

Development of a Portable NIR Spectrometer for Detecting Pesticide Residues

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Abstract

The problem of pesticide residues found in fruits and vegetables that exceed the standard is something that all sectors are interested in solving. The main reason is that farmers, consumers, and relevant authorities do not know the real-time value of the residues. The detection of the pesticide residues is not immediately known since it must have been carried out at the central laboratory, where the received result will also take so long time. To solve this problem, our research team has designed and developed a portable near-infrared (NIR) spectrometer. The developed NIR spectrometer is designed to not only detect the reflected intensity of the residues in the wavelength range from 410 [nm] to 940 [nm] using the AS7265x chipset, but also collect and analyze the normalized spectral signal using the microprocessor ESP32-WROVER-B for detecting each type of the four pesticide residues: Carbendazim, Cypermethrin, Diazinon, and Imidacloprid. From experimental results on forty pesticide residues on basil leaves and chili from the local market in Phitsanulok province, it was conclusively demonstrated that the NIR spectrometer correctly identifies a tested type of the four pesticide residues on the twenty-eight basil leaves and twenty chili, and has more stable, consistent and accurate performance for detecting the pesticide type of the forty residues than the thin-layer chromatography method utilized at the central laboratory. Furthermore, the developed NIR spectrometer exhibits remarkable versatility and the best performance of detecting each type of the four pesticide residues on the twenty-eight basil leaves and twenty-eight chili or the total fifty-six samples as well as a test run repeated 100 times per sample and at seven concentration levels. At the pesticide concentration levels of 1, 2, 3, 4 and 5 mg/l, the Accuracy, Precision and Recall values were perfect at 1.00 and standard deviation of zero in all cases. Also, the Accuracy value was greater than 0.98 and both the Precision and Recall values were greater than 0.97 with an overall standard deviation of less than 0.013 when detecting the two pesticide residue types at concentration levels of 0.05 and 0.1 mg/l. Overall, the results showed that the proposed NIR spectrometer correctly detects pesticide residues in the concentration range from 1 [mg/l] to 5 [mg/l]. As well, the total cost of the tests with the portable NIR spectrometer was about 4,395 Baht. This cost is very reasonable particularly when the price of the proposed portable NIR spectrometer is nearly half that of devices with identical specifications that are sold on the commercial market.

Keywords: portable NIR spectrometer, NIR spectroscopy, pesticide detection algorithm, pesticide residues

Introduction

All people value good health, and the key to good health is the consumption of clean and certified food and, a complete and balanced ratio of nutrients to meet the needs of the body (Oliveira et al., 2021). If the food is contaminated by toxins, it will cause food poisoning that, if sufficiently severe, can result in death (Rather et al., 2017; Huck et al., 2016). The World Health Organization (WHO) estimates that there are 385 million cases annually, of pesticide residue-induced illness worldwide, resulting in about 11,000 deaths (Boedeker et al., 2020). In 2020, pesticide residues that exceeded the maximum residue limit for pesticide (MRL) were detected in 58.5% of all samples of fruit and vegetables. Pesticide residues that exceeded the harmful levels were found in 81% of basil leaves and 100% of chili. These are both edible plants popular in local cuisine in Thailand and sold in department stores, farmer markets and modern trade markets. (Thaipan, 2020).

There are many methods for detecting pesticide residues, which are performed mainly in laboratories using Gas Chromatography or Liquid Chromatography in conjunction with Mass Spectrometry (Rohinee et al., 2016).

There are also methods that can be applied on-site using various test kits such as a GT-Test Kit, GPO-M Kit, and GPO-TM Kit. However, these methods take a long time, use a lot of chemicals, and need experts to analyze the results for detected residues (Jamshidi et al., 2016). Detection processes need to be performed quickly and produce reliable results. Therefore new techniques and processes have been developed by various research teams (Cecilie et al., 2020), including a UV-VIS-NIR spectrometer (Rathnakumar et al., 2020; Soylak et al., 2023), NIR spectroscopy (Mayr et al., 2021) and (Ye et al., 2020) as alternatives to traditional methods (Sun, 2008; Stadler et al., 2016). Although these techniques can reduce the chemical steps to analyze the related data, the size of the measurement tools is still quite large and can only be used and the results analyzed in the laboratory. Also, the price of these tools is high; up to 500,000 Baht per device.

For these reasons, spectroscopic techniques have been developed to operate on newly available portable near-infrared (NIR) spectrometers that are low-cost, provide correct detection results obtained quickly by on-site testing and are non-destructive of the tested samples. For example, Nazarloo and his colleagues have built a portable spectrometric system to detect pesticide residues in agricultural produce using a spectroradiometer, a PS-100 model produced by Apogee Instruments, INC., Logan, UT, USA for the detection of pesticide residues in tomatoes (Nazarloo et al., 2021). The device detected pesticide residues of chlorantraniliprole, indoxacarb, emamectin benzoate, carbendazim and gibberellic acid residues in lettuce, mustard green and choy sum. Although a portable visible-near infrared (VIS-NIR) spectrometer was developed by using the Nanolambda spectral sensor with a model of NSP32m-W1 ADK (Viet-Duc et al., 2022), the fast development of the portable VIS-NIR spectrometers in respond to commercial markets requirements occurred. These devices can test samples off-site and can decrease the cost down to the range of 20,000 Baht to 200,000 Baht. However, these prices are still too expensive for widespread market adoption (Market Research Future, 2023).

In previous research, spectrometers and spectral sensors have been used for pesticide residue testing and detection. For example, the AS7265x multi-spectral sensor has been confirmed to operate correctly, with performance and spectral response equal to those achieved from the laboratory-level spectrometers or similarly specified tools (Bruzze et al., 2022; Yang et al., 2020; Tran et al., 2020; Nguyen et al., 2021; Sowmya et al., 2023; Botero-Valencia et al., 2021; Shokrehodaei et al., 2021). The spectral response of the sensors with the accepted high-resolution spectral libraries in the academic world has been reflected in (Shahrabani et al., 2020). The accuracy of the spectral data obtained from these sensors has been assured, which may help public health workers use on-site NIR spectrometers developed to support both household and local pesticide residue prevention for easily detecting pesticide residues on vegetables anytime, anywhere.

In the current research, a low-cost portable VIS-NIR spectrometer was designed and developed as a special tool to measure and collect the power reflectance in the wavelength range from 410 [nm] to 940 [nm] as input spectra using the AS7565x sensor, and to analyze normalized spectra signals using the microprocessor ESP32-WROVER-B for predicting the type of the four pesticide residues: Carbendazim, Cypermethrin, Diazinon, and Imidacloprid on the basil leaves and chili. The performance of the experimental spectrometer was compared to the chemical methods used at the central laboratory of the Office of Agricultural Research and Development Region 2, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand.

Methods and Materials

Proposed Process for Detecting Pesticide Residues.

The portable near-infrared (NIR) spectrometer was designed and developed by the author team to detect pesticide residues on basil leaves and chili by the detection process shown in Fig. 1, and the experimental portable NIR spectrometer was able to perform all three main steps of the detection process; the light-to-signal converter step, the signal enhancement step and the detection step.

In the light-to-signal converter step, a light signal from the light source is changed into a spectral signal of eighteen wavelengths $\{\lambda_n\}$, where $\{\lambda_n\}$ is an index sequence of eighteen wavelengths and n is the index number of the integer set $\{1, 2, 3, \dots, 18\}$.

In the signal enhancement step, the spectral signal is recorded as a discrete-time signal or a spectral sequence, $\{x_{ij}[\lambda_n]\}$ into the microcontroller, and the unnormalized spectral data, $\{x_{ij}[\lambda_n]\}$, is then enhanced by computing the average of the four spectral data and by dividing with the ℓ_2 norm of the computed spectral data, where i is an index of the medium type, j is an index of the four spectral data. The output signal of the signal enhancement process gives the normalized spectral data $\{x_i[\lambda_n]\}$ as a representative type of pesticide residues in the next detection process.

In the detection step, the normalized spectral data $\{x_i[\lambda_n]\}$ is computed and determined to find out the wavelength location, $\lambda_{n_0} \in \{1, 2, \dots, 18\}$, at which the maximum value, m_i , of the normalized spectral data by using the controller. These (λ_{n_0}, m_i) points obtained from their spectra sequences $\{x_i[\lambda_n]\}$ can be used to specify or identify the pesticide residue on the basil leaves and chili.

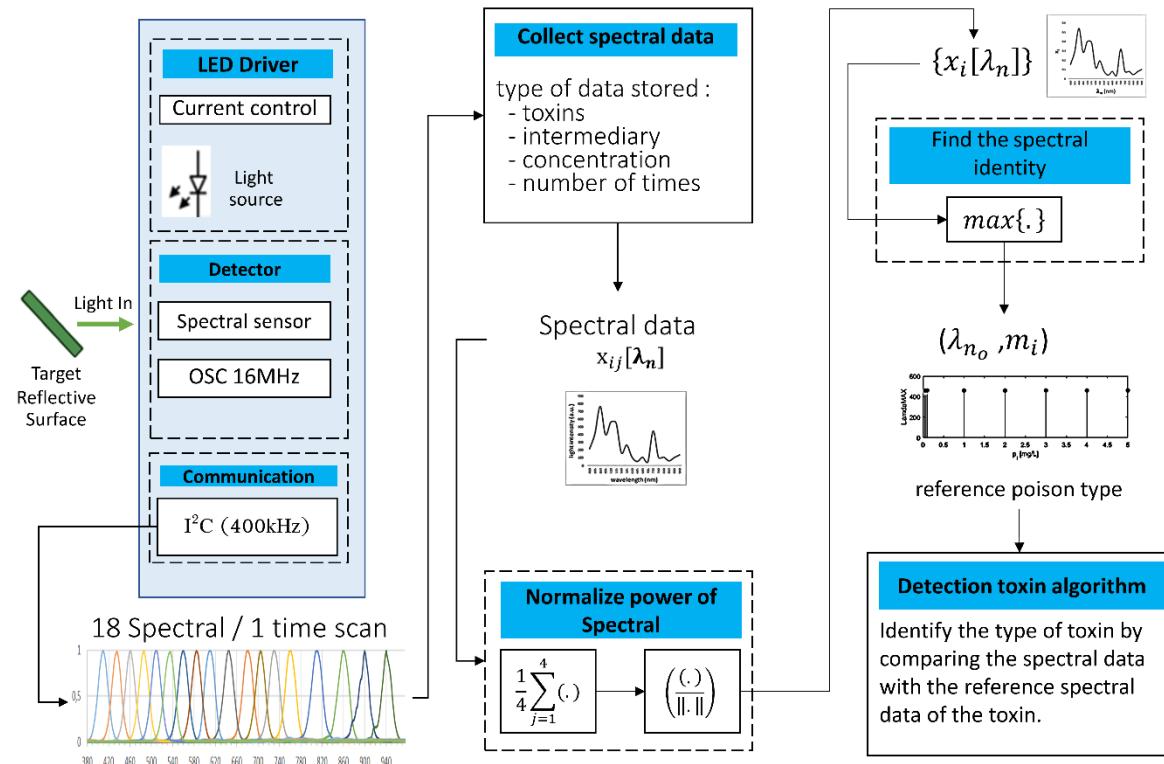


Figure 1 Overview of the proposed process to detect pesticide residues by using the developed portable NIR spectrometer

Proposed Portable NIR Spectrometer for Detecting Pesticide Residues.

For the main purpose of this research, the portable NIR spectrometer was proposed, designed, and developed to detect pesticide residues on basil leaves and chili. To develop the portable NIR spectrometer, a reflected aperture is first created shown in Fig. 2(a) to cover the light source of the triad spectroscopic sensor chipset (AS7265x SparkFun Electronics, 2023) to angle the light to correctly hit the test pesticide residues on the leaves while preventing sensor interference of the reflective intensity from external light.

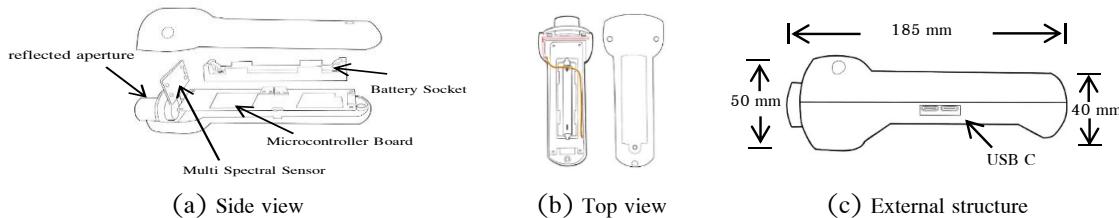


Figure 2 illustrates the structure of the developed portable VIS–NIR spectrometer

The AS7265x code of the triad spectroscopic sensor chipset was used since it is cheap and readily available in Thailand. The multi-spectra sensor installed shown in Fig. 2(a) is designed to have a reflection mode at the wavelengths from 410 [nm] to 940 [nm] with a full amplitude at a half maximum value of 20 [nm] by using the AS7265x chipset (SparkFun Electronics, 2023), and the multi-spectra sensor can fully receive the reflection intensity from the tested residues. The used chipset consists of three light emitting diodes (LEDs): 5700-Kelvin white LEDs, 405-nm UV LEDs and 875-nm IR LEDs and has a Gaussian filter to cut the waves, has electronic shutters, and also has eighteen photodiode sensors producing spectral lines at eighteen wavelengths $\{\lambda_n\}$: 410 [nm], 435 [nm], 460 [nm], 485 [nm], 510 [nm], 535 [nm], 560 [nm], 585 [nm], 610 [nm], 645 [nm], 680 [nm], 705 [nm], 730 [nm], 760 [nm], 810 [nm], 860 [nm], 900 [nm] and 940 [nm], where n is the number of the set $\{1, 2, 3, \dots, 18\}$; for example, λ_1 represents a wavelength of 410 [nm] in the case of $n = 1$, or λ_{18} represents a wavelength of 940 [nm] in the case of $n = 18$. Then, the microcontroller chipset (ESP32-WROVER-B from Espressif Systems (Shanghai) Co., Ltd., 2023), is applied as a controller of the microcontroller board shown in Fig. 2(a) to collect the reflective intensity of all the wavelengths into the spectrum obtained from the light source (the AS7265x chipset) by using the collection algorithm for the spectrum (GitHub, Inc., 2023) to normalize the power of the spectrum for enhancing spectrum, to analyze the spectra data and to store the controller commands. The processing data can also transfer between the input and the processor via an I²C bus at a clock frequency of 400 kHz. The spectra data is obtained from the average of the reflective intensity of the vegetable medium collected four times at different areas of the tested sample to reduce errors caused by the uneven surface of the medium, and the spectral data were collected between 8 a.m and 4 p.m. at a room temperature between 22 °C and 32 °C. Furthermore, the controller can also compute the normalized spectral data $\{x_i[\lambda_n]\}$ to identify the wavelength position in the format of the point pair (λ_{n_0}, m_i) , where $\lambda_{n_0} \in \{1, 2, \dots, 18\}$ is the corresponding wavelength at each of the peak values (m_i) of the spectral data. The wavelength position is detected to determine and specify the type of pesticide residues on the vegetable medium by using the point pair (λ_{n_0}, m_i) . There have been many research reports written that indicate that at the corresponding wavelength position $\lambda_{n_0} \in \{1, 2, \dots, 18\}$ at the peak value (m_i) of the normalized spectral data $\{x_i[\lambda_n]\}$ with a pesticide concentration of level i can be used as a reference wavelength to identify the type of pesticide

residues on the vegetable medium (Bhaskara, 2006; Aira et al., 2022), and there are also four research reports shown in Table 1 that give the reference wavelength that can identify the four types of pesticide residues: Carbendazim, Cypermethrin, Diazinon and Imidacloprid on a vegetable medium.

Table 1 Wavelength, λ_{n_0} at which the four pesticide residues were detected

Class of Pesticide	Wavelength, λ_{n_0} (nm)	Wavelength range	Report developed by
Carbendazim	400	350 – 2,500	Lu et al., (2021)
Cypermethrin	535	400 – 700	Mane et al. (2020)
Diazinon	900	450 – 1,000	Jamshidi et al., (2015)
Imidacloprid	835	348 – 1141	Yu et al. (2020)

Finally, this research proposed an experiment to detect the type of the four pesticide residues on chillies and basil leaves with seven levels of the tested pesticide concentration using the specially developed portable NIR spectrometer illustrated in Fig. 2. The proposed NIR spectrometer was to have a thickness– length– weight dimension of a 50-mm maximum thickness and a 185-mm length, with a total weight of 98 [gram], and with a USB– C connector to either charge the 3.7– volt lithium– ion battery with a capacity of 1,800 [mAh] and a voltage range from 3.3 [V] to 5.0 [V] installed shown in Fig. 2(a) or transmit spectrum at a maximum speed of 115,200 [baud] to communicate between sensing module and control module shown in Fig. 3.

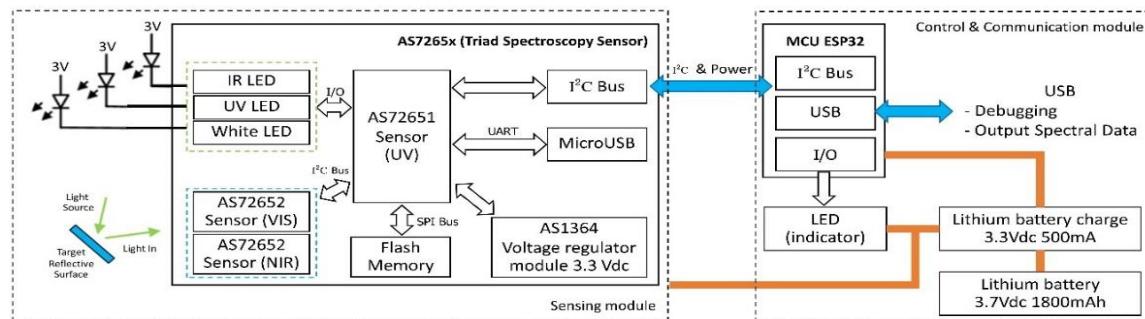


Figure 3 Communication and control module of the developed portable NIR spectrometer

Detection Performance of the Proposed NIR Spectrometer.

The performance of the developed spectrometer was tested in two ways. First, the efficiency of detecting pesticide residues on vegetables in general, and then the efficiency of detecting each of the four pesticide residue types on basil leaves and chili. The Accuracy, Precision and Recall results of the performance measurements were defined by the three following equations.

$$\text{Accuracy} = \frac{\text{Number of Correct Identifications}}{\text{Total Number of Samples}}, \quad (1)$$

$$\text{Precision} = \frac{\text{True Positive} (T_p)}{\text{True Positive} (T_p) + \text{False Positive} (F_p)}, \quad (2)$$

$$\text{Recall} = \frac{\text{True Positive} (T_p)}{\text{True Positive} (T_p) + \text{False Negative} (F_n)}. \quad (3)$$

To measure the efficiency of the experimental spectrometer in detecting the four pesticide residues on vegetables, the number of times that the spectrometer identified the existence or absence of pesticide residues

was identified. The data was then recorded into a two-class confusion matrix, illustrated in Table 2, where T_p is the number of times pesticide residues were correctly identified, and F_n is the number of times the absence of pesticide residues was correctly identified. For incorrect identification of residues, F_p is the number of times pesticide residues that did not exist were shown as being detected, and T_n is the number of times that actual pesticide residues were not detected. Eq's. (1), (2) and (3) were applied to calculate the overall efficiency of the developed spectrometer for detecting pesticide residues.

Table 2 Two-class confusion matrix used to compute the efficiency of the developed spectrometer for detecting pesticide residues

Pesticide Residues	Actually Positive	Actually Negative
	(Pesticides exist)	(Pesticides don't exist)
Predicted Positive (Pesticides exist)	T_p	F_n
Predicted Negative (Pesticides don't exist)	F_p	T_n

To measure the efficiency of the developed spectrometer for detecting the four types of pesticide residues on vegetables, the two-class confusion matrix can be expanded to the four-class confusion matrix as shown in Table 3 with the experimental data recorded as $\{n_{ik}\}$, $i \in \{1,2,3,4\}$ and $k \in \{1,2,3,4\}$ for each type of the residues. Then, the basic formulae in Eq's. (1), (2) and (3) can be used to calculate the efficiency of the developed spectrometer for the Accuracy, Precision and Recall of detecting pesticide types.

Table 3 Four-class confusion matrix used to compute the efficiency of the developed spectrometer for detecting a pesticide type

		Actual type			
Predicted type	Pesticide type	Carbendazim	Cypermethrin	Diazinon	Imidacloprid
	Carbendazim	n_{11}	n_{12}	n_{13}	n_{14}
	Cypermethrin	n_{21}	n_{22}	n_{23}	n_{24}
	Diazinon	n_{31}	n_{32}	n_{33}	n_{34}
	Imidacloprid	n_{41}	n_{42}	n_{43}	n_{44}

$$Accuracy = \begin{cases} (n_{11} + \sum_{i=2}^4 \sum_{k=1}^4 n_{ik}) / (\sum_{i=1}^4 \sum_{k=1}^4 n_{ik}) & \text{for Carbendazim type} \\ (\sum_{i=1}^4 n_{ii} + \sum_{k=3}^4 [n_{1k} + n_{k1}] + n_{34} + n_{43}) / (\sum_{i=1}^4 \sum_{k=1}^4 n_{ik}) & \text{for Cypermethrin} \\ (\sum_{i=1}^4 n_{ii} + \sum_{k=1}^2 [n_{4k} + n_{k4}] + n_{12} + n_{21}) / (\sum_{i=1}^4 \sum_{k=1}^4 n_{ik}) & \text{for Diazinon type,} \\ (n_{44} + \sum_{i=1}^3 \sum_{k=1}^3 n_{ik}) / (\sum_{i=1}^4 \sum_{k=1}^4 n_{ik}) & \text{for Imidacloprid type} \end{cases} \quad (4)$$

$$Precision = \begin{cases} n_{11} / (\sum_{k=1}^4 n_{1k}) & \text{for Carbendazim} \\ n_{22} / (\sum_{k=1}^4 n_{2k}) & \text{for Cypermethrin} \\ n_{33} / (\sum_{k=1}^4 n_{3k}) & \text{for Diazinon type,} \\ n_{44} / (\sum_{k=1}^4 n_{4k}) & \text{for Imidacloprid} \end{cases} \quad (5)$$

$$Recall = \begin{cases} n_{11} / (n_{11} + \sum_{k=2}^4 n_{k1}) & \text{for Carbendazim} \\ n_{22} / (n_{22} + n_{12} + n_{32} + n_{42}) & \text{for Cypermethrin} \\ n_{33} / (n_{33} + n_{13} + n_{23} + n_{43}) & \text{for Diazinon type,} \\ n_{44} / (n_{44} + \sum_{k=1}^3 n_{k4}) & \text{for Imidacloprid} \end{cases} \quad (6)$$

In Table 3, the $\{n_{ik}\}$ number for $i \in \{1,2,3,4\}$ and $k \in \{1,2,3,4\}$ can be described in terms of the four-class confusion matrix as follows.

True Positive (T_p), n_{11} , n_{22} , n_{33} and n_{44} , is the number of times that the right type of Carbendazim (CBZ), Cypermethrin (CPT), Diazinon (DAN) and Imidacloprid (IMP) were correctly predicted.

False Positive (F_p), the sum of $(n_{12} + n_{13} + n_{14})$, $(n_{21} + n_{23} + n_{24})$, $(n_{31} + n_{32} + n_{34})$ and $(n_{41} + n_{42} + n_{43})$, is the number of times that the right type of the CBZ, CPT, DAN and IMP were incorrectly predicted.

False Negative (F_n), the sum of $(n_{21} + n_{31} + n_{41})$, $(n_{12} + n_{32} + n_{42})$, $(n_{13} + n_{23} + n_{43})$ and $(n_{14} + n_{24} + n_{34})$, is the number of times that a wrong type of the CBZ, CPT, DAN and IMP were incorrectly predicted.

True Negative (T_n), the sum of $(n_{22} + n_{23} + n_{24} + n_{32} + n_{33} + n_{34} + n_{42} + n_{43} + n_{44})$, $(n_{11} + n_{13} + n_{14} + n_{31} + n_{33} + n_{34} + n_{41} + n_{43} + n_{44})$, $(n_{11} + n_{12} + n_{14} + n_{21} + n_{22} + n_{24} + n_{41} + n_{42} + n_{44})$ and $(n_{11} + n_{12} + n_{13} + n_{21} + n_{22} + n_{23} + n_{31} + n_{32} + n_{33})$, is the number of times that a wrong type of the CBZ, CPT, DAN and IMP were correctly predicted.

Results and Discussion

Results of Developing the Proposed Spectrometer.

The internal components of the experimental NIR spectrometer are arranged and assembled so that the light sensor is perpendicular to the testing sample. Light interference is prevented by the cover assembly. The external cover was created using a 3D printer (Flashforce Finder3), as shown in Fig. 4. The total cost of developing this spectrometer was 4,395 Baht. The cost details are listed in Table 4 showing the multispectral sensor AS7265x with a price of 3,450 Baht, the microcontroller ESP32-WROVER-B with a price of 395 Baht, the batteries with a price of 60 Baht and equipment exterior frame with a price of 490 Baht.

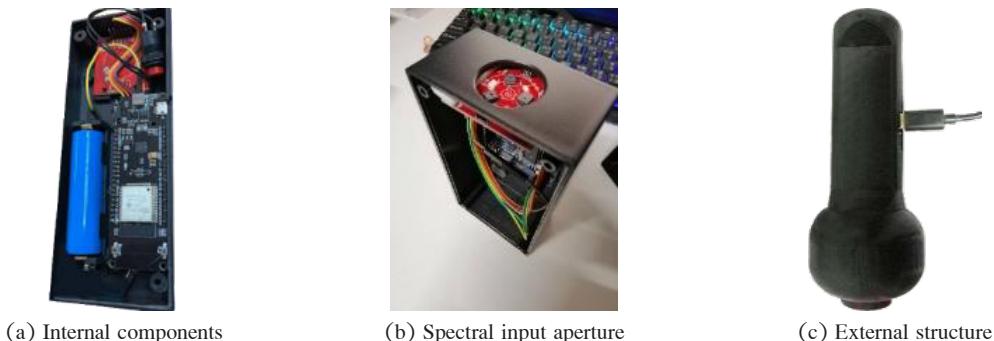


Figure 4 Internal components and structure of the developed portable NIR spectrometer

Table 4 Cost and list of materials used in the developed NIR spectrometer

Materials	Components	Total cost	Source of Materials
AS7265x	Spectral sensor	3,450	https://sparkfun.com/
ESP32-WROVER-B	Microcontroller	395	https://www.arduitronics.com/
Battery	Li-Ion (1800 mAh)	60	https://www.aliexpress.com/
Case	Enclosure	490	Knowledge Centric Co., Ltd.
<u>4,395</u>			

In addition, the characteristics and price of the developed spectrometer were compared to devices with the same specifications available on the commercial market. The comparisons are shown in Table 5. The cost of the

experimental spectrometer is 2%, 5%, 13% or 22% of the price of the other devices listed but the developed NIR spectrometer can achieve the same Accuracy, Precision and Recall results as those other devices.

Table 5 Specification comparison between portable VIS-NIR spectrometers available on the market and the developed spectrometer

brand/ model	HOPOOCOLOR OHSP350S	Lisun LMS-6000SF	Texas Instrument DLPNIRNANOEV	Torchbearer T21B7U10034FMP1	Developed Spectrometer
cost	THB 208,404.00	THB 84,890.14	\$999.00 (USD)	THB 20,006.64	THB 4,395
Light source	Include	Include	Include	Include	Include
Detector	CCD	CCD	InGaAs	CCD	photodiode
Wavelength	350–950nm	350–950nm	900–1,700 nm	340–1000nm	410 – 940nm
Processing	inside	inside	inside / PC	PC	inside
Display	5 Inches LCD	5-inch LCD	PC	PC	LED light
Size	138.5*81*23mm	135*80*23mm	36*58*62mm	53*27*24mm	145*50*50mm
Weight	430g	430g	84g	20	98g
Bandwidth	2 nm (FWHM)	0.2 nm	10 nm	5nm	20 nm

Sample Preparation Results for Detecting Pesticide Residues.

To prepare specimens used in the detection process for each type of four pesticide residues: Carbendazim, Cypermethrin, Diazinon and Imidacloprid, sample pesticide residues were obtained from the Agricultural Research and Development Laboratory, Area II, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand. All were packaged in brown opaque bottles as shown in Fig. 5. Each bottle has a volume of 10 [ml] and each type of residue had seven different concentration levels: 0.05 [mg/l], 0.1 [mg/l], 1 [mg/l], 2 [mg/l], 3 [mg/l], 4 [mg/l] and 5 [mg/l].

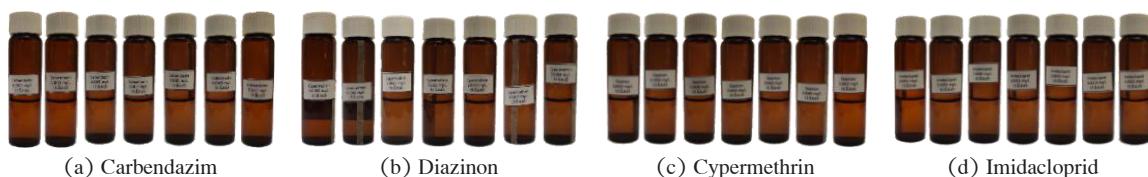


Figure 5 Seven bottles per a type of seven concentration levels: 0.05, 0.1, 1, 2, 3, 4 and 5 [mg/l]

Fifty-six pesticide samples on basil leaves and chili were prepared by washing these with running water for eight hours to remove impurities and then dried for 8 hours. The pesticide residues at the seven concentration levels were then mixed on each of the basil leaves and chili to get 56 testing samples. Each sample was contaminated with one of the four pesticide residues: Carbendazim, Cypermethrin, Diazinon and Imidacloprid at each concentration of the seven levels: 0.05, 0.1, 1, 2, 3, 4 and 5 [mg/l].

Detection Results for Identifying a Pesticide Property.

To determine the properties of the four types of pesticide residues on the sample leaves using the experimental spectrometer, sample preparation was begun by using seven pesticide concentration levels of 0.01, 0.1, 1, 2, 3, 4 and 5 [mg/l] of each pesticide of Carbendazim, Cypermethrin, Diazinon and Imidacloprid residues; that is, twenty-eight residues on basil leaves as Sample#1 thru Sample#28 shown at the top row of Fig. 6 and the more twenty-eight residues on chili as Sample#29 thru Sample#56 shown at the bottom of Fig. 6.

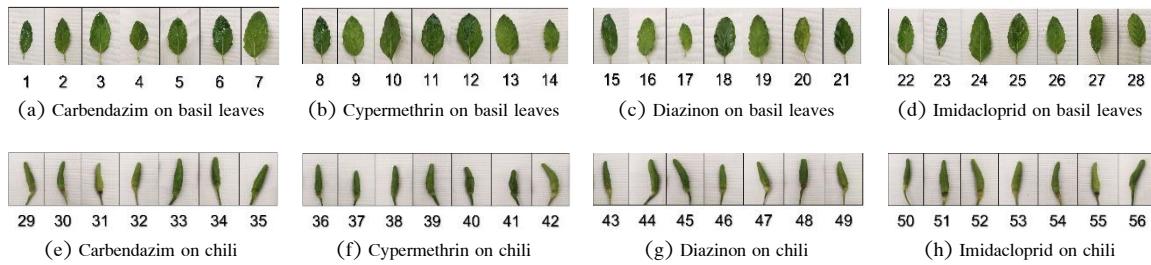


Figure 6 Fifty-six pesticide samples on the basil leaves and chili at each of 0.05, 0.1, 1, 2, 3, 4 and 5 [mg/l]

The 56 samples were each scanned 25 times per position per sample at four scanned positions per sample, 100 times per sample, as shown in Fig. 7, to collect the reflective intensity via the multi-spectra sensor measuring from the tested residues by using the AS7265x chipset, which consists of three light emitting diodes and eighteen photodiode sensors producing spectral lines at eighteen wavelengths: 410 [nm], 435 [nm], 460 [nm], 485 [nm], 510 [nm], 535 [nm], 560 [nm], 585 [nm], 610 [nm], 645 [nm], 680 [nm], 705 [nm], 730 [nm], 760 [nm], 810 [nm], 860 [nm], 900 [nm] and 940 [nm] denoted as a wavelength sequence $\{\lambda_n\}$, where n is the number of the set $\{1, 2, 3, \dots, 18\}$, and the collected reflective intensity of all the wavelengths into the spectrum by using the collection algorithm for enhancing the spectrum to give a plot of the normalized spectral signal $\{x_i[\lambda_n]\}$ and λ_n shown in Fig. 8.



Figure 7 Pesticide residues scanned by using the proposed portable spectrometer

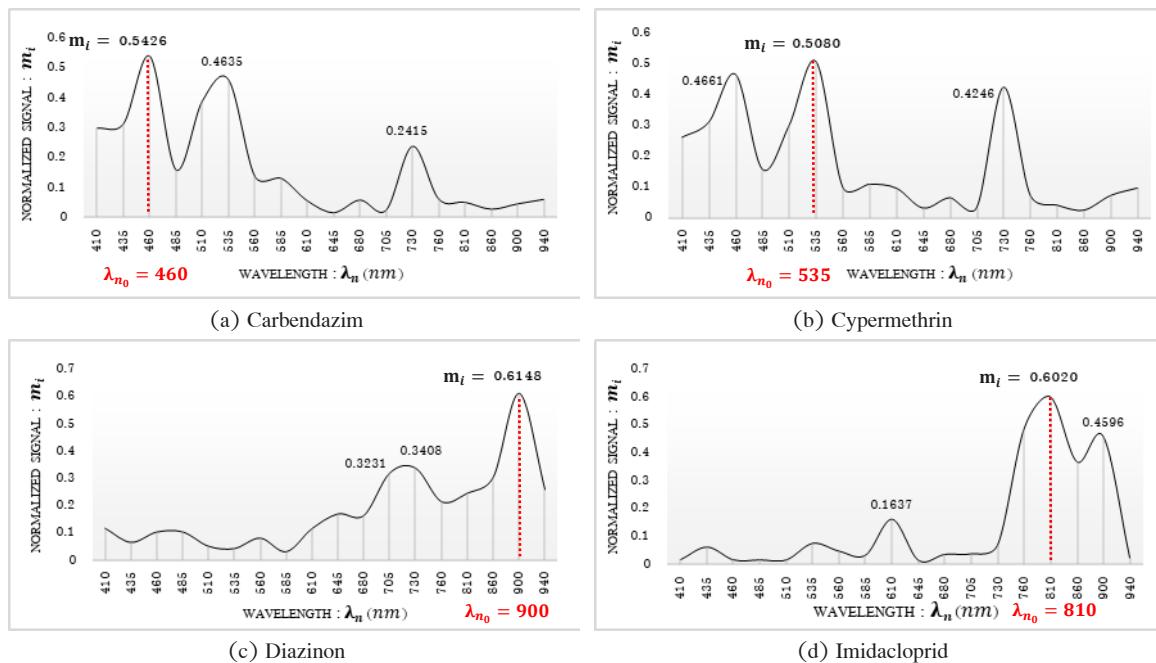


Figure 8 A plot of the normalized spectral signal and wavelength for a type of the four pesticide residues on the leaves

Using the plot of the normalized spectral signal ($x_i[\lambda_n]$) and wavelength λ_n shown in Fig. 8 find out the corresponding wavelength λ_{n_0} at each of the peak values (m_i) of the spectral signal in the format of the point pair (λ_{n_0}, m_i) , where $\lambda_{n_0} \in \{1, 2, \dots, 18\}$ and $i \in \{1, 2, \dots, 7\}$ is the level index of seven pesticide concentrations: 0.01, 0.05, 1, 2, 3, 4 and 5 [mg/l] to specify a type of four pesticide residues: Carbendazim, Cypermethrin, Diazinon and Imidacloprid on the basil leaves and chili. The wavelength λ_{n_0} corresponding to the peak value m_i obtained from the proposed spectrometer is determined in Table 6.

Table 6 The (λ_{n_0}, m_i) point of the peak values and their wavelengths obtained from scanning the total fifty-six pesticide residues on the basil leaves and chili run at 100 times/residue

Medium type	Concentration (mg/l)	$\lambda_{n_0}(\text{nm})$				m_i			
		CBZ	CPT	DAN	IMP	CBZ	CPT	DAN	IMP
Basil leaves	0.05	460	535	900	810	0.5111	0.4933	0.6539	0.6015
	0.1	460	535	900	810	0.5115	0.4987	0.6559	0.6025
	1	460	535	900	810	0.5560	0.5534	0.6850	0.6129
	2	460	535	900	810	0.6212	0.5969	0.7096	0.6261
	3	460	535	900	810	0.6661	0.6278	0.7227	0.6347
	4	460	535	900	810	0.6946	0.6814	0.7288	0.6404
	5	460	535	900	810	0.7129	0.7058	0.7383	0.6395
Chili	0.05	460	535	900	810	0.4702	0.4759	0.5916	0.5758
	0.1	460	535	900	810	0.4727	0.4790	0.5931	0.5794
	1	460	535	900	810	0.5426	0.5080	0.6148	0.6020
	2	460	535	900	810	0.5850	0.5296	0.6370	0.6284
	3	460	535	900	810	0.6280	0.5622	0.6548	0.6451
	4	460	535	900	810	0.6558	0.5845	0.6623	0.6563
	5	460	535	900	810	0.6559	0.6027	0.6729	0.6605

From Fig. 8 and Table 6, the four wavelengths (λ_{n_0}) at the peak positions of the spectral maximum values (m_i) of pesticide residues on the sample leaves for Carbendazim is 460 nm, Cypermethrin 535 nm, Diazinon 900 nm, and Imidacloprid 810 nm, and the standard deviation of the wavelength of all types of pesticides is equal to zero. Therefore, the wavelength at the spectra peak value could be used to specify a property of each type of the four pesticide residues on the sample basil leaves and chili.

When compared with wavelength, λ_{n_0} at which pesticide residues were detected as shown in Table 1, four wavelengths at the peak position of the spectral peak values of fruit and vegetable residues for Carbendazim was 400 nm, as reported by (Lu et al., 2021), Cypermethrin 535 nm (Mane et al., 2020), Diazinon 900 nm (Jamshidi et al., 2015) and 835 nm for Imidacloprid (Yu et al., 2020).

Although the medium used for the four pesticides was different, each of Cypermethrin and Diazinon gave the same wavelength at the peak of the spectral signal, and each of Carbendazim and Imidacloprid had only two small different wavelength ranges of 60 and 25, respectively.

Results of Evaluating the Performance of the Proposed Spectrometer.

To measure and evaluate the performance of the developed spectrometer, 40 samples were tested for the detection of pesticides without classifying the pesticide type and concentration of residues on 20 basil leaves and 20 chili. The 40 samples were picked randomly from either a local agriculture market or a local supermarket in Phitsanulok Province, Thailand. The 40 samples were tested for the existence of pesticide residue by using the developed spectrometer as a predicted class and the thin-layer chromatography method as an actual class from the central laboratory under the supervision of officials following the Agricultural Commodity Standards Act 2008 at the Agriculture and Cooperatives Office, Phitsanulok province, where the count is $T_p = 4$, $T_n = 16$, $F_p = F_n = 0$ for the pesticide residues on the 20 basil leaves and $T_p = 3$, $T_n = 17$, $F_p = F_n = 0$ for the pesticide residues on the 20 chili samples, as described in the sub-section of "Detection performance of the proposed NIR spectrometer".

The Accuracy, Precision and Recall were calculated by Eq. (1), Eq. (2) and Eq. (3) and the results were recorded as mean \pm standard deviation, as shown in Table 7. It was found that the developed spectrometer has the best efficiency for detecting pesticide residues on both basil leaves and chili of all forty samples, where a mean of Accuracy, Precision and Recall is equally 1.000 and the corresponding standard deviation is equal to zero.

Table 7 Detection performance of the proposed spectrometer to forty pesticide residues on the basil leave and chili

Sample type	Accuracy	Precision	Recall
Chili	1.00 \pm 0	1.00 \pm 0	1.00 \pm 0
Basil	1.00 \pm 0	1.00 \pm 0	1.00 \pm 0
$\mu \pm SD$	1.00 \pm 0	1.00 \pm 0	1.00 \pm 0

To measure and evaluate the performance of the experimental spectrometer for detecting each type of the four pesticide residues: Carbendazim, Cypermethrin, Diazinon and Imidacloprid on the sample basil leaves and chili, the fifty-six pesticide residues with the seven concentration seven levels: 0.05, 0.1, 1, 2, 3, 4 and 5 [mg/l] mixed on each of the sample leaves were used as the testing samples. The experimental spectrometer was used to detect each type of the four pesticide residues in the 56 samples as discussed in the sub-section of "Detection Performance of the Proposed NIR Spectrometer", and the count result was recorded into the four-

class confusion matrix used to calculate the Accuracy, Precision and Recall from Eq. (4), Eq. (5) and Eq. (6). The calculation result with the format mean \pm standard deviation in the basil leaves residues are shown in Table 8 and the chili residues are shown in Table 9.

Table 8 Detection performance on twenty-eight pesticide residues on the basil leaves run at 100 times/residue

Conc. (mg/l)	Carbendazim			Cypermethrin			Diazinon			Imidacloprid		
	Accuracy	Precision	Recall	Accuracy	Precision	Recall	Accuracy	Precision	Recall	Accuracy	Precision	Recall
0.05	0.993	0.980	0.990	0.993	0.990	0.980	0.990	0.980	0.980	0.990	0.980	0.980
0.1	0.998	1.000	0.990	0.998	0.990	1.000	0.995	0.990	0.990	0.995	0.990	0.990
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
5	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
μ	0.999	0.997	0.997	0.999	0.997	0.997	0.998	0.996	0.996	0.998	0.996	0.996
SD	0.003	0.007	0.005	0.003	0.005	0.008	0.004	0.008	0.008	0.004	0.008	0.008

Table 9 Detection performance on twenty-eight pesticide residues on the chili run at 100 times/residue

Conc. (mg/l)	Carbendazim			Cypermethrin			Diazinon			Imidacloprid		
	Accuracy	Precision	Recall	Accuracy	Precision	Recall	Accuracy	Precision	Recall	Accuracy	Precision	Recall
0.05	0.988	0.970	0.980	0.988	0.980	0.970	0.988	0.970	0.980	0.988	0.980	0.970
0.1	0.993	0.980	0.990	0.993	0.990	0.980	0.993	0.980	0.990	0.993	0.990	0.980
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
4	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
5	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
μ	0.997	0.993	0.996	0.997	0.996	0.993	0.997	0.993	0.996	0.997	0.996	0.993
SD	0.005	0.012	0.008	0.005	0.008	0.013	0.005	0.012	0.008	0.005	0.008	0.013

It was found that the experimental spectrometer had the highest efficiency for detecting pesticide residues on both basil leaves and chili of all 56 samples at the five concentration levels: 1, 2, 3, 4 and 5 [mg/l], where a mean of Accuracy, Precision and Recall is equally 1.000 and a corresponding standard deviation is equal to zero. For the 0.05 and 0.1 mg/l concentrations of the two pesticides, the experimental spectrometer had a good efficiency for detecting pesticide residues on basil leaves and chili in all 56 samples where the mean of the Accuracy values is greater than 0.98 and both the Precision and Recall values are greater than 0.97 with the overall standard deviation of less than 0.013 in case of detecting a residue type of the two pesticide concentration levels: 0.05 and 0.1 [mg/l]. The result showed that the experimental NIR spectrometer not only correctly detects the pesticide residues of the pesticide concentration range from 1 [mg/l] to 5 [mg/l]. This is an excellent outcome for a device that costs only 4,395 Baht. Therefore, in terms of effectiveness, usefulness and cost, the portable NIR spectrometer that was developed is superior to currently available devices, and methods.

Conclusion and Suggestions

The portable NIR spectrometer designed and developed by the research team has a dimension of 50 mm maximum thickness and 185mm in length, a total weight of 98 grams, a USB-C connector to either charge the 3.7-volt lithium-ion battery with a capacity of 1,800 [mAh] and a voltage range from 3.3 [V] to 5.0 [V], and the proposed spectrometer transmits the spectral signal at a maximum speed of 115,200 [baud] to communicate between sensing and control modules. The total cost is at least 4,395 Baht, and this cost leads to the reasonable price of the proposed portable NIR spectrometer, between 2% and 22% of the cost of devices with identical specifications sold on the commercial market.

The experimental results from 56 sample pesticide residues with seven concentration levels, each tested 100 times/ residue, the developed spectrometer also has the highest performance for detecting each of the four pesticide residues on both basil leaves and chili with five concentration levels: 1, 2, 3, 4 and 5 [mg/l], where the Accuracy, Precision and Recall values are 1.000 with a standard deviation of zero each, but for the case of two pesticide concentration levels: 0.05 [mg/l] and 0.1 [mg/l], the Accuracy, Precision and Recall values in overall are greater than 0.97 with a standard deviation of less than 0.013.

Furthermore, the developed spectrometer used as a predicted class showed superior performance than the thin-layer chromatography method used as an actual class in these experiments.

There is no doubt that the developed portable NIR spectrometer is superior in terms of cost and performance to existing methods and devices currently available, and is a valuable contribution to the science of harmful pesticide residue detection.

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Author Contributions

Author 1 (Suchart Yammen): conceptualization of the research, Formulated the topic of the research, collection of data and review of the manuscript.

Author 2 (Natthasak Yaemsuk): Wrote the first draft of the manuscript, development of methodology, developed the methodology, collected and analysed data, interpreted the analysed data, and reviewed and edited the manuscript.

Conflict of Interests

The authors declare no conflicts of interest.

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