Authentication of organic Lampung robusta ground roasted coffee by UV-visible spectroscopy and PLS-DA method

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Abstract. In this research, a potential application of UV-visible (UV-Vis) spectroscopy combined with partial least squares-discriminant analysis (PLS-DA) method to discriminate Lampung robusta coffee with different fertilizer treatment was evaluated. The fully red ripened coffee beans were selectively harvested by hand from coffee plantation located in Lampung Barat of Lampung province from two different fertilizer treatments: chemically fertilized and organically fertilized. A number of 200 ground roasted coffee samples of each treatment (1 gram of each samples) was used as samples, respectively. The all coffee samples were extracted using hot distilled water. The aqueous coffee samples were pipetted into 10 mm of cuvette and the spectral data was obtained using a UV-Vis spectrometer in the range of 190-1100 nm. Principal component analysis (PCA) and PLS-DA method was used as unsupervised and supervised classification methods to discriminate the organic and non-organic coffee. The results showed that using the first two principal components (PCs), a clear separation between organic and non-organic coffee samples was achieved using modified spectral data in the range of 230-450 nm. The classification of organic and non-organic coffee using PLS-DA method resulted in high accuracy both for calibration and prediction steps. The overall result showed that UV-visible spectroscopy combined with PLS-DA method could be used as a low-cost, relative fast and green method to discriminate between organic and non-organic Lampung robusta ground roasted coffee.

1. Introduction

Recently, the awareness of eating a healthy food has increased [1]. For this reason, the market for organic food has increased during the past decade [2]. According to Barbosa *et al.* [3] organic food can be defined as a product that has been produced according to some standards by which the use of pesticides and inorganic fertilizers is prohibited. In fact, this organic farming system with the absence of pesticides and inorganic fertilizer is more expensive than the conventional system [4]. Therefore, organic food products tend to retail at a higher price [4]. This premium price and the increasing demand thus make organic food products susceptible to fraud. It was reported that non-organic products are easily labeled as organic products since there is no reliable visual difference between them [5], no

exception for Lampung ground roasted coffee. As seen in Figure 1, it is very difficult to differentiate between organic (left) and non-organic (right) Lampung ground roasted coffee. For this reason, the development of a robust analytical method to authenticate organic ground roasted coffee is highly needed.

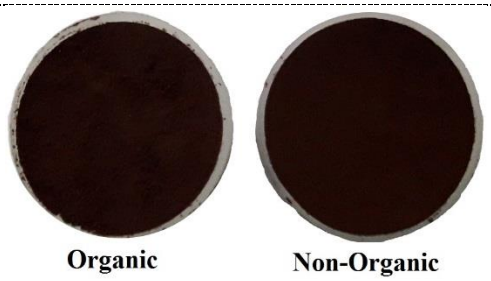

Figure 1. Lampung ground roasted coffee of organic (left) and non-organic (right) samples.

Several analytical methods have been tried to discriminate between organic and non-organic food. Analytical methods based on determination of trace element in food can be used to differentiate between organic and non-organic food. The examples of trace element based methods for organic food authentication are compound-specific isotope analysis (CSIA) [6], inductively coupled plasma-mass spectrometry (ICP-MS) [7], instrumental neutron activation analysis (INAA) [8] and isotope ratio mass spectrometry (IRMS) [9].

One of the most widely used analytical method for organic food authentication is spectroscopy based method within its different regions (UV-Vis, NIR, MIR, X-ray and THz) [10]. For example, the combination of mid-infrared (MIR) spectroscopy and multivariate analysis was used by Cozzolino *et al.* [11] to discriminate between organic and conventional wines grown in Australia. Song *et al.* [12] investigated the use of low-cost NIRS standard recognition techniques in order to differentiate 60 samples of Gala apples cultivated in organic and conventional systems. An accuracy of 96.00% was obtained in the classification of these apple samples. Bortoleto *et al.* [13] investigated the potential of energy-dispersive X-ray fluorescence (EDXRF) combined with chemometrics analysis (PCA) of the spectral data to discriminate between organic and conventional coffee and tomato samples.

For ground roasted coffee, UV-visible spectroscopy has been used for discrimination between fresh and expired coffee [14], peaberry versus normal coffee [15], civet versus non-civet coffee [16-17], Gayo wine versus Gayo normal coffee [18] and decaffeinated versus non-decaffeinated coffee [19]. UV-visible spectroscopy also has been used for authentication of several Indonesian specialty coffees both in qualitative and quantitative studies [20-22]. However, the use of UV-visible light (190-780 nm) for authentication of organic food is very limited. PLS-DA (partial least square-discrimination analysis) is a versatile algorithm that has demonstrated great success in classification purpose. For this reason, the objective of this current research is to evaluate the use of UV-visible spectroscopy and PLS-DA for authentication of organic Lampung ground roasted coffee.

2. Materials and Methods

2.1. Samples

The fully red ripened coffee beans were selectively harvested by hand from coffee plantation located in Lampung Barat of Lampung province from two different fertilizer treatments: chemically fertilized (non-organic) and organically fertilized (organic). For organic fertilizer, two different types of fertilizer were used: organic 1 was made from microbial based organic fertilizer and organic 2 was made from compost based organic fertilizer. A number of 200 ground roasted coffee samples of each treatment (1 gram of each samples) was used as samples, respectively. The sample preparation including grinding

and sieving was done according to previous reported work [17]. The samples were randomly divided into two sample sets, calibration and validation set (501 samples) and prediction set (99 samples).

2.2. Extraction procedures and spectral measurement

An aqueous extraction procedure of the coffee samples was done as described by Suhandy and Yulia [15-17]. UV-Visible spectra of the aqueous extracts were measured using a UV-Vis spectrometer (Genesys™ 10S UV-Vis, Thermo Scientific, USA) in the range of 190-1100 nm with spectral resolution of 1 nm at a room temperature. This spectrometer was equipped with a quartz cell with optical path of 10 mm. This spectrometer has total six holders (five sample holders and one reference holder). To generate each sample absorbance data, reference spectra was measured by putting 3 mL of distilled water and was followed by sample measurement by putting 3 mL of coffee aqueous samples.

2.3. PLS-DA method

The original (raw) spectra and modified spectra were used for further analysis. The modified spectra were obtained by applying two different spectral pre-treatments: moving average (MOV) with 9 segments for averaging and mean normalization. For classification and discrimination, PLS-DA (partial least squares-discriminant analysis) method was used. This method works based on PLS algorithm with a dummy response variables: Y=1 is belong to class and Y=0 is not belong to class. The calculation of PLS-DA model was done using a multivariate analysis program The Unscrambler® version 9.8 (CAMO AS, Norway). Accuracy and error of each model was calculated both for calibration and prediction step. Accuracy of the classification can be defined as the number of correct classifications over the total number of classifications. Error is the number of incorrect classification divided by the total number of classifications.

3. Results and Discussions

3.1. Spectra of organic and non-organic Lampung ground roasted coffee samples

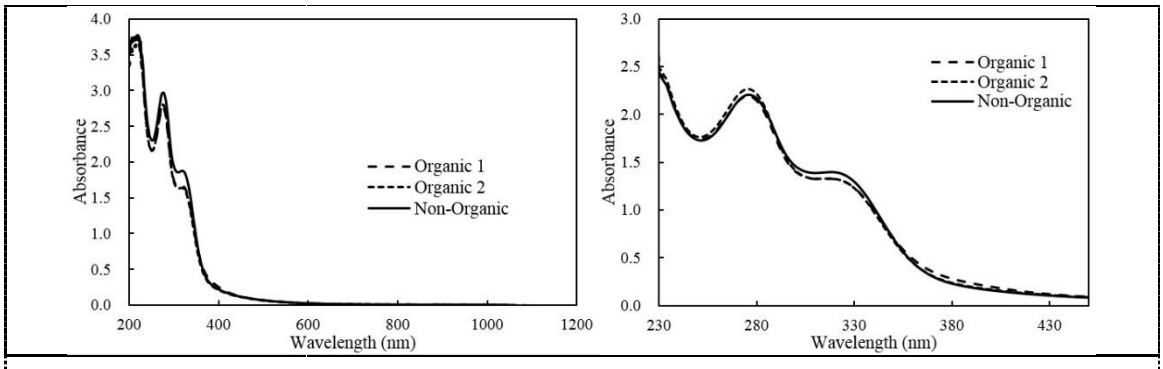

Figure 2. Spectra of organic and non-organic coffee samples for original spectra in the range of 190-1100 nm (left) and modified spectra in the range of 230-450 nm (right).

Figure 2 (left) showed a typical average original spectra of organic and non-organic coffee samples in the range of 190-1100 nm. The shape of spectra was similar to previous reported works [12-14]. Due to high noise in the range of 190-230 nm and very low absorbance intensities in the range of 450-1100 nm, the spectral data in the range of 230-450 nm was selected for further analysis. To improve the quality of original spectra, two different spectral pre-treatments were used: moving average (MOV) with 9 segments for averaging and mean normalization. The modified spectra was demonstrated in Figure 2 (right). Several peaks with high absorbance intensity were identified at 252 nm, 278 nm, 310 nm and 325 nm. The high absorbance intensities at wavelength of 252 nm and 278 nm are associated with the absorbance of caffeine in ground roasted coffee [24-25].

3.2. Results of PCA

Principal component analysis (PCA) was applied to evaluate the differences between the types of fertilizer (organic and non-organic) based on the UV-visible spectra. PCA was applied for both original and modified spectra and the results were demonstrated in Figure 3. The scores plot for the two first principal components, PC1 and PC2, represent 89% of the total spectral variation in which PC1 explained 62% and PC2 explained 27% of the data variance for original spectra (Figure 3 left). It was showed that the samples of organic and non-organic coffee could not be separated using original spectra in the range of 190-1100 nm. However, using modified spectra in the range of 230-450 nm, the separation between organic and non-organic coffee was achieved using PC1 (51%) and PC2 (43%) of the total variance (Figure 3 right). The organic coffee samples (organic 1 and organic 2) were concentrated on the positive side of the PC1, whereas the non-organic coffee samples were agglomerated on the negative side of PC1.

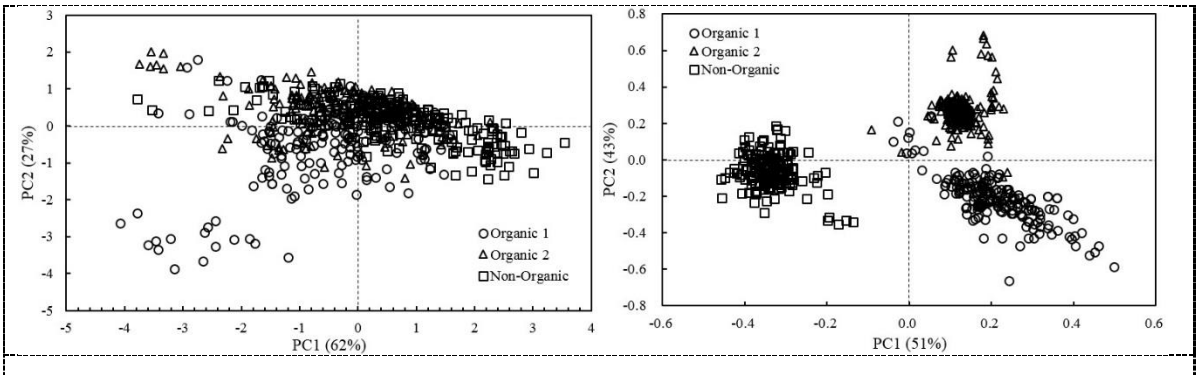

Figure 3. Score plot of PC1 and PC2 of coffee samples using original spectra in the range of 190-1100 nm (left) and using modified spectra in the range of 230-450 nm.

Before developing PLS-DA model, it is important to remove outlier which can be accomplished using information about the residual analysis and leverage. For this, an influence plot from PCA result was depicted in Figure 4. This plot was a two dimensional plot with sample leverage value in x-axis and sample residual value in y-axis. Samples with high leverage and high residual are damaging to the model. Based on Figure 4, it is noted that there is one sample (x) having high value both in leverage and residul. This sample was removed from further analysis (PLS-DA).

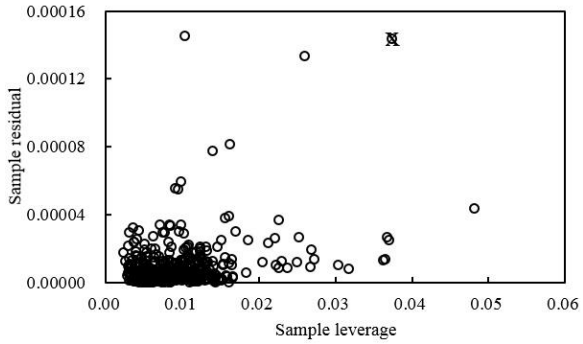

Figure 4. Influence plot of organic and non-organic coffee samples for modified spectra in the range of 230-450 nm.

3.3. Results of PLS-DA

A PLS-DA model was developed using modified spectra in the range of 230-450 nm for each class (organic 1, organic 2 and non-organic). The result was summarized in Table 1. The quality of the model

is quite good with low RMSECV and RMSEP. The accuracy of the model is high (0.98 ~ 1.00) for all classes.

Table 1. PLS-DA results for discrimination between organic and non-organic samples in calibration and prediction samples.

Pre-treatment of spectral data	Latent variables	Class	RMSEC	RMSEP	Calibration		Prediction	
					Accuracy	Error	Accuracy	Error
MOV 9s + Normalize (mean) in the range of 230-450 nm	10	Organic 1	0.144543	0.135872	0.98	0.02	0.99	0.01
	4	Organic 2	0.130362	0.124202	0.99	0.01	1.00	0.00
	4	Non-Organic	0.086744	0.105027	1.00	0.00	1.00	0.00

4. Conclusion

The application of using UV-visible spectroscopy, in combination with PLS-DA method for discrimination of organic and non-organic Lampung robusta ground roasted coffee samples has been shown. The separation of organic and non-organic coffee samples can be achieved by applying PCA on modified spectra in the range of 230-450 nm. All PLS-DA models resulted in high accuracy both in calibration and prediction. This research conclude that UV-visible spectroscopy along with PLS-DA method can be promoted to establish authentication system for Lampung organic coffee.

Acknowledgment

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References

[1] De Lima M D and Barbosa R 2019 Methods of authentication of food grown in organic and conventional systems using chemometrics and data mining algorithms: a Review *Food Anal. Methods*. **12** 887–901.

[2] Siderer Y, Maquet A and Anklam E 2005 Need for research to support consumer confidence in the growing organic food market *Trends Food Sci. Technol.* **16** 332−43.

[3] Barbosa R M, Batista B L, Barião C V, Varrique R M, Coelho V A, Campiglia A D and Barbosa F Jr 2015 A simple and practical control of the authenticity of organic sugarcane samples based on the use of machine-learning algorithms and trace elements determination by inductively coupled plasma mass spectrometry *Food Chem*. **184** 154–9.

[4] Tres A, van der Veer G, Perez-Marin M D, van Ruth S M and Garrido-Varo A 2012 Authentication of organic feed by near-infrared spectroscopy combined with chemometrics: A feasibility study *J. Agric. Food Chem.* **60** 8129–33.

[5] Charlebois S, Schwab A, Henn R and Huck C W 2016 Food fraud: An exploratory study for measuring consumer perception towards mislabeled food products and influence on self-authentication intentions *Trends Food Sci. Technol.* **50** 211–8.

[6] Laursen K H, Mihailova A, Kelly S D, Epov V N, Bérail S, Schjoerring J K, Donard O F X, Larsen E H, Pedentchouk N, Marca-Bell A D, Halekoh U, Olesen J E and Husted S 2013 Is it really organic? – Multi-isotopic analysis as a tool to discriminate between organic and conventional plants *Food Chem.* **141** 2812–20.

[7] Maione C, de Paula E S, Gallimberti M, Batista B L, Campiglia A D, Jr F B and Barbosa R M 2016 Comparative study of data mining techniques for the authentication of organic grape juice based on ICP-MS analysis *Expert Syst. Appl.* **49** 60–73.

[8] Turra C, Fernandes E A N, Bacchi M A, Tagliaferro F S and França E J 2006 Differences between elemental composition of orange juices and leaves from organic and conventional production systems *J. Radioanal. Nucl. Chem.* **270** 203–8.
[9] Muccio Z and Jackson G P 2009 Isotope ratio mass spectrometry *Analyst* **134** 213–22.
[10] Callao M P and Ruisánchez I 2018 An overview of multivariate qualitative methods for food fraud detection *Food Control* **86** 283–93.
[11] Cozzolino D, Holdstock M, Dambergs R G, Cynkar W U and Smith P A 2009 Mid infrared spectroscopy and multivariate analysis: A tool to discriminate between organic and non-organic wines grown in Australia *Food Chem*. **116** 761–5.
[12] Song W, Wang H, Maguire P and Nibouche O 2016 Differentiation of organic and non-organic apples using near infrared reflectance spectroscopy – A pattern recognition approach *SENSORS IEEE* 1–3.
[13] Bortoleto G G, De Nadai Fernandes E A, Tagliaferro F S, Ferrari A A and Bueno M I M S 2008 Potential of x-ray spectrometry and chemometrics to discriminate organic from conventional grown agricultural products *Proc. Second Scientific Conf. of International Society of Organic Agriculture Research (ISOFAR)*, Modena, pp. 000–000.
[14] Yulia M and Suhandy D 2018 Identification of fresh and expired ground roasted robusta coffee using UV-visible spectroscopy and chemometrics *MATEC Web of Conf.* **197** 09003.
[15] Suhandy D and Yulia M 2017a Peaberry coffee discrimination using UV-visible spectroscopy combined with SIMCA and PLS-DA *Int. J. Food Prop.* **20** S331–9.
[16] Suhandy D and Yulia M 2017b The use of partial least square regression and spectral data in UV-visible region for quantification of adulteration in Indonesian palm civet coffee *Int. J. Food Sci*. **2017** 1–7.
[17] Yulia M and Suhandy D 2017 Indonesian palm civet coffee discrimination using UV-visible spectroscopy and several chemometrics methods *Journal of Physics: Conf. Series* **835** 012010.
[18] Suhandy D and Yulia M 2018 The classification of arabica gayo wine coffee using UV-visible spectroscopy and PCA-DA method *MATEC Web of Conf.* **197** 09002.
[19] Yulia M, Asnaning A R and Suhandy D 2018 The classification of ground roasted decaffeinated coffee using UV-VIS spectroscopy and SIMCA method *IOP Conf. Ser.: Earth Environ. Sci*. **147** 012010.
[20] Suhandy D, Yulia M and Kusumiyati 2018 Chemometric quantification of peaberry coffee in blends using UV–visible spectroscopy and partial least squares regression *AIP Conf. Proc.* **2021** 060010.
[21] Yulia M, Asnaning A R, Waluyo S and Suhandy D 2018 Partial least squares with discriminant analysis and UV– visible spectroscopy for qualitative evaluation of Arabica and Robusta coffee in Lampung *AIP Conf. Proc.* **2021** 060021.
[22] Suhandy D and Yulia M 2018 The potential of UV-visible spectroscopy and chemometrics for determination of geographic origin of three specialty coffees in Indonesia *AIP Conf. Proc.* **2021** 040001.
[23] Suhandy D, Yulia M and Kusumiyati 2019 The authentication of peaberry and civet ground roasted robusta coffee using UV-visible spectroscopy and PLS-DA method with two different particle sizes *IOP Conf. Ser.: Earth Environ. Sci.* **258** 012043.
[24] Belay A, Ture K, Redi M and Asfaw A 2008 Measurement of caffeine in coffee beans with UV/vis spectrometer *Food Chem.* **108** 310–5.
[25] Clarke R J and Macrae R 1985 Coffee chemistry (Vol. 1) (Amsterdam: Elsevier).