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Portable NIR Spectroscopic Application for Coffee Integrity and Detection of Adulteration with Coffee Husk

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Abstract: Reliable and user-friendly discrimination of coffee bean integrity and quantification of adulteration in the coffee bean processing value chain would be vital for ensuring consumer trust in quality control and traceability management. In this research, a portable short-wave NIR spectroscopy coupled with chemometric data analysis was employed under different pre-treatments to develop a rapid detection technique. Different pre-processing treatments (multiplicative scatter correction; MSC, standard normal variant; SNV, first derivative; FD) together with multivariate techniques; support vector machine (SVM), linear discriminant analysis (LDA), neural network (NN), and random forest (RF) were comparatively assessed using accuracy and correlation coefficient (R) for discrimination and quantification. The results showed that the FD-LDA model had 97.78% and 100 % in both the calibration set and prediction set. In comparison, the SPA-PLS model had R = 0.9711 and 0.9897 in both the calibration set and prediction set. The outcome of this study showed portable short-wave NIR spectroscopic techniques could be used for examining the integrity of coffee.

Keywords: coffee; adulteration; pure; portable NIR spectroscopy; chemometric

Citation: Boadu, V.G.; Teye, E.; Amuah, C.L.Y.; Lamptey, F.P.; Sam-Amoah, L.K. Portable NIR Spectroscopic Application for Coffee Integrity and Detection of Adulteration with Coffee Husk. *Processes* **2023**, *11*, 1140. https://doi.org/10.3390/pr11041140

Academic Editors: Min-Pei Ling and Tai-Sheng Yeh

Received: 22 February 2023
Revised: 31 March 2023
Accepted: 3 April 2023
Published: 7 April 2023

1. Introduction

Food fraud has now been reported in every food commodity and has become a global food safety concern, with adulteration topping all forms of food fraud [1]. Food adulteration form of food fraud is the action of manufacturers to increase the profit of authentic products with low-quality products by removing costly components to increase the amount of the product with cheap materials [2]. Often this fraudulent act is targeted at widely used consumer commodities such as coffee due to its ease of adulteration, which includes techniques such as adding flavors or aromas and using an unknown addictive to boost its volume, among others. Coffee, unfortunately, has one of the highest reported numbers of fraud instances among beverages [3,4]. Roasted coffee is frequently and, in various ways, adulterated. To reduce the price of coffee blends, it may be necessary to alter the quality of the beans (taking into account the species, region of origin, and defective beans) as well as to add additional ingredients such as coffee husk, stems, maize, barley, chicory, wheat middling, brown sugar, soybeans, rye, and triticale [5].

Coffee is an important raw material traded globally and one of the most popular consumed beverages [6]. Food safety concerns have recently been on a high agenda of many consumers, and coffee quality assessment is impelled by the need to supply consumers with consistently high-quality products at affordable prices [7]. This, therefore,

has called for far greater scrutiny to provide undeniable coffee integrity. However, some form of adulteration goes on unnoticed, with the majority being an adulteration of roasted coffee with coffee husk [8]. This act is further influenced by the increasing demand for coffee propelled by its consumption in emerging markets around the world, especially Russia, Australia and South Korea [9]. Since only the person handling the food is aware that the item has been altered, they are the only ones with knowledge, but they might not have the expertise to assess whether such alteration puts the customer at risk. These practices are prohibited everywhere and not only have negative economic effects [10].

Therefore, coffee roasters, consumers and quality control officials need to rise to the task of ensuring the integrity of coffee consumed worldwide and not only focus on massive production to catch up with the shortfall in supply. Hence, user-friendly and suitable analytical techniques are needed, for quality, safety and economic reasons, as well as to prevent coffee fraud and ensure integrity, thus promoting consumer confidence and encouraging and maintaining coffee beverage consumption worldwide. These were made possible by employing different wet chemistry methods, including compositional data analysis (volatile compounds, fatty acid profile, chlorogenic and caffeine content) [11], analysis of total xylose [8] and other known compositions. Furthermore, other researchers have used methods such as chromatographic and enzymatic methods, while anion-exchange chromatography with pulsed amperometry detection is mostly preferred as the most powerful technique [8]. However, these aforementioned techniques are quite expensive, elaborate, time-consuming and often not applicable for onsite real-time analysis.

Researchers have used different analytical methods to detect adulteration of coffee. UV-Vis spectroscopy was employed by [12] to successfully detect adulteration in the form of husk and sticks in the ground roasted coffee samples. Again, the following equipment was used by other researchers in adulteration detection in coffee; normal-phase HPLC with fluorescence [13], PCR-capillary electrophoresis [14] and Gas chromatography solid-phase micro-extraction [15].

NIR technology offers a great replacement for the conventional methods used for industrial coffee quality control. Due to sensitivity, non-destructiveness, speed, minimal sample preparation requirements, and lack of the use of toxic solvents, NIR data reveals itself as a potentially efficient tool for the detection of coffee adulteration. Various food items are detected using this technique [16]. NIR was utilized to identify coffee that contained adulterated arabica beans made of barley [17], corn [18], and Robusta [19,20]. The non-destructive detection of coffee containing adulterants such as barley and maize was conducted using FT-NIR spectroscopy [17,21]. Ebrahimi-Najafabadi et al. [17] employed portable NIR to detect 2% *w/w* of barley, and ref. [18] identified 5% of corn in roasted coffee. Moreover, ref. [19] demonstrated that it could accurately determine the 5–8 wt.% of corn, sticks, and Robusta coffee in arabica coffee.

Even though it is speedier than wet chemistry, it can be difficult, particularly in developing nations, to rely only on pricey, stationary laboratory-based equipment. For these reasons, the coffee authenticity drive is looking for a faster, low cost and onsite method. Portable NIR spectroscopy could be a very useful tool to solve this challenge. The development in NIR downsizing has opened up new possibilities for NIR applications ideal for in-person, lab, and industrial examination. Large, stationary laboratory-based NIR tools have become portable as a result of this. Portable NIR is more affordable, less complicated to use, and requires simple equipment than convectional, lab-based spectrum measuring spectrometers. The benefits of this instrument include their movability, strength, and ability to permit in-field and product-to-product evaluation and regulation. Online and in situ analysis are just a couple of the extra benefits above conventional instrument designs. Moreover, they have important benefits in terms of size, weight, resilience, spectrum range, and low manufacturing process [22]. They are helpful, once more, in circumstances where process monitoring and emergency response are necessary. Its shortcomings, however, include greater detection limits, reduced sensitivity, a strong impact of environmental factors on instrument performance, and a significant risk of sample contamination in

the field [23]. Nowadays, several methods involving portable spectroscopy have been developed for rapid and in-field food analysis. Because of their analytical capabilities, cost, and capability for in-the-field real-time investigation, portable NIR and Raman equipment are of special interest [24]. The features of the sample's physical and chemical properties are recorded by these instruments together with irrelevant data and interference signals. Raman spectroscopy is based on the scattering phenomena, whereas NIR is based on the absorption of light. The advantage of portable NIR over Raman spectroscopy is that the latter has limitations, such as the adverse effects of fluorescence, lack of sensitivity, and less value for precise product identification [25]. Santos et al. [26] used a portable NIR spectrometer to quantify and distinguish between crude and derivative oils in mixes containing used motor oil, gasoline, and diesel. Moreover, refs. [27,28] used it to identify forensic elements and estimate the quantities of soil plastic pollution, respectively. Using portable NIR spectroscopy and chemometrics methods, ref. [29] created a supervised classification model for separating Robusta from arabica coffee in the field of coffee research. The application of portable micro NIR spectroscopy in conjunction with sensory analysis was also proposed by [30] as a new analytical technique for observing the attributes of Robusta coffee grown in agroforestry systems.

It has not been utilized frequently, as far as we know, for onsite identification of adulterants in coffee. Consequently, the goal of the study was to assess the effectiveness of using chemometrics and portable NIR spectroscopy together to detect coffee husk in samples of Robusta coffee.

2. Materials and Methods

2.1. Sample Collection

Robusta coffee and coffee husk were gathered for this study from several locations in African countries that produce coffee. These samples consist of 90 adulterated samples created by accurately adding coffee husk (5–30% w/w) to 40 samples of Robusta coffee, 40 samples of coffee husk, and 40 samples of Robusta coffee. According to [31], the coffee samples were roasted for 1 h at 200 °C. To make the coffee husk's color resemble that of roasted coffee, it was first roasted. A home electric coffee bean roaster was used to roast the beans and husk (Jiawanshun, China). Using a multipurpose grinder, the coffee husk and Robusta coffee were ground separately (QE-100, Zhejiang YiLi Co., Ltd., Jiangsu, China). All of the sample groups were well-labeled and transported to the agriculture laboratory at the University of Cape Coast.

2.2. Spectra Collection

In the laboratory, a portable NIR spectrometer (SCIO^{TM}) in the range of 740–1070 nm was used to capture the spectrum of each sample from the three different coffee categories (Robusta coffee, husk coffee, and adulterated coffee, all in the powdered state) with a resolution of 1 nm for data collection assisted by a smartphone (Samsung A21). 50 g of each sample was gathered in a Ziplock bag and subjected to five scans, and the spectra were averaged to provide a mean spectrum as the original spectrum of the samples used. The scanning was carried out in a steady state of humidity and ambient temperature of 31 °C at the laboratory of the Food fraud center of the school of Agricultural, University of Cape Coast.

2.3. Chemical Composition Determination

The proximate composition, antioxidants and polyphenols of all the samples were determined using accepted procedures by those used by other authors [32]. All the parameters of the sample were carried out in triplicate and averaged to represent one sample.

2.4. Spectra Data Processing

All the computation, chemometrics analysis and graphs were performed with MATHLAB (2021a, MathWorks Inc., Natick, MA, USA) using the windows 10 Basic software

package for all data processing. In this study, three pre-processing techniques—first derivative (FD), multiplicative scattered correction (MSC), and SNV (standard normal variate) were utilized in comparison. Other authors have employed these pre-processing techniques. Consult the earlier research of other writers for more information on the theory underlying the pre-processing techniques that were employed [33,34].

2.5. Principal Component Analysis (PCA)

After pre-processing, PCA was employed as an unsupervised pattern method of identification to analyze potential data trends in a dimensional space in the form of a score plot. PCA compresses data into a major component that includes practical interpretable variables. It is also a well-known approach for lowering the dimensions of the data matrix. The top three PCs in a PCA hold crucial information and frequently initiate crucial information with minimal to no redundant data.

2.6. Data Partitioning

The spectral data set for pure Robusta coffee (40), adulterated samples (90) and pure coffee husk (40) were downloaded individually, and two sets (the training set and the test set) of each category were created. A total of 58 samples were chosen as the testing set when the model was being tested, and 112 samples were chosen as the training set when the model was being built. Three spectra were randomly chosen from every five samples as a training set, while the other samples were utilized as a test set to prevent bias in the division.

2.7. Multivariate Data Modelling

The study's main objective is to identify and quantify coffee promptly. Accurately recognizing Robusta coffee, coffee husk, and adulterated coffee is the identification problem. Support vector machine (SVM), linear discrimination analysis (LDA), neural network (NN), and random forest (RF) were some of the identification techniques that were compared to solve this problem. Please check the authors for more details on the ideas underlying these identification techniques [35–37]. To compare various forms of partial least square regression (PLS, iPLS, biPLS, GaPLS, and SPA-PLS), the quantity of coffee husk adulteration in Robusta coffee was determined. These different multivariate modeling approaches were compared and evaluated after their application using the test set performance data because each has strengths and shortcomings of its own. Please refer to the authors for further information on the ideas behind the quantitative models employed in the study [33–38].

2.8. Model Development Evaluation

To evaluate how well the qualitative and quantitative models performed, various statistical approaches were applied. As conducted by previous authors, the true positive rate (TPR), true negative rate (TNR), false positive rate (FPR), and false negative rate (FNR) were used to examine the performance of the identification models [39]. The predictive performance of the quantitative models was examined using the correlation coefficients of calibration and prediction sets (R), as well as the root mean squared errors of cross-validation and prediction, respectively (RMSECV and RMSEP), which were employed by other researchers [40,41].

There was a significant difference in all the parameters measured for coffee and coffee husk except for moisture. Ash (6.26%), lipids (6.23%), and fiber (6.19%) in coffee husk were higher than in coffee. Proteins, carbohydrates, polyphenols and antioxidants were higher in the coffee than in the coffee husk. Comparing the proximate composition of the husk to the literature, ash was higher than values recorded by (5.4%) [42] and in the range of (6.2%) [43]. Protein was higher than all values recorded in the literature (7.0% and 11.0%) for [42] and [44], respectively. The addition of coffee husk to the coffee decreases the level of antioxidants and polyphenols since coffee has a higher amount of polyphenols and antioxidants, as recorded in Table 1. Antioxidants and polyphenols

may significantly improve quality of life by assisting in the prevention or delaying of degenerative diseases [45,46]. Husk and other impurities lower the quality of ground and roasted coffee, which adversely affects the beverage's flavor, fragrance, acidity, bitterness, and other sensory qualities [47,48].

Table 1. Chemical composition of Robusta coffee and husk.

Parameters	Robusta Coffee	Husk
Moisture (%)	2.54 ± 0.32 [a]	3.24 ± 0.59 [a]
Ash (%)	3.62 ± 0.28 [a]	6.26 ± 0.20 [b]
Protein (%)	16.19 ± 0.11 [a]	14.59 ± 0.19 [b]
Lipid (%)	5.46 ± 0.29 [a]	6.23 ± 0.10 [b]
Fiber (%)	5.76 ± 0.09 [a]	6.19 ± 0.06 [b]
Carbohydrate (%)	68.98 ± 0.66 [a]	66.73 ± 0.38 [b]
Polyphenols (mg/kg)	4373.30 ± 65.80 [a]	354.30 ± 29.0 [b]
Antioxidant (mg/kg)	4416.80 ± 18.50 [a]	739.67 ± 7.43 [b]

Note: Values represent mean and ± SD of the three replicates. Where letters in the same row represent non-significant difference while different letters show significant difference at $p < 0.05$.

3. Results and Discussion

3.1. Spectral Profile Examination

As depicted in Figure 1, the spectral profile of the coffee samples used in this study had a distinct fingerprint. The raw spectra for Robusta coffee, coffee husk, and adulterated coffee are displayed in Figure 1a. This chart made it clear that Robusta coffee's spectrum was distinct from that of coffee husk and adulterated coffee. Figure 1b shows that all three samples (Robusta coffee, coffee husk, and adulterated) overlapped at 790 nm and 980 nm. This indicates that the samples exhibit some differences in physical and chemical properties, as shown in Table 1. From Table 1, it could be observed that the chemical parameters of the pure samples (coffee) showed significant differences compared with the adulterant (husk) except for moisture content. However, coffee is frequently adulterated with coffee husk because of these similarities in other slightly similar properties such as lipids and caffeine. Moreover, the wavelength range from 740 to 900 nm represents 3rd overtone Aromatic C-H, C-C and C=C which is associated with proteins, carbohydrates and lipids. Furthermore, in the region, 740 nm to 1070 nm 2nd and 3rd overtone RNH and ROH represent proteins, antioxidants, and polyphenols of coffee samples used [7]. The entire utilized wavelength range (740–1070) contains aromatic C–H, C–C, C=C, N–H, and O–H chemical bonds that may be connected to polyphenols, antioxidants, proteins, lipids, and carbohydrates.

To ensure that the samples were distinct from one another, the mean spectrum of the scanned samples was calculated, as shown in Figure 2. It was seen that the Robusta coffee samples clearly distinguished themselves from the coffee husk and adulterated samples at wavelengths between 750 nm and 1050 nm in Figure 2a. When the light of various wavelengths is radiated to organic matter, a portion of the light at a certain wavelength is absorbed. The amount of light absorbed depends on the composition of the irradiated organic materials in the case of coffee, husk, and adulterated samples. They have different compositions, such as polyphenols, proteins, lipids, carbohydrates, and moisture. This causes different absorption responses for each. This range of band corresponded to the band previously observed in spectra for roasted coffee and husk [49]. In Figure 2b, absorbance was lower for coffee and higher for coffee husk. The spectra for the adulterated samples were found in between the spectra for coffee and coffee husk. This could be a result of variations in their chemical composition.

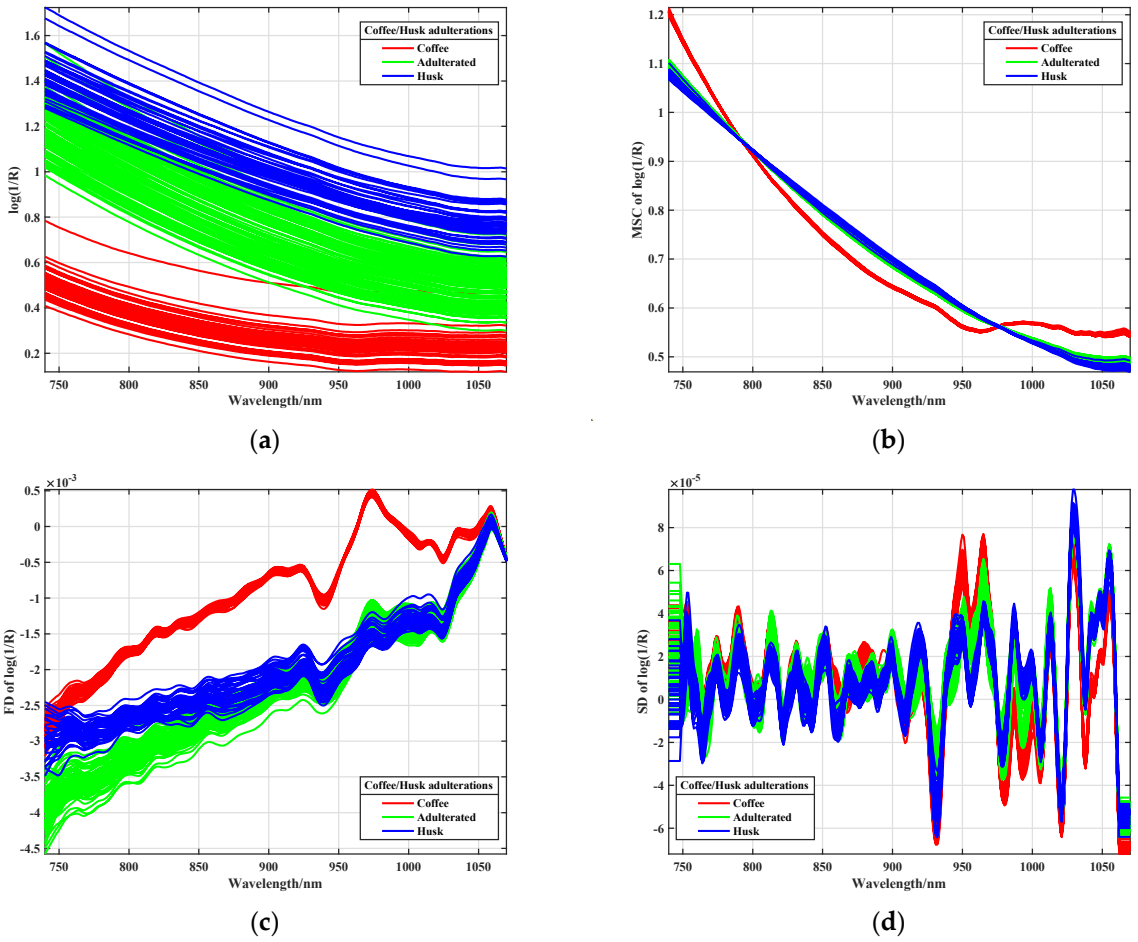


Figure 1. Raw spectral profile of Robusta coffee and adulterants: (**a**) raw, (**b**) MSC, (**c**) FD and (**d**) SD.

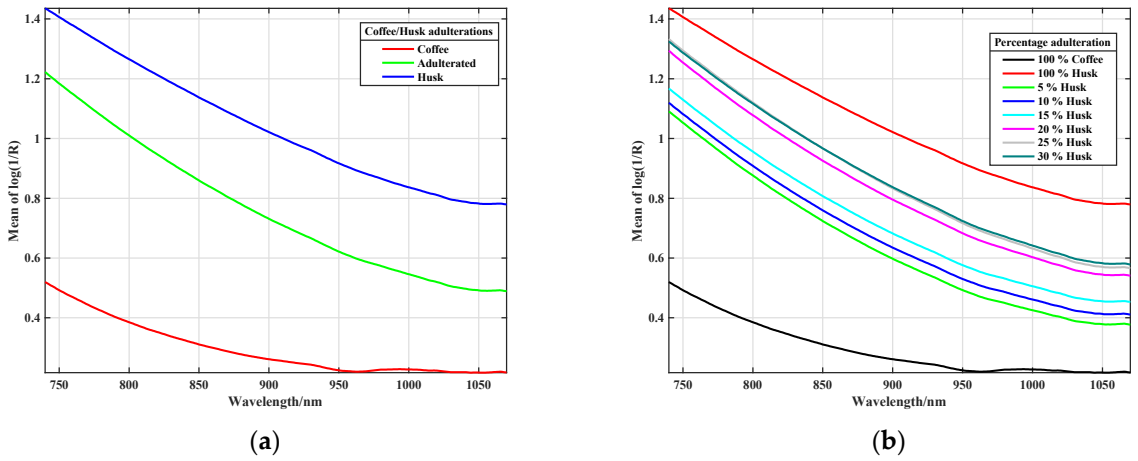


Figure 2. Mean coffee category spectral profiles in their raw form (**a**) and adulterated levels (**b**).

3.2. Principal Component Analysis (PCA)

In this study, roasted robusta coffee and coffee husk were subjected to principal component analysis to reveal the underlying natural pattern as a PCA score plot. Figure 3 displays the PCA for samples of roasted coffee, coffee husk, and adulterated coffee. The PCA is an unsupervised pattern. It typically determines the primary phenomena in the dataset and the direction of variation that is most important in the data set space [50]. With a pretreatment result of 99.96%, MSC outperformed all other preprocessing methods,

followed by FD (99.79%) and SNV (99.95%) for the top three PCs. As can be observed in the PCA score plot in Figure 3, all three samples were clustered for MSC, as shown in Figure 3a. MSC outperformed alternative pretreatments because it can correct the scatter, addictive and multiplicative effects of other pretreatments [51].

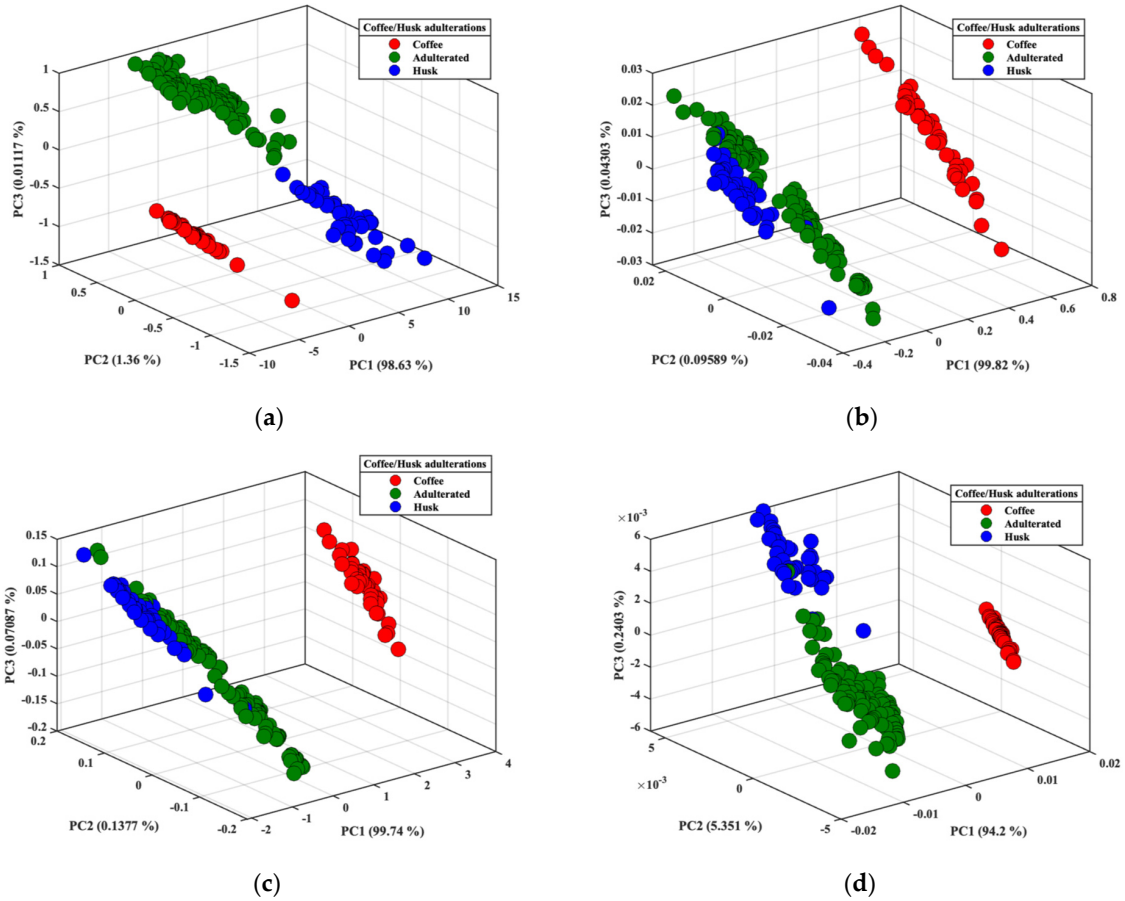


Figure 3. PCA score scatter Robusta coffee and adulterants: (**a**) raw, (**b**) MSC, (**c**) SNV and (**d**) FD.

The PCA eigenvector plot explained the cluster trend observed in the PCA score plot, as can be seen in Figure 4. The key peaks responsible for the neat clustering are situated between 950 and 1000 nm for PC1, 920 and 930 nm for PC2, 930 and 960 nm, 960 and 980 nm, and 990 and 1100 nm for PC2 for PC3, according to the loading plot of FD-PCA Eigenvectors. The second and third overtone regions' RNH, ROH, CH2, and CH3 are represented by these significant peaks [7].

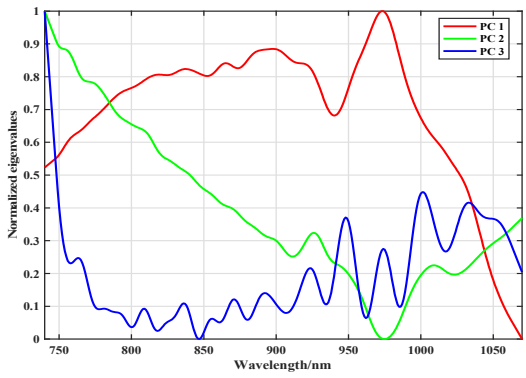
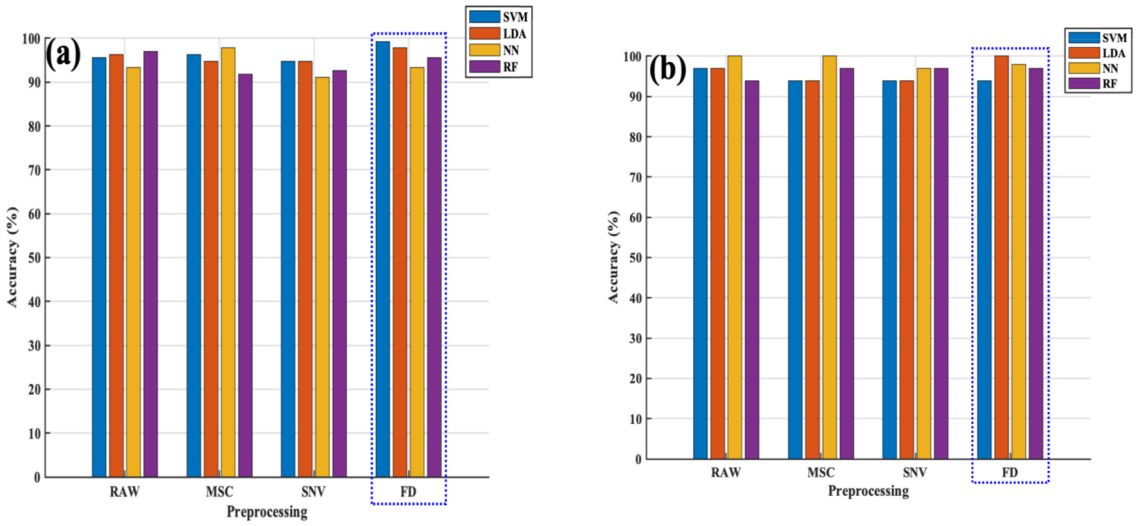


Figure 4. FD-PCA Eigenvectors for the coffee samples.

3.3. Identification Model

Identification models were also constructed and assessed in comparison. Support vector machine (SVM), linear discrimination analysis (LDA), neural network (NN), and random forest were among these models (RF). The models produced the best results with preprocessing techniques such as FD, MSC, and SNV. Figure 5 shows that the performance of every identification model was considerably above a 90% identification rate. The first derivative spectra preprocessing treatment, however, outperformed the others when the raw spectra data set was processed, achieving 97.78% and 100% in both the calibration set and the prediction set using LDA, as shown in Table 2. Again, the model was assessed by the true positive rate (TPR), true negative rate (TNR), false positive rate (FPR), and false negative rate (FNR). It is always desirable for the false positive rate to be at a minimum while the true positive rate is maximized [52]. For all the models, the true positive rate was 100%, and the false negative rate was less than 1%. The capacity of linearly discriminating functions, which highlights the ratio of class variance and lowers the ratio of within-class variation, is what gives LDA its best performance [53].



(**a**) (**b**)

Figure 5. Accuracy in (**a**) calibration set and (**b**) prediction set for SVM, LDA, NN and RF models of Coffee samples.

Table 2. Optimum discrimination accuracy for the models developed.

Model	Preprocessing	Sets	Accuracy (%)	Error (%)	TPR (%)	TNR (%)	FPR (%)	FNR (%)
SVM	FD	Calibration	99.26	0.74	100.00	100.00	0.00	0.00
		Prediction	93.94	6.06	100.00	100.00	0.00	0.00
LDA	FD	Calibration	97.78	2.22	100.00	100.00	0.00	0.00
		Prediction	100.00	0.00	100.00	100.00	0.00	0.00
NN	FD	Calibration	96.30	3.70	100.00	99.05	0.00	0.95
		Prediction	96.97	3.03	100.00	100.00	0.00	0.00
RF	FD	Calibration	95.56	4.44	100.00	100.00	0.00	0.00
		Prediction	96.97	3.03	100.00	100.00	0.00	0.00

4. Multivariate Quantification of Adulterant

To more precisely quantify the authenticity and levels of adulteration in the samples, various partial least square regression models, including PLS, iPLS, biPLS, Si-PLS, GaPLS,

and SPA-PLS, were utilized for quantitative analysis. PLS could provide accurate predictions and extract relevant information. These methods were improved and contrasted. With R = 0.97 for the calibration set, R = 0.98 for the prediction set, and RPD (ratio performance deviations) of 7.05, the results in Table 3 showed that the SPA-PLS model provided the best adulteration prediction results for the samples that had been tampered with. These results concur with those of other researchers who tackled a related problem using even a wider wavelength [12,49]. Among these models, the SPA (successive projections algorithm) chooses variables with the least amount of collinearity by using straightforward projection operations. It is a cutting-edge variable selection algorithm that has also been used to successfully address collinearity issues [54].

Table 3. Comparison of different PLS quantification models.

Models	Variables	Calibration Set			Prediction Set			RPD
		R	RMSECV	Bias	R	RMSEP	Bias	
PLS	331	0.9626	10.7187	0.9867	0.9858	5.2485	0.7422	6.0179
iPLS	16	0.9701	9.6209	0.2049	0.9704	8.2453	−0.8647	3.8306
biPLS	49	0.9682	9.9263	0.1241	0.9708	8.2086	−0.6206	3.8478
Si-PLS	50	0.9799	7.888	0.0056	0.9824	6.0610	−1.4073	5.2111
GaPLS	331	0.9674	10.0189	−0.1527	0.9792	7.1855	−3.1656	4.3956
SPA-PLS	10	0.9711	9.4455	0.8695	0.9897	4.4753	0.6329	7.0576

The optimum spectrum selection of the essential wavelengths that produce the research's accurate results, which are 756–768 nm, 790–799 nm, 844 nm, 891–906 nm, 982–995 nm, and 1042 nm, is illustrated in Figure 6c to explain this phenomenon. These wavelengths match the various chemical characteristics of the coffee that set it apart from the coffee husk. More significantly, the third overtone CH_3, CH_2, and ROH ranges from 756–768 nm, 790–799 nm, 844,891–906 nm, and 844,891–1042 nm are linked to carbohydrates, while the second overtone R-NH, aromatic-CH, CH2, and CH3 ranges from 982–995 nm and 1042 nm are linked to proteins, lipids, polyphenols, and antioxidants. The aforementioned qualities offer incredibly distinctive chemical traits that can be utilized to precisely identify the grade classes and make predictions about the integrity of the coffee. This provides more evidence for the claim made by [19] that polyphenolic substances were crucial in the identification and application of their spectrum data, which allowed for the precise observation and determination of distinct samples.

The ratio of random variation in the samples to the degree of expected prediction errors is described as residual prediction deviation (RPD). RPD is more advantageous when comparing models on different data sets or in absolute terms. It was calculated for the calibration and prediction sets and produced values that showed how well or poorly the models were able to predict outcomes. Values of residual prediction deviation greater than 2.4 indicate calibration models with good predictive capacity, whereas values less than 1.5 are considered poor [55,56]. The SPA-PLS model, which has the best PRD value of the other models at 7.05, as shown in Table 3, has all of the recorded values higher than 2.4. Figure 6b shows the residual plot for the SPA-PLS for both the calibration and prediction plots with 95% confidence bounds. This plot shows the differences between the measured percentage of adulteration and the predicted percentage of adulteration. More than 90% of the calibration data scatter around the mean (fit) line, with the remaining outside the confidence bounds. These data points can be considered to be outliers. The same can be said for the prediction data.

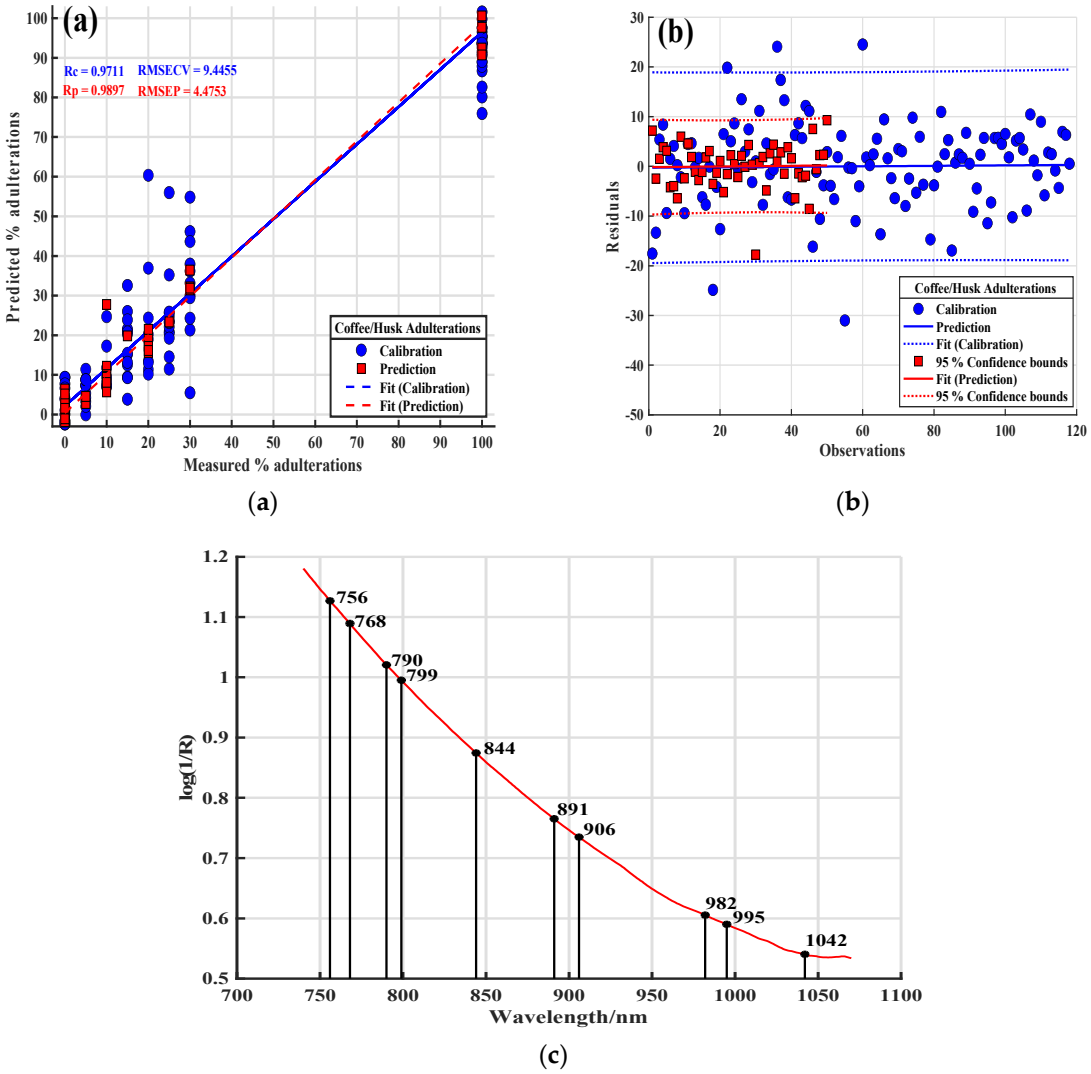


Figure 6. Scatter plots of SPA-PLS model with NIR estimation and experimental concentration (**a**) and residual plot (**b**) and (**c**) model plot.

5. Conclusions

This research work has demonstrated the potential of miniaturized short-wave NIR spectroscopy for coffee integrity in Ghana and could be used as a technique for rapid, onsite and affordable coffee examination. The best technique was found to be first derivative (FD) pre-processing modeled with linear discriminate analysis (FD-LDA). Thus, FD-LDA was superior (97.78% and 100% in both the calibration set and prediction set) to the others used for qualitative determination of coffee integrity (discrimination of pure coffee from adulterated ones). While for quantitative detection of coffee adulterants (quantification of the percentage of adulterants; 5–30%) in authentic coffee, the SPA-PLS model had R = 0.9711 and 0.9897 in both the calibration set and prediction set. The results obtained in this study showed only feasibility and additional research is required to confirm the performance across different locations and varieties.

Author Contributions: Funding acquisition, Conceptualization, investigation, methodology, formal analysis, and writing—original draft: V.G.B. and E.T.; validation, visualization and data curation: C.L.Y.A. and F.P.L.; resources, writing—review, editing, supervision project administration: E.T. and L.K.S.-A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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