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An approach to chemical fertilizer detection in coffee cherries using photoacoustic spectra and artificial intelligence

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ABSTRACT

Coffee consumption has increased worldwide, and the rise in coffee trading has served as a key economic motivator for producers to add value and expand their market presence, thereby enhancing the value of their products. Among the implemented strategies to increase the value of coffee, the free pesticide product label stands out due to the market's tendency to consume this product. In this work, artificial intelligence techniques were employed to analyze the photoacoustic spectra of cherry coffee to determine if chemical-fertilizer traces are present in the coffee cherries. Spectra were divided into bands to improve the artificial algorithm's response. Subsequently, logistic regression, random forest classifier, support vector machines, and decision tree classifier algorithms were applied. The results indicate that principal component analysis offers the highest accuracy in detecting inorganic fertilizers at wavelengths of 320-330 nm and 560-620 nm in the analyzed samples. Consequently, photoacoustic spectrum analysis using artificial intelligence techniques represents a viable option for detecting inorganic fertilizers in coffee at the cherry stage rather than beans or powder.

Keywords: Artificial intelligence; Organic coffee; Spectrum analysis.

INTRODUCTION

Coffee trading has become a significant global industry, with a total of 9.68 million 60-kg bags traded in October 2021 (International Coffee Organization, 2021b). The increased trading has made optimizing coffee production processes a tremendous economic motivation. Various efforts have been made to increase coffee's value, including improving sowing processes, enhancing the drying stage, controlling the roasting stage time, and conserving the final product (International Coffee Organization, 2021a).

In the struggle to increase the value of coffee, producers are adding value by offering specific features such as fair trade, origin denomination, and organic product label, leading to new research areas to cover all

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those features; coffee has been the subject of several studies aimed at detecting defects (Dias *et al.*, 2018), roasting degree (Alessandrini *et al.*, 2008; Delin Orduña *et al.*, 2016; Dias *et al.*, 2018; Yeretzian *et al.*, 2002), aroma (Baggenstoss *et al.*, 2008; Czerny & Grosch, 2000; Gonzalez-Sanchez *et al.*, 2023; Schenker *et al.*, 2002; Yeretzian *et al.*, 2002), and adulterants presence (Cesar *et al.*, 1984).

The chemical-free fertilizer label, also known as an "organic product," has introduced a new approach to production and, to the coffee's final value. The organic product label indicates that the product has been cultivated in accordance with specific standards, including respect for natural harvest cycles, the avoidance of genetically modified organisms, and, most importantly, the exclusion of pesticides and chemical fertilizers.

Despite the organic product label, indicating the absence of chemical fertilizers, the presence of chemicals associated with fertilizers in coffee has become a problem. Therefore, several studies have been proposed to detect fertilizers in beans (Rosencwaig, 1978, 1980) and powder (Cesar *et al.*, 1984; Gordillo-Delgado *et al.*, 2016; Rosencwaig, 1980). Despite the promising results in detecting chemical fertilizers on coffee beans and powder, no studies have used coffee cherries as a sample.

On the other hand, photoacoustic spectroscopy is a non-destructive technique based on sample light absorption (Rosencwaig, 1978, 1980). A frequency-modulated light beam is focused on the sample at a specific wavelength and modulation frequency. The sample is periodically heated, and due to the incident light, it undergoes a modulated thermal expansion at the same frequency as the exciting light. Thermal expansion depends on the sample's thermal and elastic properties, as well as its absorption at the exciting wavelength. The sample absorption spectrum is obtained by varying the excitation wavelength within a specified interval. In photoacoustic spectroscopy, the light modulation frequency is in the sound range; as a result, the sample's thermal expansion can be monitored using a microphone.

Photoacoustic spectroscopy (PAS) is characterized by using a reduced sample and provides spectral information of the sample directly from the time domain signal (Kistenev *et al.*, 2017). Because the photoacoustic signal comprises both amplitude and phase, it provides two information sources: the amplitude, which is related to the sample's optical absorption, thermal properties, and thermal wave scattering, and the phase, which is related to the thermoelastic properties of the sample (Ishihara *et al.*, 2003).

Several applications have emerged from the use of photoacoustic studies, including the detection of gases (Linhares *et al.*, 2019), the study of crystal defects (Zegadi *et al.*, 1992), piezoelectric materials (Lara-Hernandez *et al.*, 2017), and pigments in archaeological samples (Jiménez-Pérez *et al.*, 2004). Depending on their color, photoacoustic spectroscopy enables the determination of optical properties in food, which is a crucial parameter in the agrifood industry because quality and flavor are closely related to its color (Arana *et al.*, 2015). The PAS technique, applied to food and plants, enables the determination of their properties, concentrations, and the presence of chemical compounds and adulterations (Hernández-Aguilar *et al.*, 2019; Hernández *et al.*, 2023; Ikegwu *et al.*, 2023); therefore, the methodology is considered an analytic method. The photoacoustic technique has been successfully applied to coffee-related studies, ranging from quality powder to prepared coffee infusions (Cesar *et al.*, 1984; Dias *et al.*, 2018; Hernández-Aguilar *et al.*, 2019; Tepepa *et al.*, 2009).

Several studies have employed the spectroscopic method (ATR-FTIR) combined with chemometrics to detect the adulteration of sibutramine in tea and coffee, utilizing hierarchical group analysis and key compounds. The result showed a group of vibratory bands associated with chemical compounds of sibutramine (Cebi *et al.*, 2017). Arabica coffee and its classification by groups and high-quality fingerprints of coffee by implementing the Nuclear magnetic resonance (NMR) method (Arana *et al.*, 2015).

Photoacoustic spectroscopy does not require sample preparation; with a suitable measurement chamber, samples can be solid, liquid, or gas. In contrast, infrared techniques (IR, FTIR) often require extensive sample preparation, such as grinding a solid sample into a fine powder and pressing it into a pellet, or dissolving a sample in a specific solvent that is transparent to IR.

On the other hand, several applications of artificial intelligence (AI) have emerged in agricultural and food analysis. Shaikh and colleagues reported on the use of AI models to forecast crop yields, allowing farmers to plan and optimize their production (Shaikh, Rasool, & Mir, 2025). Applications of AI in irrigation and fertilizer management have been reported by Kumar and coworkers (Kumar, Farooq, & Qureshi, 2024). Food quality control also benefits from the use of AI. Shaik reported the automation of sorting and grading products using AI algorithms, whereas Konfo describes the use of AI in detecting herbicides (Konfo et al., 2023).

Since studying the possible presence of chemical fertilizers in coffee before any process can yield economic benefits, the working hypothesis is that Photoacoustic spectra combined with AI can discriminate the presence of fertilizers in coffee cherries. Thus, this study proposes examining coffee cherries using PAS and artificial intelligence to detect specific chemicals in coffee.

MATERIALS AND METHODS

Photoacoustic spectroscopy

The experimental setup uses a 1 kW Xenon lamp (Oriel), as shown in Figure 1. Because the lamp emission spectra strongly affect measurements, the lamp spectra were obtained in advance using black charcoal as a reference sample and used to normalize the photoacoustic signals (Flores-Cuautle *et al.*, 2013; Lara-Hernandez *et al.*, 2017). The photoacoustic signal was obtained using a lock-in amplifier (SR-850) with a frequency modulation of 17 Hz; all measurements were performed at room temperature (23 °C). This work performed photoacoustic spectra measurements in the 300 to 800 nm range with a 1 nm step. The selected band enables the acquisition of information about carboxyl groups, which absorb near 300 nm, allowing for the differentiation of aldehydes, ketones, carboxylic acids, and ester functional groups. The photoacoustic spectra were obtained in triplicate for all samples, and the spectra subject to IA analysis are the result of averaging the spectra of the three samples. In this work, the amplitude and phase components were employed in the IA analysis.

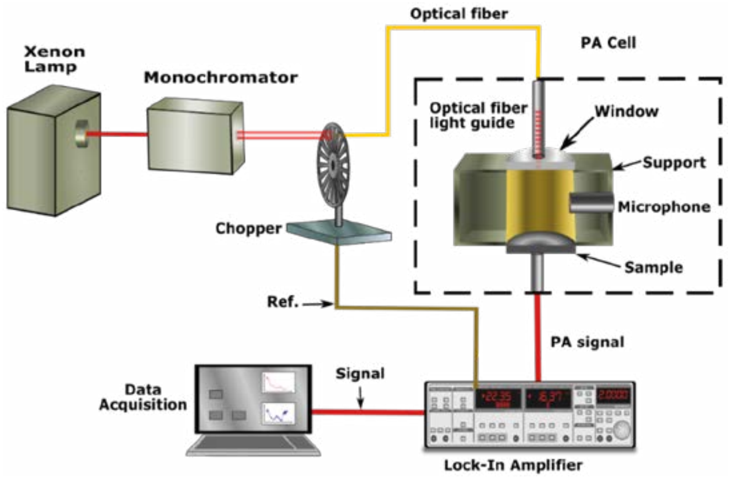

Figure 1. Scheme of the experimental setup used to determine the photoacoustic spectra of the studied samples.

Samples

Samples were collected from the so-called high mountain region in Veracruz, Mexico, as shown in Figure 2. The high mountains region is around 1300 meters above sea level; therefore, the weather is favorable for the coffee crop. All samples considered in the study were analyzed at cherry stage and red and green cherries were included. This study comprises two certified organic coffee varieties as a sample reference: Colombia and Costa Rica (S4, S5). Samples fertilized with chemicals, using two fertilizers —one organic and one inorganic— were also included in this study. Table 1 shows the main features considered in each sample. The study included one sample taken from a cliff that is difficult to access.

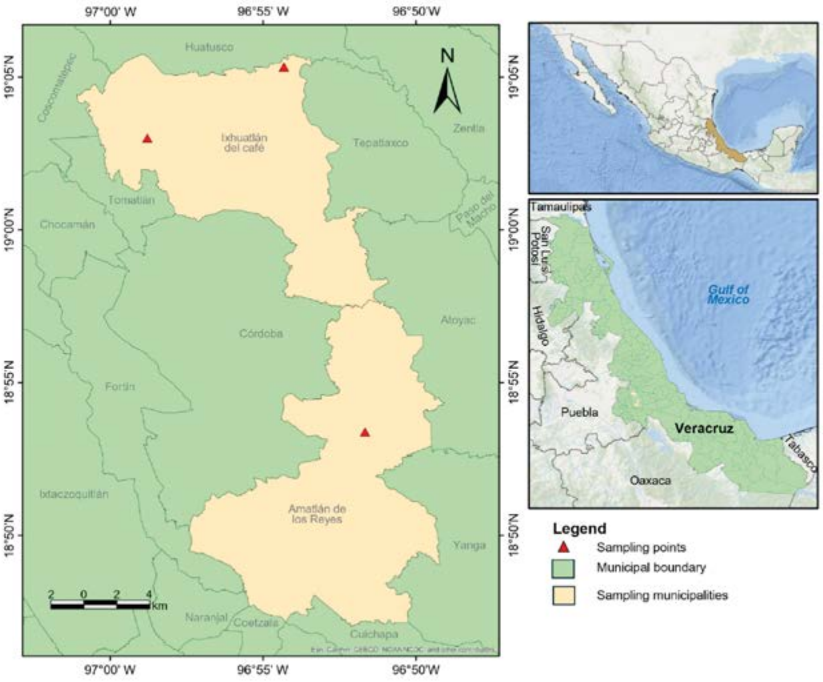

Figure 2. Geographical localization of the samples' collection point.

Table 1. Analyzed samples and main features.

Sample code	Main feature	Fertilizer?
S1	A robusta sample taken from a cliff, it is considered a fertilizer-free sample.	NO
S2	A robusta sample taken from a field with ten years of abandonment could contain traces of fertilizer.	NO
S3	A Robusta sample, nitrophosca, and black manure are used as fertilizer.	YES
S4	Certified Colombia variety sample	NO
S5	Certified Costa Rica variety sample	NO
S6	Robusta sample from the local farmer using fertilizers	YES
S7	Colombia variety from local farmers using fertilizers	YES
S8	Black fertilizer	NO
S9	Nitrophosca fertilizer	YES

Artificial intelligence

The artificial intelligence scheme for detecting fertilizers in coffee cherries through photoacoustic spectra is divided into two sections: data preprocessing and machine learning.

Data preprocessing

Variable selection: The amplitude and phase of the photoacoustic spectra were used as inputs. The light wavelength ranged from 300 to 700 nm, and 800 data points were acquired for each analyzed sample, from which 400 points correspond to amplitude and 400 to phase.

Corrupted data: Corrupted or null values can impact the training and performance of machine learning algorithms. Therefore, data correction was carried out by identifying and removing null values. Interpolation using the two closest points was used to estimate the missing or corrupt data.

Data Reduction: An algorithm was designed to reduce the amount of data from the photoacoustic spectrum signals. Data reduction was performed using an averaging window.

Normalization: Maxpoling was carried out using 1D signal convolution to reduce the number of variables (wavelengths) used for the analysis. It was possible to compress the signal from 400 data points per coffee sample to 40 data points per coffee sample. The analysis used ten coffee samples, resulting in a 10×40 data matrix. A data arrangement was used as a training target for each coffee sample, where 0 or 1 was assigned (0=coffee with fertilizer, 1=Organic Coffee).

Data Splitting was performed, with 75% of the data intended for training and 25% for testing. Specialized libraries were used to perform this random separation of the data. Random separation enables more reliable results regarding the precision obtained.

Machine learning

The Scikit-learn, NumPy, Pandas, Matplotlib, SciPy, Plotly, Seaborn, and CatBoost libraries were utilized to develop the intelligent system within the Python programming environment, facilitating the design, training, and testing of the AI algorithms employed.

Because there is no best AI algorithm for all problems, different algorithms were tested to find one that suits this particular application better. Logistic regression, Decision tree, Random Forest, KNN, RFE, LASSO, Chi2, and Catboost algorithms were tested to determine which one best fits the study of the photoacoustic spectrum.

Correlation Analysis: Pearson correlation was used to estimate the relationships among amplitude and phase of the photoacoustic spectrum of the samples at all wavelengths.

Feature Importance: The feature importance analysis was conducted to determine the importance and correlation of each input variable. The feature importance analysis identifies the most critical and relevant variables for the classification process.

Model Cross-Validation: This technique involves an algorithm that generates groups of variables to evaluate the model. This methodology enables us to identify data groups with significant variance that could impact the model's precision.

Model Estimation: Machine Learning algorithms were used to classify organic coffee and coffee with inorganic fertilizers.

Hyperparameter optimization: A random search algorithm was employed to determine the optimal hyperparameters. Random Search defines a search space in the bounded domain and randomly samples points.

RESULTS

Data preprocessing: Optical photoacoustic spectra are shown in Figure 3 for sample reference, sample without fertilizers (S1, S4, S5), abandoned field (S2), sample with fertilizers (S3, S6, S7), and spectra from two main fertilizers used in the region (S8, S9).

Figure 4 shows the amplitude signal spectra after data reduction. An average window was implemented for data reduction, varying the number of samples within the window; for simplicity, only the signals' amplitudes are presented.

Correlation analysis

Pearson correlation analysis of the amplitude and phase of the photoacoustic signals indicates that the 380-560 nm wavelength band exhibits the highest amplitude correlation. The lowest correlation was found in the range of 300 to 380. Figure 5 shows the representation of the principal components for the studied wavelengths.

Feature importance

A feature importance analysis was conducted to determine the importance and correlation of each input variable with the output. The feature importance analysis identifies the most critical and relevant variables for the classification process. Each spectrum was divided into wavelength bands of 10 nm each to implement the feature analysis. Each algorithm proposed in this study was applied to the data bands, and the number of matches was calculated for each algorithm and wavelength band. Figure 6 illustrates a graph that classifies the importance of each wavelength in the classification process.

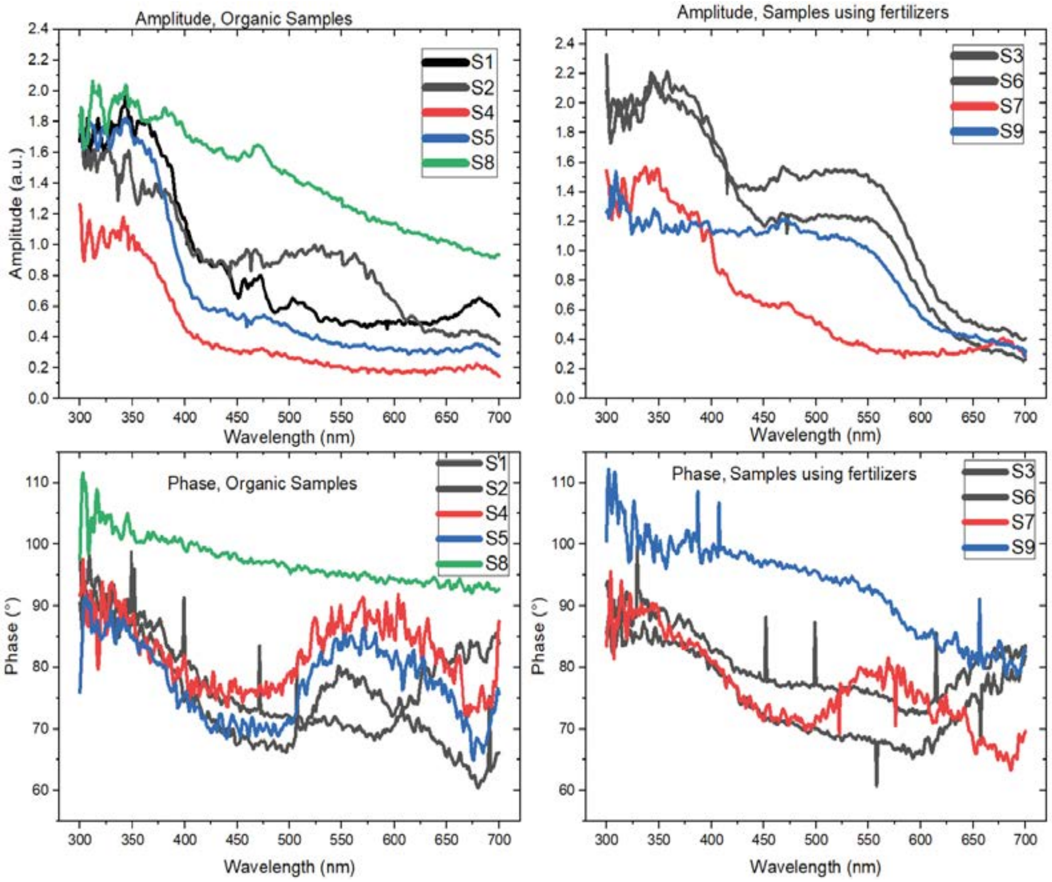

Figure 3. Optical absorption spectra from fertilizers and the analyzed samples; left) images, amplitude, and phase of organic samples, right) samples using chemical fertilizers.

Principal components analysis

Principal component analysis identifies which frequency bands are most significant in determining whether a coffee sample is organic or contains fertilizers. Various methodologies were selected to identify the critical features at the amplitude and phase wavelengths, where most methodologies for analyzing essential features were in agreement. In terms of amplitude, the most influential bands were 320-330 nm and 560-620 nm. In phase, the most influential bands were 530 nm, 610 nm, 380-400 nm, 340 nm, and 550 nm. Figure 7 shows the results of the crucial characteristics of the coffee samples, specifically the amplitude and phase of the photoacoustic signals.

Since the selected hyperparameters significantly impact the machine learning algorithms, an automated hyperparameter tuning method was employed to select the training parameters. The hyperparameters used in each of the analyzed machine learning algorithms are provided in supplementary material S1.

Because the photoacoustic signal provides a means to detect the presence of inorganic fertilizers, this study lays the groundwork for a potential organic coffee certification. This certification could provide economic benefits to the producer while providing certainty to the final consumer.

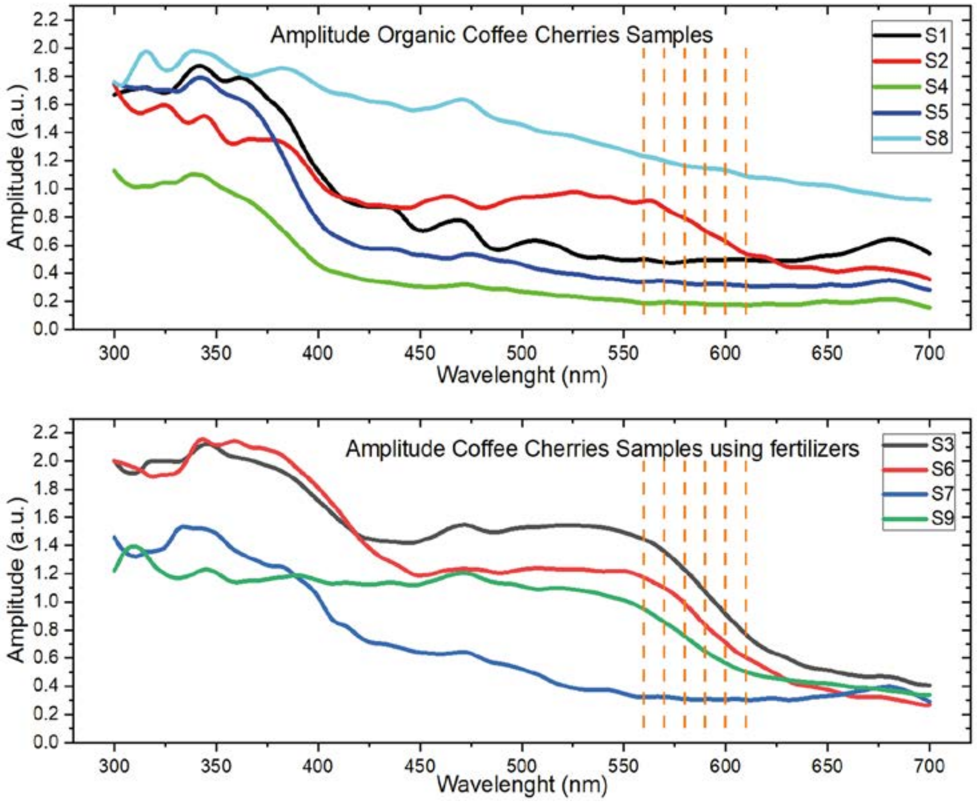

Figure 4. Spectra of the amplitude signals after data reduction, the dotted orange lines indicate the wavelengths using markers.

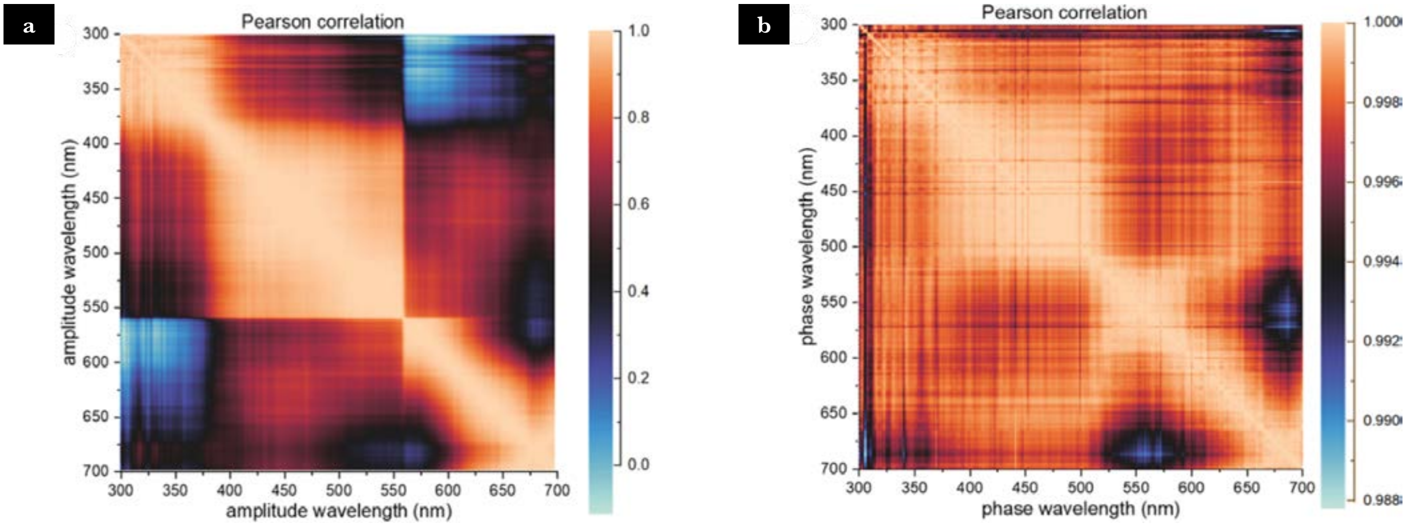

Figure 5. Principal components analysis: a) Signal amplitude, b) Phase.

DISCUSSION

The photoacoustic signal consists of two parts: amplitude and phase, each providing distinct information, as the amplitude is related to the optical absorption coefficient. In contrast, the phase is mainly related to the depth of absorption of the thermal wave

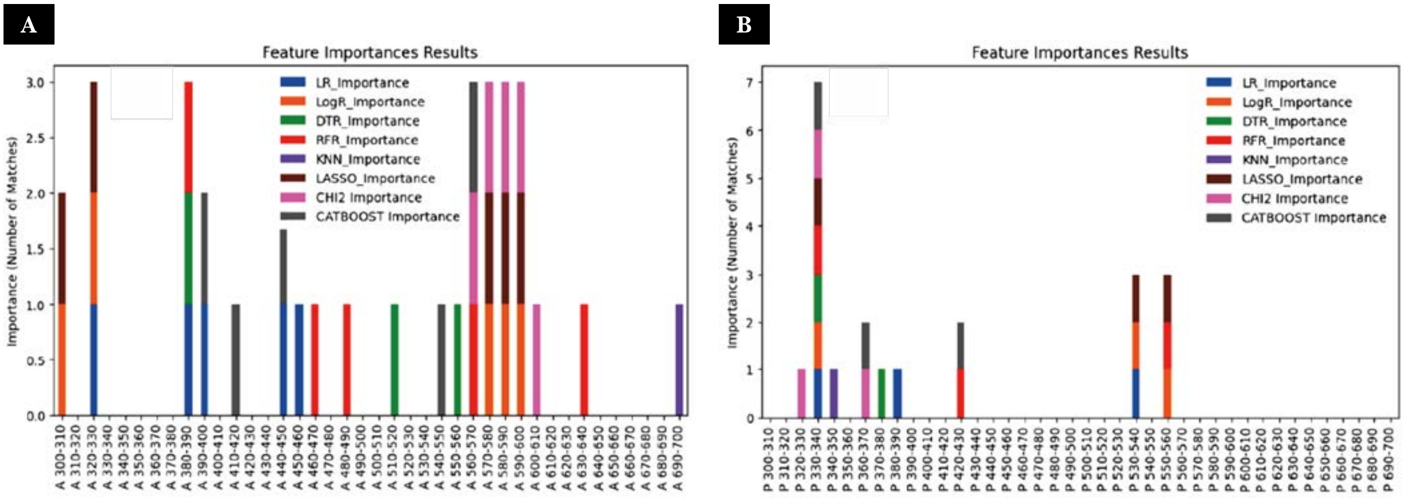

Figure 6. Graph of feature importance of the signals for the different IA techniques: A) amplitude, B) phase.

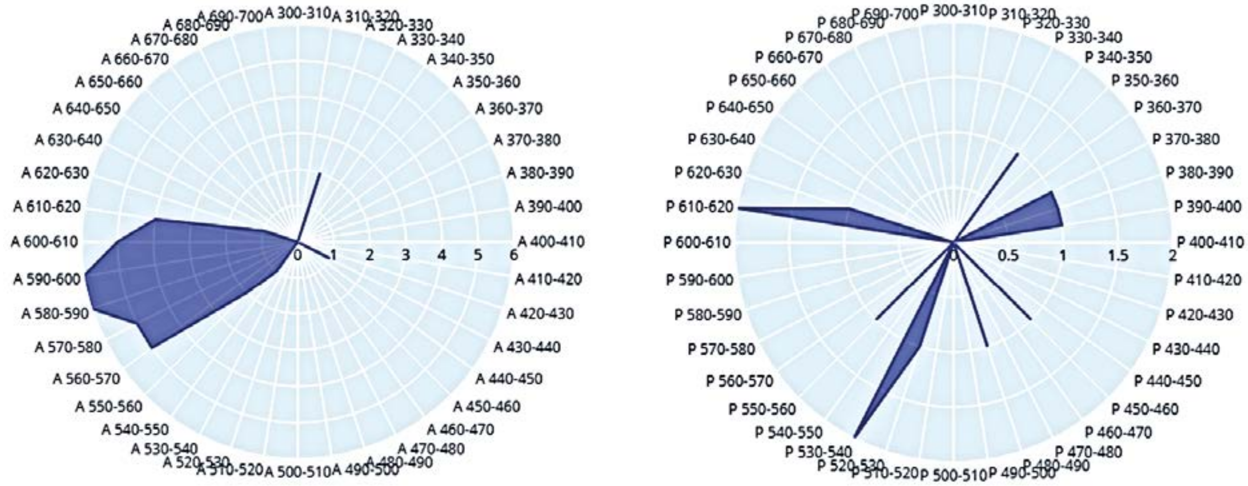

Figure 7. Graph of Principal Components of the signals.

in the sample. Since the optical absorption originates from the amplitude, this signal component is more susceptible to changes in the absorption coefficient of the sample, including color, light power, and others. In principal components analysis, helpful information can be obtained in the 570-620 nanometer range. For the phase, the bands that provide more information about the possible presence of inorganic compounds are located at 530-540 and 610-620 nanometers. Feature importance reveals several wavelength bands where discrimination between inorganic and organic presence can occur. The amplitude signal shows four wavelength bands where the importance is higher.

However, as mentioned, the signal amplitude is particularly sensitive to color changes in the sample, which can lead to erroneous results. Samples comprising green and red cherries were used in this analysis to avoid issues with absorption coefficients.

The combination of photoacoustic with IA in this specific application eliminates the need for searching characteristic peaks or specific absorption bands, thus facilitating the determination of the presence of inorganic fertilizers.

Because the purpose of this work is not fertilizer quantification or specific compounds detection, a profiling approach was used (Kistenev *et al*., 2017; van der Schee *et al*., 2015); in a similar way to that in clinical settings, a profiling strategy was used to set a positive or negative flag in fertilizer content. The PAS in combination with IA under profiling strategy appears to be a reliable technique for organic coffee certification or as a quality control test.

Because there is a lack of a totally controlled free inorganic fertilizer field that provides samples, further validation of the results is still necessary. On the other hand, due to environmental variability, the obtained results are limited; however, they serve as proof of concept for further studies.

CONCLUSIONS

Photoacoustic spectroscopy (PAS) combined with artificial intelligence (AI) represents a viable and efficient method for detecting inorganic fertilizers. The spectral range of 300-800 nm provides an optimal window for PAS, allowing precise differentiation of fertilizer compounds based on their optical absorption characteristics. Among the machine learning algorithms evaluated, principal component analysis (PCA) proved to be the most reliable for distinguishing fertilizer types due to its robustness in handling complex spectral data and reducing dimensionality without significant information loss. Notably, coffee cherries serve as an effective biological stage for detecting inorganic fertilizers, suggesting their potential as natural bioindicators in sustainable agricultural monitoring systems.

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