

Multi-Spectral NIR-LED-Based Spectrometer Prototype Detects Chemical and Pesticide Residue in Mango and Banana Fruit [†]

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[†] Presented at the 12th International Electronic Conference on Sensors and Applications (ECSA-12), 12–14 November 2025; Available online: <https://sciforum.net/event/ECSA-12>.

Abstract

In the Philippines, chunks of calcium carbide are usually used as a ripening agent for mango samples, while chlorpyrifos is used to control pests and diseases in banana fruits. However, both of these agents can cause harm to human health. The acetylene gas from the calcium carbide produced during the ripening process of mango and the chlorpyrifos residue in the banana fruit can be inhaled and touched by humans. Likewise, considering the country's economic standing, the development of low-cost and portable instruments is encouraged. To address these issues, a multi-spectral near-infrared light-emitting diode-based spectrometer was developed. This study aims to determine the calcium carbide residue and chlorpyrifos detection capability in mango and banana fruit, respectively, using the developed spectrometer prototype. The prototype is a spectrometer system that uses a graphical user interface, a DC power supply, and a black box. Fruit samples were scanned inside the black box and irradiated by the near-infrared lights from the circuit board. Partial least square regression and linear discriminant analysis showed 81.33% calcium carbide residue prediction capability and 88.9% correct classification, while it shows 74% chlorpyrifos residue prediction capability and 80% correct classification. Therefore, the multispectral near-infrared light-emitting diode-based spectrometer prototype has the chance to detect calcium carbide chemical residue in mango fruit and chlorpyrifos in banana fruit non-destructively.

Keywords: multi-spectral; LED; NIR; banana; mango; calcium carbide; chlorpyrifos

Academic Editor(s): Name

Published: date

Citation: Rodriguez-Macadaeg, F. Multi-Spectral NIR-LED-Based Spectrometer Prototype Detects Chemical and Pesticide Residue in Mango and Banana Fruit. *Eng. Proc.* **2025**, volume number, x. <https://doi.org/10.3390/xxxxx>

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1. Introduction

Food can be contaminated at any point from production to consumption. Food producers are the primary party responsible for delivering safe food to the middleman and/or directly to consumers. However, many food-borne diseases or poisoning are caused by content adulteration; improper preparation or mishandled food at home, in food service establishments, markets, or even on farms; pesticide contamination; and artificial foods [1].

For example, one of the most exported fruits in the Philippines is the banana. The country has been recognized as one of the most efficient banana producers, offering the highest quality standard in terms of taste and aesthetic appearance [2]. However, the existence of bunchy top and Fusarium diseases is a threat to all banana growers [3,4]. Due to these diseases, the frequent use of pesticides and fungicides is practiced in order to attenuate and protect the banana trees from these diseases and to increase production.

Brodan is a widely used pesticide within the country in various crops, with an active ingredient, chlorpyrifos. Nonetheless, these chemicals pose a threat and health hazard to consumers since bananas are eaten as fresh fruit [5]. Chlorpyrifos is one of the pesticides listed by the Philippine National Standard- Bureau of Agriculture and Fisheries Standards (PNS-BAFS) to watch out regarding pesticide limits. According to them, the maximum residue limit of chlorpyrifos in banana is 2 mg/kg [6].

On the other hand, calcium carbide (CaC_2) is used as a source of acetylene gas, which is a mango ripening agent [7]. However, acetylene gas may affect the neurological system of humans by inducing prolonged hypoxia. According to Per et al. (2022), the findings are headache, dizziness, mood disturbances, sleepiness, mental confusion, memory loss, cerebral edema, and seizures for prolonged exposure [8]. Moreover, CaC_2 powder contains traces of arsenic and phosphorus as per study conducted by Lakade et al. (2018) [9]. According to the Food Safety and Standards Authority of India (2011), the allowable arsenic amount in any mango fruit pulp is 0.2 ppm [10].

To control the exportation and consumption of banana fruits with chlorpyrifos pesticide and mango fruits with calcium carbide above the maximum residue limit and to limit their exposure to humans during handling, processing, and transportation, a fast, non-destructive, affordable testing and detection instrument is needed.

Various studies were conducted to detect pesticide residues in fruits and vegetables. Some of these studies involve using innovative technologies and methods. One to mention is the near-infrared spectroscopy. Near-infrared spectroscopy (NIRS) is a non-destructive detection technique, precise and rapid, that has shown potential in the determination of numerous foods and food products' properties chemically and physically. An earlier study conducted by Rodriguez et al. (2020) showed the potential of using NIRS for detecting pesticide residues that contain varying concentrations of chlorpyrifos-methyl in rough, brown, and milled rice using a commercial full wavelength (950–1650 nm) NIR instrument (Pertin DA7200, Pertin Industries, Springfield, IL) [11]. While the NIR spectroscopy technique is simple and the commercially available instrument can be readily adapted with the development of calibrations, there is a need in countries such as the Philippines, for a fast and reliable technique or instrument that is low-cost and made of locally available parts and which is preferably portable to allow testing at various handling and pre-consumption points [12].

The developed multi-spectral NIR-LED based Spectrometer Prototype was based on the simulated LED instruments with the DA Pertin 7200 NIR spectrometer fitted with 980, 1050, 1200, 1300, 1450, 1550, 1600, and 1650 nm [12]. Its evaluation as to actual experimental sample scanning is important to know its potential to detect calcium carbide residue in mango fruits and chlorpyrifos pesticide residue in banana fruits.

2. Materials and Methods

2.1. Fruit Samples

Pesticide-free-matured mangoes and bananas were harvested from a backyard located at Bacnotan, La Union, Philippines. There were 63 and 33 mango and banana fruit samples used, respectively. Mango fruits, three (3) each replicate, were treated with calcium carbide at different concentrations (0, 0.5 g, 1 g, 2 g, 3 g, 4 g, and 10 g), then wrapped in separate newspapers and placed inside a box for 3 days or until they ripened. On the other hand, banana fruits were treated with 10 mL of chlorpyrifos at different concentrations (0, 0.05, 0.1, 0.2, 0.5, 0.8, 1, 2, 3, 4, and 10 times 3.0 tablespoons of Brodan per 16 L of water) of each replicate. It was contained in an open zip lock polyethylene, 18 cm by 18 cm bags to avoid contamination, and allowed to dry for 4 h at room temperature before scanning.

2.2. Instrumentation (Multi-Spectral NIR-LED Based Spectrometer Prototype)

The prototype consists of the 12 V DC Power supply, laptop (GUI), and the black box with the multi-spectral NIR LEDs circuit board. All the data gathered through the microprocessor interface were saved using the graphical user interface for partial least square regression and linear discriminant analysis. The black box should ensure that no light will enter the box. The circuit board is composed of Near Infrared Light Emitting Diodes (700, 980, 1050, 1200, 1300, 1450, 1550, 1600, and 1650 nm) with InGaAs detector, amplifier, transistors, and capacitors. The board was interfaced with a microprocessor board that process digital and analog I/O signals.



Figure 1. Multi-spectral NIR-LED based Spectrometer Prototype.

2.3. Data Analysis

Quantitative and qualitative spectral data analyses were performed using Parles v.3.1 software and NCSS software, respectively. For the quantitative analysis, partial least squares (PLS) regression was performed. This includes pre-processing of spectral data using Standard Normal Variate (SNV), Multiplicative Scattering Correction (MSC), and Mean Centering. The PLSR should provide the beta regression coefficient and the prediction model of the analyzed spectra. For the qualitative analysis, linear discriminant analysis was performed to indicate the correct classification of the samples.

3. Results

Figures 2 and 3 show possible spikes in chlorpyrifos and calcium carbide at 1050, 1200, 1450, 1550, and 1600 nm. Furthermore, slight differences were observed among the spectra gathered. However, by spectral subtraction, it is possible that the prototype was poorly detected or differentiated between different chlorpyrifos and calcium carbide concentrations.

On the other hand, qualitative analysis revealed 80.0% correct classification of banana fruits with different chlorpyrifos concentrations, while 88.9% correct classification was achieved for the pure chunks of calcium carbide.

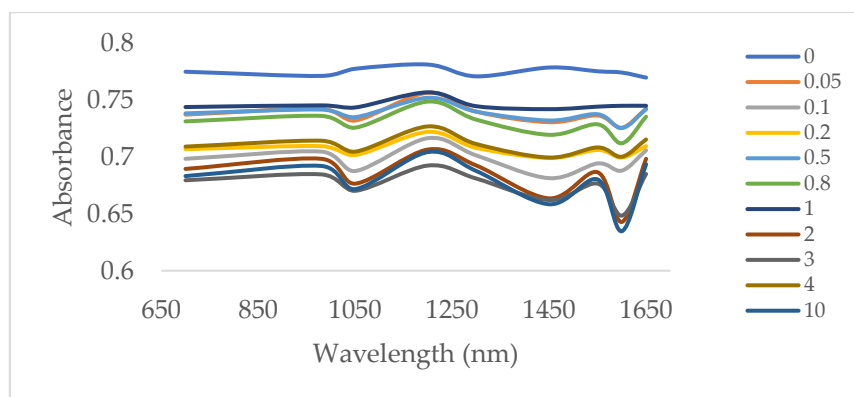


Figure 2. Banana fruits with chlorpyrifos pesticide raw spectra.

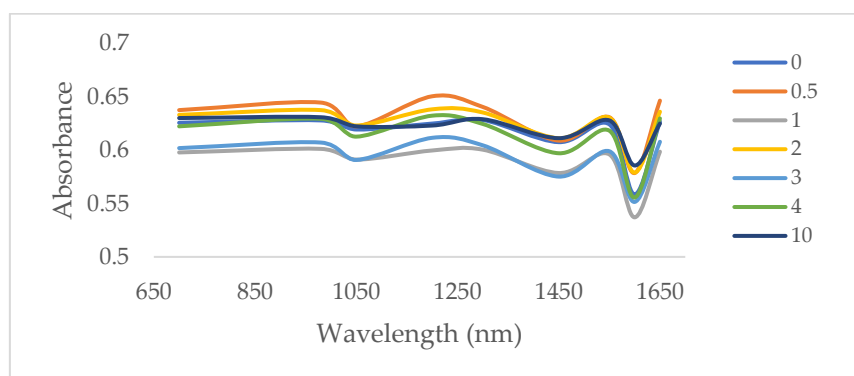


Figure 3. Mango fruits with calcium carbide raw spectra.

The spectra data were pre-treated with mean centering and pre-processed with SNV and MSC. Figure 4 shows the PLS beta or regression coefficients of calcium carbide in mango fruit at an optimum number of factors. The wavelengths that are relevant to the identification of the presence of calcium carbide were identified. For instance, at 1300 nm peak pertains to methylene, and at 1600 nm, the peak pertains to alkenes, which are related to the chemical composition of acetylene gas produced by calcium carbide [13].

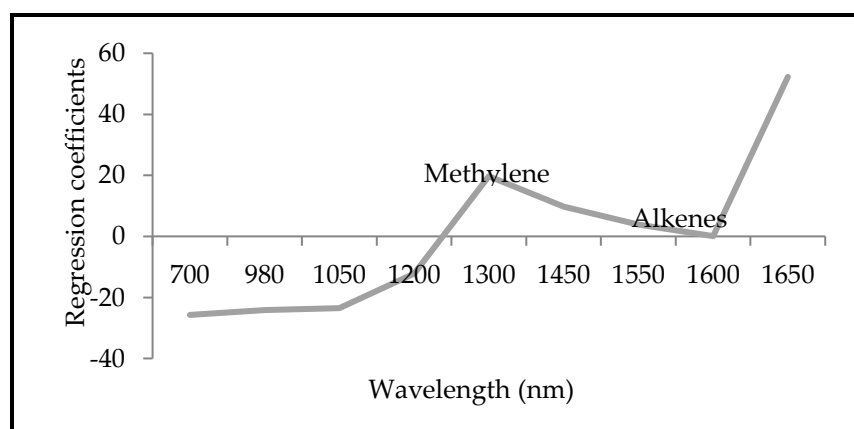


Figure 4. Regression beta coefficient for mango fruits with calcium carbide.

On the other hand, Figure 5 shows the PLS beta or regression coefficients of chlorpyrifos in banana fruit at an optimum number of factors. The wavelengths that are relevant to the identification of the presence of chlorpyrifos were identified. For instance, at 1050 nm, the peak pertains to methylene, at 1300 nm, the peak pertains to methyl, and at 1450

nm, the peak pertains to carbonyl, amines, and polymeric compounds, which are related to the chemical composition of the chlorpyrifos pesticide [13].

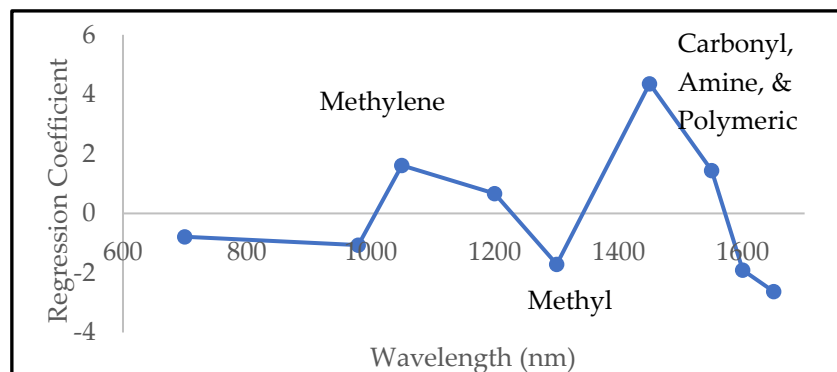


Figure 5. Regression beta coefficient for banana fruits with chlorpyrifos.

Moreover, quantitative analysis revealed the prototype's predictive capability of 81.33% and 74% for mango fruits with calcium carbide and banana fruit with chlorpyrifos pesticide residue, respectively.

4. Discussion

Although predictive capability and correct classification of banana fruits with chlorpyrifos pesticide and mango fruits with calcium carbide at different concentrations were acceptable, the prototype is not yet recommended for application, but only good for approximate calibrations [14]. This may be attributed to the noise received by the amplifier during scanning [15]. There is a possibility that the voltage signal that is registered to be the analog input/output signal of the prototype directly affects the spectra gathered [16].

Therefore, further study was needed to improve the design and functionality of the developed prototype, such as the use of another graphic unit interface, a voltage source, and an amplifier to amplify the signal, reduce the noise of the device, and increase voltage capacity to improve the analog and digital input/output signals.

Funding:.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Acknowledgments: The author would like to thank U.S. Department of Agriculture- Agriculture Research Service, Manhattan, Kansas for their continuous support, guidance, and technical help during this research. Don Mariano Marcos Memorial State University for the review, conduct, and guidance during the conduct of the study. To Lea Ruth M. Banan and Sunshine Baltazar for their dedication, time, and effort during the conduct of the studies.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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