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The Potential of UV-Visible Spectroscopy and Chemometrics for Determination of Geographic Origin of Three Specialty Coffees in Indonesia

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Abstract. The growing global trading market for specialty coffee increases the need for better coffee quality evaluation methods. Several Arabica coffees in Indonesia have high commercial value. For this reason, the development of analytical methods with high sensitivity and accuracy for detection of its adulteration was important. This research evaluated the potential of UV-visible spectroscopy and partial least squares discriminant analysis (PLS-DA) for determining the geographic origin of three specialty coffees (Gayo, Kintamani and Wamena) in Indonesia. In this research, 296 coffee samples from three different origins (Gayo, Kintamani and Wamena) were used. All coffee samples were ground using a home-coffee-grinder. We sieved all coffee samples through a nest of US standard sieves (mesh number of 40) on a Meinzer II sieve shaker for 10 minutes to obtain a particle size of 420 µm. All samples were extracted with distilled water and then filtered. For each sample, 3 mL of extracted sample then was pipetted into 10 mm cuvettes for spectral data acquisition. The spectral data were acquired using a Genesys 10s UV-visible spectrometer in the range of 190-1100 nm. A PLS-DA classification model was estimated to classify the origin of specialty coffees by their UV-visible spectra. The best PLS-DA model accurately classified the specialty coffee samples of the prediction sample set with prediction ability of 100% of correct classification for Gayo, Kintamani and Wamena, respectively. The results demonstrate that UV-visible spectroscopy coupled with PLS-DA provides a sensitive and accurate analytical method to distinguish ground roasted coffee samples geographically.

Keywords: Coffee, geographic origin, partial least squares discriminant analysis, UV-visible spectroscopy.

INTRODUCTION

Several types of coffee beans in Indonesia coming from certain regions, such as Arabica Gayo coffee (Aceh), Arabica Kintamani coffee (Bali) and Arabica Wamena coffee (Papua), have been classified as specialty coffee. Those coffees are very special and unique in taste. For this reason, the prices are higher than for other, non-specialty coffee. In order to protect the authenticity of those specialty coffees, the Indonesian government has developed the concept of "geographical indication" or GIs since regulated in Law No. 20/2016 on Trademarks (TM) and Geographical Indication (GI). Geographical Indication (GI) is a sign that indicates the place of origin of goods and/or products, which due to geographical environment factors, including nature, the humans who produced it or the combination thereof provides a specific reputation for quality and certain characteristics of the produced goods and/or products. So far, more than 54 well-known Indonesian products have followed the GI route and been officially registered as GIs in Indonesia by the relevant governmental authority. For coffee products, presently there

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are 19 products that have been registered and granted the GIs. For example, Arabica Gayo coffee is registered and received the GI number ID G 000000005, and Arabica Kintamani coffee has the GI number ID G 000000001.

Most of those specialty coffees are traded in the form of ground roasted coffee (powder), as it is ready and easier for consumers to prepare for daily usage. However, when it is in the form of ground roasted coffee, it is almost not feasible to discriminate between specialty coffee coming from one origin and specialty coffee from another origin with the naked eye. For this reason, adulteration of specialty coffee could become a serious problem. Food adulteration is one types of food fraud which can be defined as lowering the quality of food by intentional or unintentional substitution of food with some inferior foreign material or by removal of some value added food substitute from the main food item.[1,2] The risk of food adulteration is a major concern in the food industry not only for economic but also for safety reasons.[1] To avoid the serious problem of food adulteration, there is a need to develop a food authentication system to ensure and protect the authenticity of high-priced products (including specialty coffee).

One important issue in the area of food authentication is development of the method for authentication. Authentication itself can be defined as the process that verifies that a food is in compliance with its label description. Several methods have been reported to assess the authenticity of food products, including spectroscopy (UV-visible, NIR, MIR and Raman), chromatography (HPLC, GC, GC–MS, GC-FTIR, and GC-TOFMS) and the electronic nose and electronic tongue.[2-4] For authentication of coffee, several different analytical methods have been used such as near infrared spectroscopy, mid infrared spectroscopy and gas chromatography.[5-8] However, no reported work has been done on the authentication of ground roasted coffees produced in different regions in Indonesia. In addition, although UV-visible spectroscopy has been used for quality evaluation of ground roasted coffee, no record has been found in the literature on its application for the discrimination of Indonesian ground roasted coffees.[9-11] Therefore, the main objective of the current research was to develop a supervised classification method using partial least squares discriminant analysis (PLS-DA) capable of discriminating coffees produced in Indonesia according to their origin using UV-visible spectroscopy.

MATERIALS AND METHODS

Coffee Samples

Indonesian specialty Arabica coffees (Gayo, Kintamani and Wamena) were purchased from a local market in Bandar Lampung, Lampung, Indonesia (roasted coffee bean). Sample preparation including grinding and sieving was performed based on the procedure described in previous published works [9-10]. Altogether, 296 samples (each sample consist of 1 g weight) of either Gayo, Kintamani or Wamena were prepared. A standard aqueous extraction of the coffee samples was then performed in accordance to previous works [9-11]. After cooling to room temperature (for 20 min), all extracts were then diluted in a 1:20 (mL: mL) proportion with distilled water.

Spectral Acquisition

Spectral data of aqueous coffee samples were recorded using a UV-visible spectrometer (Genesys™ 10S UV-Vis, Thermo Scientific, USA). Spectra were obtained in transmittance mode and performed at room temperature (27-28°C). Spectral data were collected over the range 190 to 1100 nm with 1 nm of wavelength accuracy. All the spectral data were then imported into The Unscrambler® X (30 days trial version – CAMO Software, Oslo, Norway).

Spectral Treatment

Before the application of the PLS-DA method, spectral data pre-processing was applied. Different pre-processing methods were applied: moving average smoothing (segment: 9) (MOV), standard normal variate (SNV), multiplicative scatter correction (MSC) and Savitzky-Golay 1st derivative (ordo: 2; window: 9) (SG 1d).

Data Analysis

The dataset (spectral data) was randomly divided into two subsets: a calibration set (240 samples) and prediction set (56 samples). The calibration set was used to develop classifier model based on the PLS-DA method. Prediction set was used to evaluate the performance of the developed PLS-DA model.

Development of PLS-DA Model

The PLS-DA model was developed using the PLS algorithm with the matrix Y (variable Y) containing information about the sample classes (Gayo, Kintamani and Wamena class). For each class, the value is assumed to be 0 or 1, depending on whether or not it belongs to the class represented for that column.[9] For this reason, evaluation of the PLS-DA model was conducted in a manner similar to PLS model evaluation using the following parameters: coefficient of determination (R^2) both in calibration and validation, root mean square error of calibration (RMSEC), and root mean square error of cross-validation (RMSECV).[12] A calibration model with R^2 value greater than 0.91 is considered to be an excellent calibration, while an R^2 value between 0.82 and 0.90 results in good prediction [12]. To avoid over-fitting cases in the PLS-DA model, a small difference between RMSEC and RMSECV is required [13-14]. To evaluate the performance of the PLS-DA model, the percentage of correct classifications (%CC) was calculated based on the previous work.[15]

RESULTS AND DISCUSSION

Spectral Analysis of Specialty Coffees with Different Origins

Figure 1 shows the average original spectra (left) and pre-processed spectra (right) of the aforementioned three specialty coffees. In general, the absorbance intensity was high in the range of 190-400 nm. This spectral range is associated with $n \rightarrow \pi^*$ electronic transition of caffeine, chlorogenic acids, and trigonelline molecules.[16] In next step, we used spectral data in the range of 250-450 nm for principal components analysis (PCA) and PLS-DA analysis.

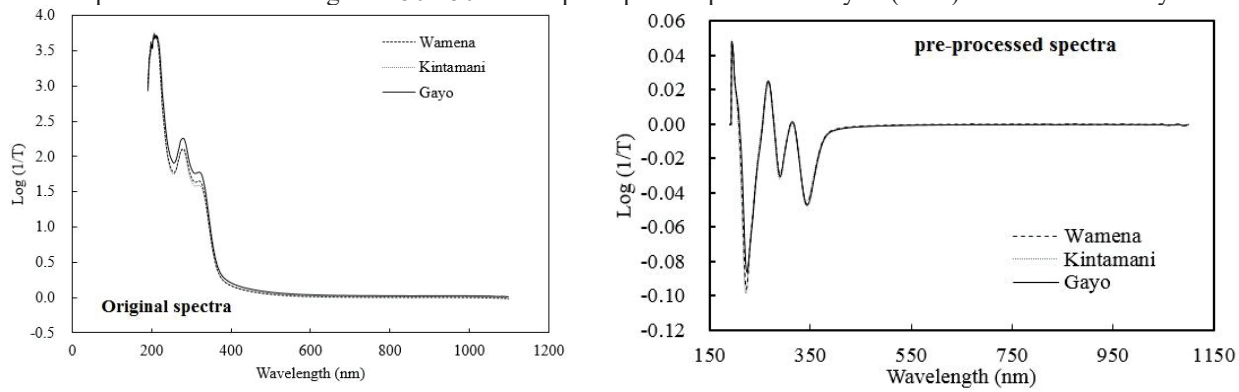

FIGURE 1. The original and pre-processed spectral data (average) of three different specialty coffees in the range of 190-1100 nm. Original spectra (a) Pre-processed spectra (b).

Unsupervised Classification Using Principal Component Analysis

The result of the PCA is plotted in Figure 2 (a). PC1 explained 69% of the total variance in the data set, while PC2 explained 24%. The cumulative percentage of variance (CPV) explained of the first two principal components was 93% of the total variance in the whole spectral dataset, which meets the general requirements of CPV more than 70%–85% for PCA analysis.[17] Kintamani coffee samples were well separated from the Wamena and Gayo coffee samples, as shown in Figure 2. In contrast, the Kintamani coffee samples were close to the Wamena coffee samples alone. Two outliers (samples located at upper right: Gayo coffees) were observed and excluded in further calculations.

Figure 2 (b) shows the loadings of PCA about the sample groups for specialty coffee samples. The PCA loading elucidates the data structure in terms of correlations between the modeled variables. In this study, we identified three relevant wavelengths with high loadings values for coffee sample discrimination to explain the variance of the model. The first wavelength is around 275 nm, which corresponds to the C=O chromophore absorbance of caffeine.[16] The second wavelength is 325 nm, and it corresponds to the absorbance of trigonelline and caffeic acid.[16] The third important wavelength is 350 nm, and it is close related to the absorbance of chlorogenic acid (CGA).[9]

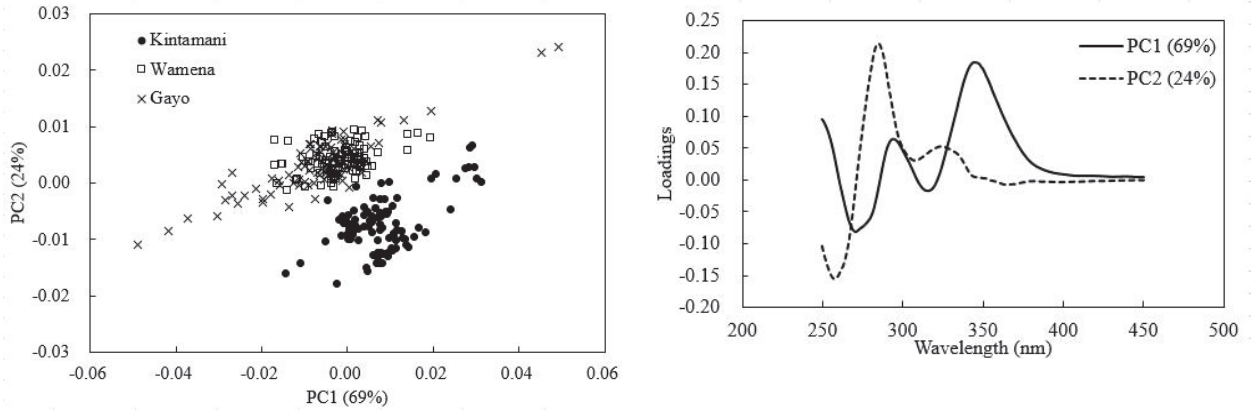

FIGURE 2. The PCA score plots of the three different coffee samples groups based on pre-processed spectral data (a) and loading plot of first two PCs (PC1 and PC2) from PCA analysis (b).

Supervised Classification using PLS-DA Method

The PLS-DA model was developed for each spectral type (original and pre-processed spectra) in the range of 250-450 nm. The results are summarized in Table 1. It can be seen that the best PLS-DA model was obtained using pre-processed spectra (combination of MOV+SNV+MSC+SG 1d) with eight, six and seven latent variables (LVs) for the Gayo, Kintamani and Wamena class, respectively. The PLS-DA model for the Kintamani class had the highest quality with $R^2 = 0.984$ for calibration and $R^2 = 0.957$ for validation.

TABLE 1. PLS-DA result for geographical origin using original and pre-processed spectra in the range of 250-450 nm using calibration and validation sample set (240 samples). The best model is marked in bold.

Spectral data pre-processing method	LV	Class	$R^2_{calibration}$	$R^2_{validation}$	RMSEC	RMSECV
Original spectra	8	Gayo	0.833	0.802	0.192861	0.210729
	15	Kintamani	0.987	0.964	0.053340	0.089200
	8	Wamena	0.838	0.773	0.189526	0.225465
MOV 9s	6	Gayo	0.704	0.608	0.256264	0.296223
	11	Kintamani	0.972	0.962	0.078475	0.092007
	6	Wamena	0.711	0.652	0.253415	0.279151
SNV	7	Gayo	0.821	0.787	0.199214	0.218579
	4	Kintamani	0.957	0.953	0.097552	0.102213
	6	Wamena	0.773	0.748	0.224573	0.237526
MSC	7	Gayo	0.823	0.781	0.198196	0.221629
	4	Kintamani	0.957	0.954	0.097352	0.102020
	6	Wamena	0.777	0.751	0.222752	0.236018
MSC + SG 1d (ordo:2; windows:9)	7	Gayo	0.749	0.723	0.236250	0.249363
	4	Kintamani	0.957	0.954	0.097303	0.101822
	6	Wamena	0.715	0.684	0.251667	0.266261
MOV 9s+ SNV+MSC+SG 1d (ordo:2; windows:9)	**8**	**Gayo**	**0.873**	**0.843**	**0.167853**	**0.184941**
	6	**Kintamani**	**0.984**	**0.957**	**0.060111**	**0.098242**
	7	**Wamena**	**0.889**	**0.876**	**0.156712**	**0.166681**

Classification of Geographical Origin using PLS-DA

Figure 3 shows the results of prediction obtained by PLS-DA for the Gayo class, Kintamani class and Wamena class, respectively. For the Gayo class, the predicted Y values close to one (between 0.5 and 1.5) indicate that the samples belong to the Gayo class, while the predicted Y values close to zero (between -0.5 and 0.5) point out that the samples belong to the not Gayo class (Kintamani and Wamena coffee). For the Kintamani class, the predicted Y values close to one (between 0.5 and 1.5) indicate that the samples belong to the Kintamani class, while the predicted Y values close to zero (between -0.5 and 0.5) indicate that the samples belong to the not Kintamani class (Gayo and Wamena coffee). For the Wamena class, the predicted Y values close to one (between 0.5 and 1.5) indicate that the samples belong to the Wamena class, while the predicted Y values close to zero (between -0.5 and 0.5) point that the samples belong to the not Wamena class (Gayo and Kintamani coffee). If the predicted Y value is not located in the zone between -0.5 to 1.5, the sample cannot be identified. We found that although there is one sample in Wamena class located on the border line in the predicted set, the classification using PLS-DA is accurate (100% the percentages of correct classification for all samples), as shown in Figure 3.

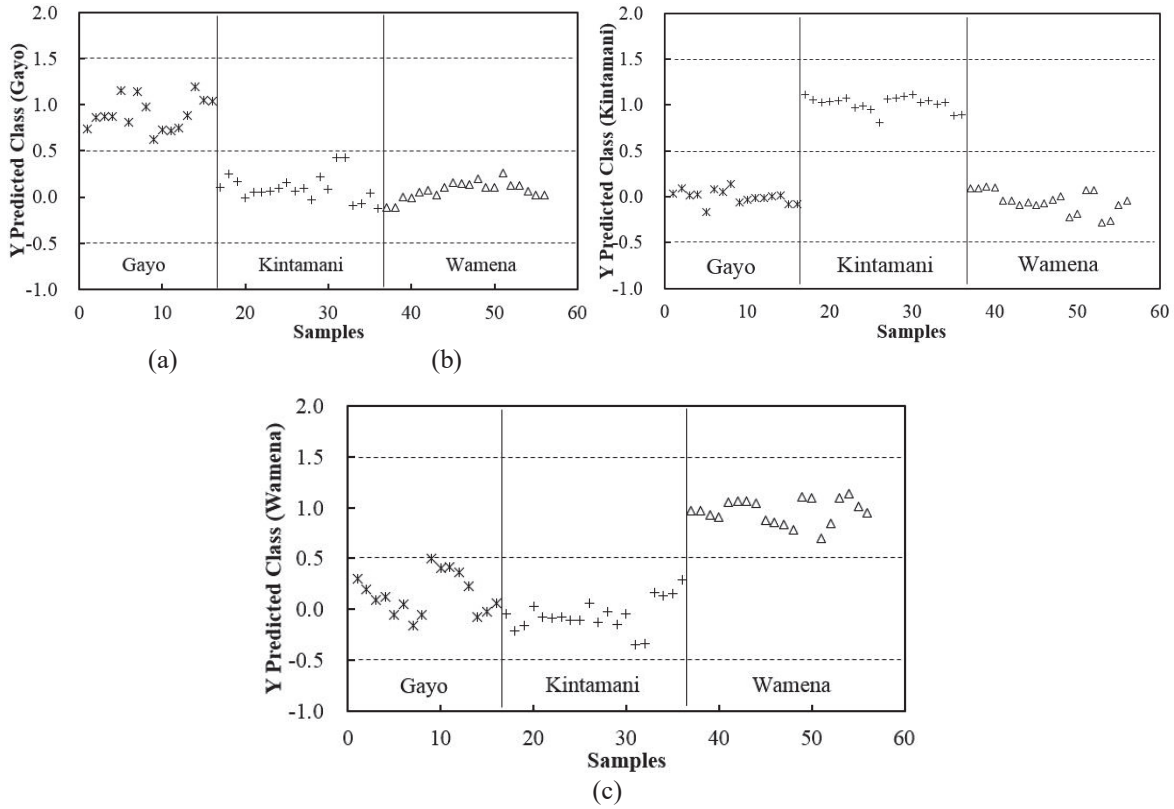

FIGURE 3. PLS-DA classification for Y predicted class. (a) Gayo (*), (b) Kintamani (+), and (c) Wamena (∆).

SUMMARY

The feasibility of employing UV-visible spectroscopy and PLS-DA method for discrimination between Arabica Gayo, Kintamani and Wamena ground roasted coffee was confirmed. The best PLS-DA model accurately classified the specialty coffee samples of the prediction sample set with prediction ability of 100% of correct classification for Gayo, Kintamani and Wamena, respectively. This promising result may open the way for a potential application of UV-visible spectroscopy for authentication of ground roasted coffee in the near future.

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