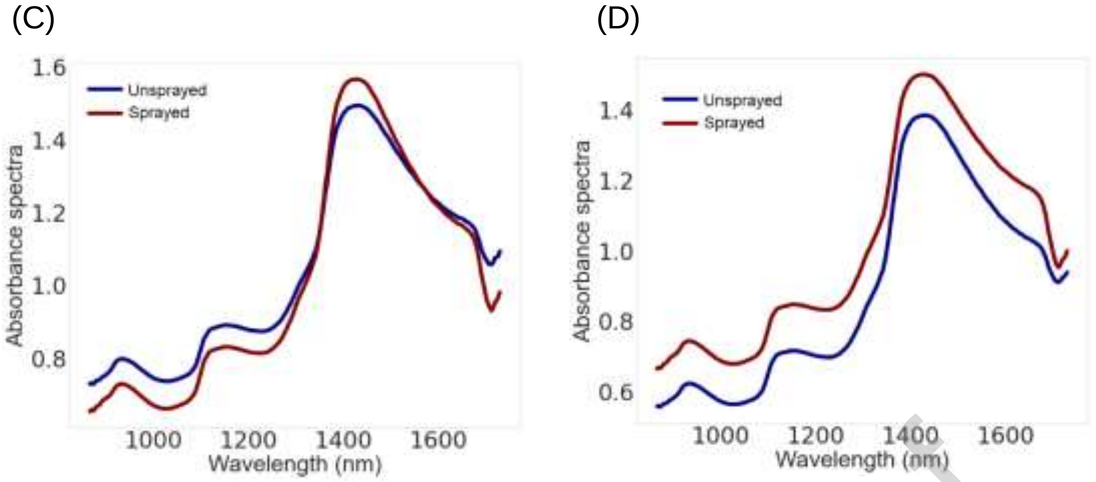
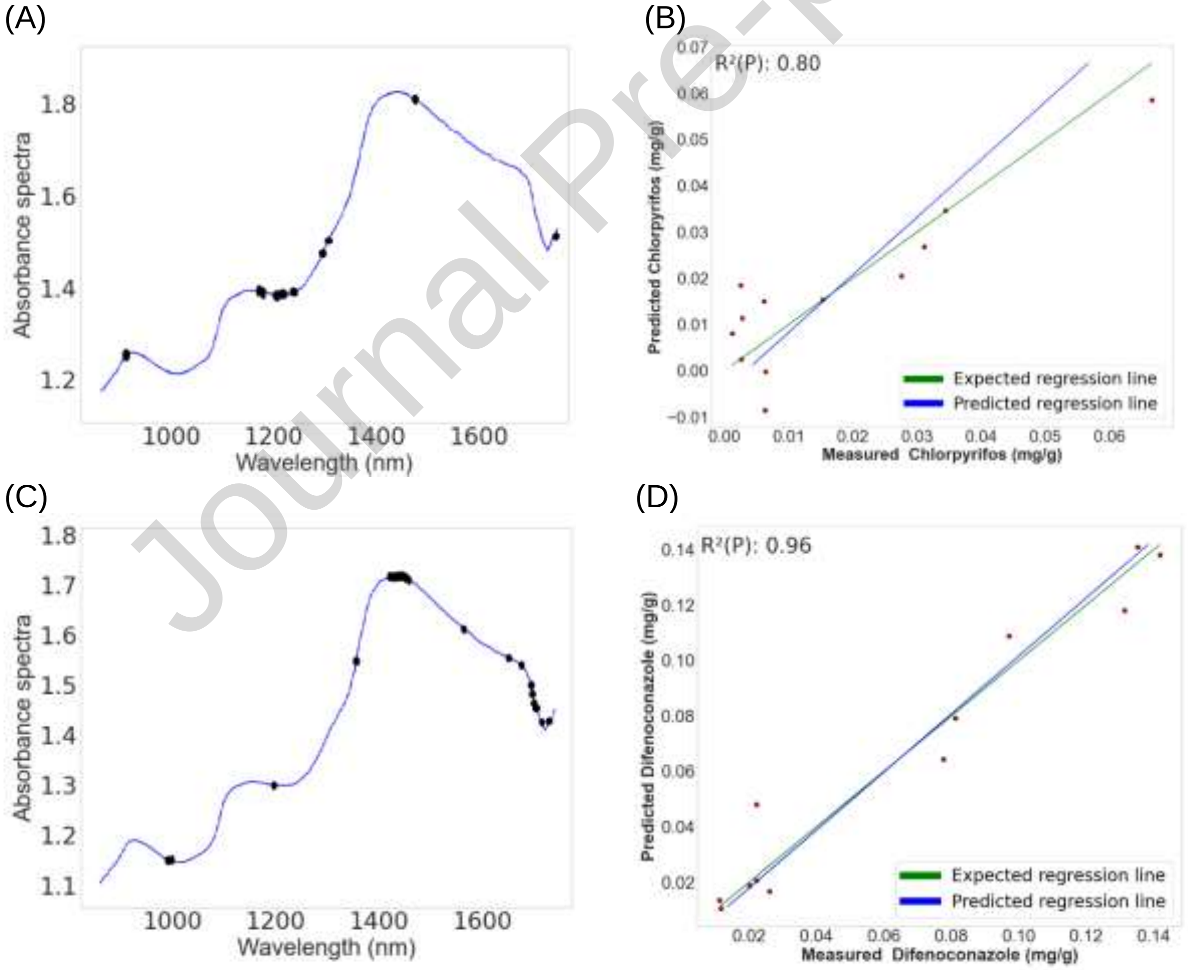


Figure 5. Average raw absorbance spectra for strawberries unsprayed or sprayed with pesticides azoxystrobin (A), chlorothalonil (B), chlorpyrifos (C), and difenoconazole (D).



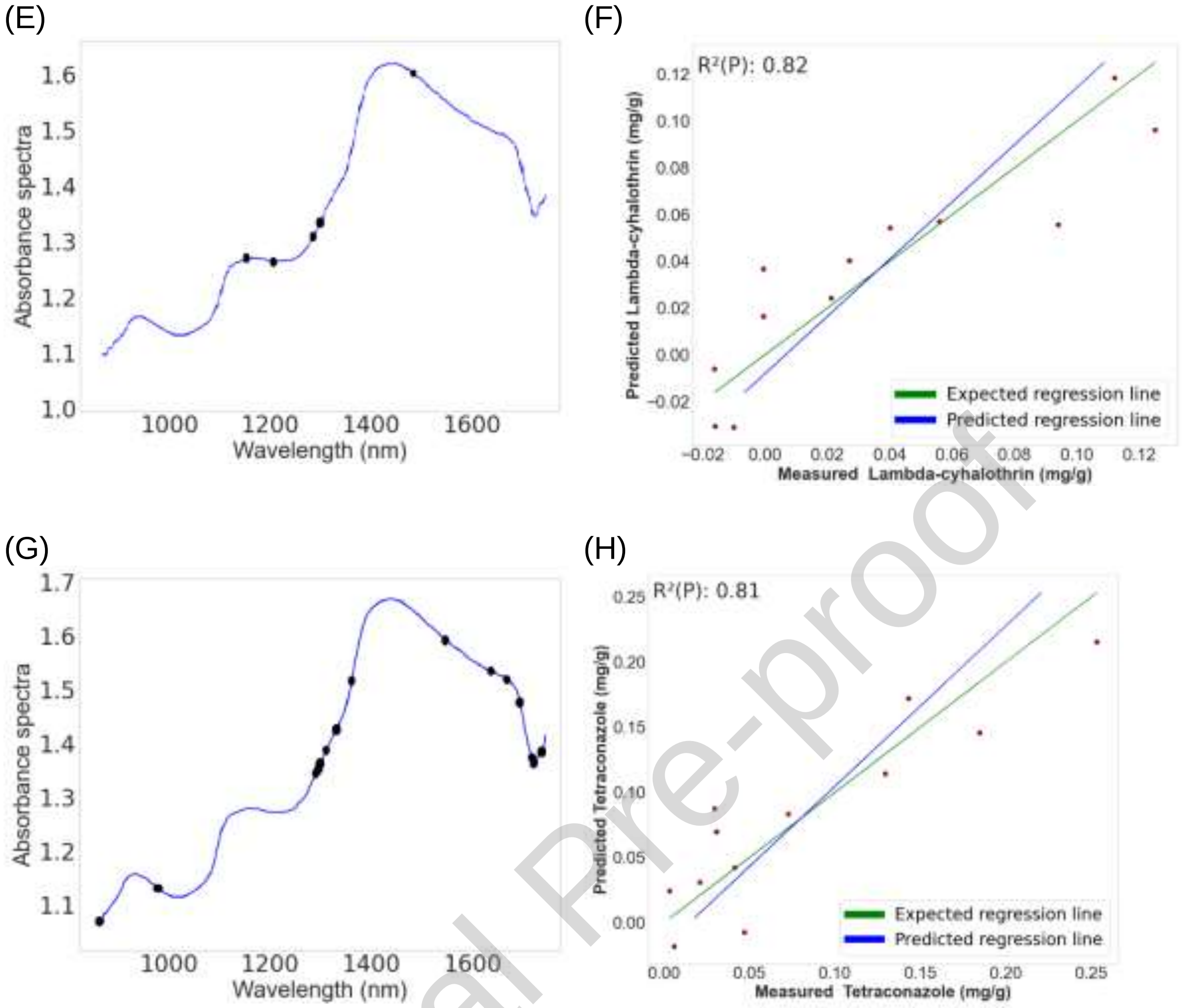
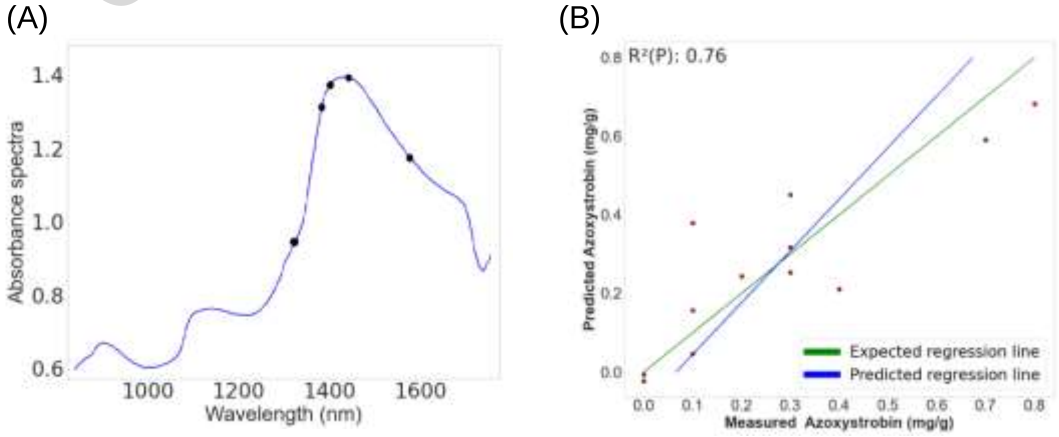


Figure 6. Selected wavelengths by RFE and scatter plots of pesticide concentrations in cherry tomatoes measured by reference methods versus predicted by OPLS models for chlorpyrifos (A, B), difenoconazole (C, D), lambda-cyhalothrin (E, F) and tetraconazole (G, H).



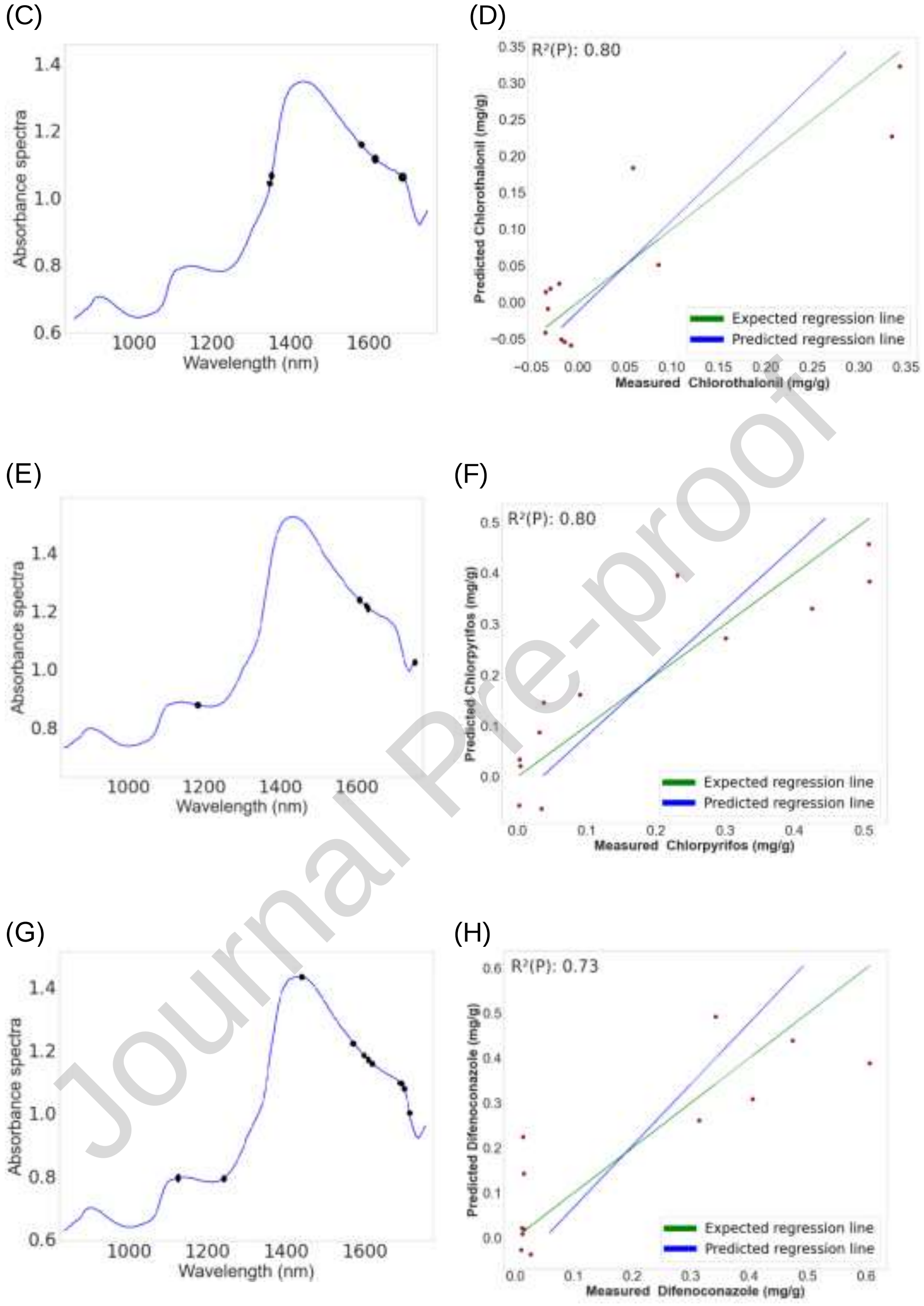


Figure 7. Selected wavelengths by RFE or SFM and scatter plots of pesticide concentrations in strawberries measured by reference methods versus predicted by OPLS models for azoxystrobin (A, B), chlorothalonil (C, D), chlorpyriphos (E, F) and difenoconazole (G, H).

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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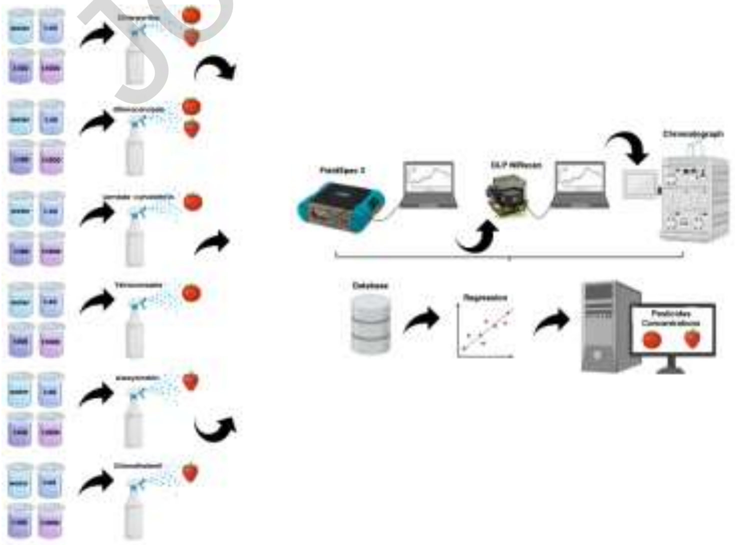

Graphical abstract

HIGHLIGHTS

NIRS and data mining can be used to detect pesticides residues in fresh fruits.

Models developed with specific wavelengths are highly accurate in pesticide analysis.

Portable NIR is a rapid and non-destructive method for pesticide analysis in fruits.