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The Qualitative and Quantitative Analysis of Adulteration in Specialty Coffee from Tanggamus Lampung Using UV-Visible Spectroscopy and Chemometrics

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Abstract. In Tanggamus region, Robusta coffee is mainly planted in the mountainous area (more than 600 meters above sea level) resulted in a high quality of Robusta coffee. In 2014, Robusta coffee from Tanggamus region got a certificate of geographic indication from Indonesian government and regarded as one of Indonesian specialty coffee. In ground roasted coffee, it is difficult to discriminate between specialty coffee and normal coffee (non-specialty coffee). To establish a fair trading of specialty coffee from Tanggamus region, it is highly desired to develop an easy and cheap analytical method for specialty coffee authentication. In this research, we utilize UV-visible spectroscopy and chemometrics methods to discriminate specialty coffee from normal coffee both quantitatively and qualitatively. A number of 180 samples of Tanggamus specialty coffee with different adulteration level was prepared. All samples were subjected to an extraction procedure using a hot distilled water. Spectral acquisition was done using a UV-visible spectrometer in the range of 190-1100 nm. Principal component analysis (PCA) and partial least squares (PLS) regression was applied for qualitative and quantitative analysis, respectively. The result of qualitative analysis showed that the samples can be clustered into three groups of adulteration (low, middle and high) using PC1 and PC2 with total 96% of explained variance. The best calibration model was achieved using preprocessed spectra with R^2=0.99 and RMSECV=2.08%. The result of prediction was accepted with SEP=2.38% and RPD=7.292.

INTRODUCTION

As one of the most popular beverages, coffee has important economic role in the world trade, no exception Indonesia. The consumption of coffee has increased rapidly recently with about 1.4 billion cups of coffee are consumed worldwide every day especially for premium grade or high quality of coffee or specialty coffee [1-2]. Quality of specialty coffee is a complex relationship of many factor from planting to roasting [3]. Both agronomic and human factors significantly affect the final taste of specialty coffee. In Lampung, Robusta coffee are planted in high land (275-1000 meter above sea level) and processed by local experienced farmer resulted in a unique taste of specialty Tanggamus Lampung Robusta coffee [4]. Since 13 May 2014, Lampung Robusta coffee got certificate of geographical indication (GI) ID G 000 000 026 from Indonesian government with the area of production included West Lampung, Tanggamus and Way Kanan regency [4].

The high price and popularity of specialty coffee comparing to normal non-specialty coffee is one of the main reasons of doing adulteration. The adulteration is usually carried out after roasting and grinding in the form of coffee powder [5-6]. By using unaided eye, it is hard to discriminate between authentic and adulterated ground roasted coffee [6]. Traditionally, the quality evaluation of specialty coffee is performed using cup tasting by experts or cuppers.

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However, this method suffers some drawbacks such as bias from one cupper to another cuppers, high subjectivity, and inconsistent may happen due to health condition of cuppers [3].

Several analytical methods have been successfully reported to be used for detection and authentication of adulteration in ground roasted coffee. High-performance anion-exchange chromatography was used to detect roasted soybean and wheat in coffee adulteration [7-8]. Using portable NIR spectroscopy Correia *et al.* [9] studied the quantification of adulteration in Brazilian coffee with different types of adulterant and resulted in a high coefficient determination of 0.86 and 0.98 for peels/sticks and corn as adulterant, respectively. Nuclear magnetic resonance (NMR) spectroscopy was effectively used to check four adulterants (corn, coffee husks, barley and soybean) in commercial Brazilian arabica blends [10]. Low cost and simple analytical method based on voltammetric electronic tongue was presented to detect adulterations (coffee husks and sticks) in ground roasted Brazilian coffee with an excellent predictive power (root mean square error of prediction/RMSEP = 0.05%) [11].

On the other hand, UV-visible spectroscopy has been used for authentication of ground roasted specialty coffee such as Indonesian civet coffee [12], discrimination between peaberry and normal coffee [13], classification of Indonesian specialty coffee with different geographic origins [14-15], discrimination between fresh and expired ground roasted coffee [16], authentication of organic ground roasted coffee [17] and classification of ground roasted decaffeinated coffee [18]. In this present research, an evaluation of UV-visible spectroscopy for classification and calculation of adulteration level in ground roasted Tanggamus Lampung coffee was demonstrated.

MATERIALS AND METHODS

Coffee Samples and Adulteration

A number of 180 samples of Tanggamus Lampung specialty coffee with different adulteration level was prepared. The adulteration was created intentionally by adding normal coffee (not Tanggamus Lampung specialty coffee) with different adulteration level of 10%, 20%, 30%, 40%, 50% and 60% (w/w). Each adulteration level consists of 30 samples with 1 g weight for each sample. All samples were subjected to an extraction procedure using hot distilled water as described by previous reported works [12-14].

For PCA (principal component analysis) calculation, there is no need to separate the samples. However, for PLSR (partial least squares regression) analysis, samples were randomly divided into three sets: 90 samples for calibration, 60 samples for validation and 30 samples for prediction. Detail explanation of each sample set was shown in Table 1. From Table 1 it was clear that all sample sets had skewness very close 0 means that a symmetrical distribution data was achieved.

TABLE 1. Descriptive statistics for the adulteration level in UV-visible datasets used to develop and predict the adulteration in Tanggamus Lampung coffee.

Items	Calibration set (%)	Validation set (%)	Prediction set (%)
Number of samples (n)	90	60	30
Minimum	10	10	10
Maximum	60	60	60
Mean	35	35	35
Standard deviation (SD)	17.17	17.22	17.37
Skewness	-3.079×10^{-8}	-9.587×10^{-7}	4.919×10^{-7}

Spectral Data Acquisition and Spectral Preprocessing

The UV-visible spectral data of 180 Tanggamus Lampung coffee samples with different adulteration level were acquired in transmittance mode using a benchtop UV-Vis spectrometer in the range of 190-1100 nm with 1 nm of resolution (Genesys™ 10S UV-Vis, Thermo Scientific, USA). Three spectral preprocessing transformations were used to remove irrelevant spectral information coming from highly overlapped original spectra: 3-point moving average (MA 3s) followed by multiplicative scatter correction (MSC) and mean normalization (MN). The purpose of

moving average is to reduce noise and increase the signal noise to ratio (SNR) [19]. The MSC was utilized to remove the baseline drift from spectra caused by scattering (different in particle distribution inside the aqueous sample) and variations in particle sizes and optical length variables [20]. To correct the UV-visible spectral fluctuation a mean normalization was used [21].

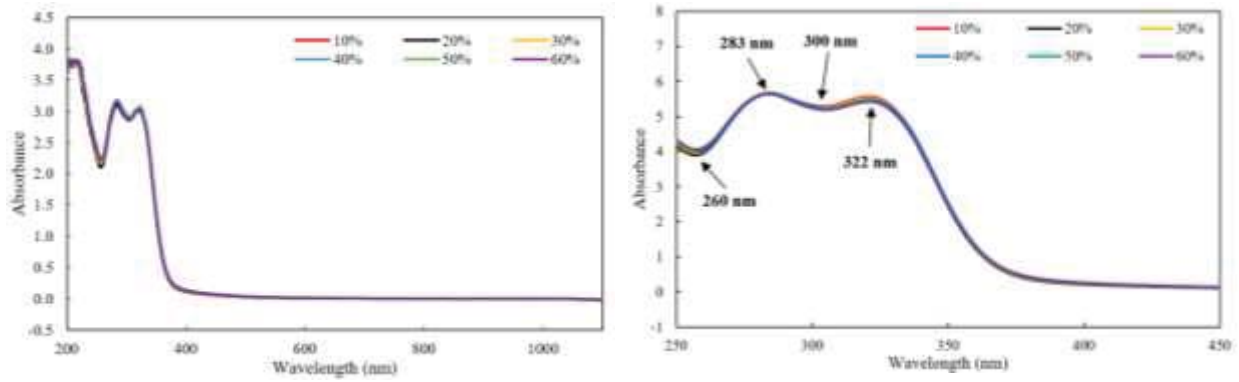
Chemometrics Analysis

Unsupervised classification was performed using principal component analysis (PCA) using preprocessed spectral data. The score of first two PCs (PC1 versus PC2) was usually plotted to evaluate the separation of the samples based on different adulteration level. The calculation of adulteration level could be done by applying partial least squares regression (PLSR). Several statistic parameters were used to evaluate the quality of calibration model. First, the optimal number of factor or latent variables was determined by the root mean square error of cross validation (RMSECV) [22]. The coefficient of determination of calibration and validation (R^2_{cal} and R^2_{val}), SEC (standard error of calibration) and SEV (standard error of validation) was considered for model evaluation according to Yulia *et al.* [23]. The performance and reliability of the prediction was determined by the coefficient of determination in prediction (R^2_{pred}), SEP (standard error of prediction) and RPD value. RPD is the ratio of the standard error in prediction (SEP) to the standard deviation of the prediction samples set (SD) [24]. The PLSR model to be excellent when RPD >3, fair when 1.5 < RPD < 3, and nonreliable when RPD <1.5 [24]. The calculation of chemometrics (spectral preprocessing, PCA and PLSR) was done by using The Unscrambler 9.7 (64-bit) (Camo Software AS, Oslo, Norway).

RESULTS AND DISCUSSION

Analysis of Coffee Spectral Data with Different Adulteration Level

The averaged original spectra (a) and preprocessed spectra (b) of Tanggamus coffee samples with different adulteration level were demonstrated in Figure 1. It was hard to see the spectral difference as a function of adulteration level. The all spectra almost had similarity in shape and intensity. The spectral window at wavelength of 190-250 nm was noisy with very high absorbance while absorbance intensity at 450-1100 nm was very close to 0. For this reason, the spectral window at 250-450 nm was selected for further analysis (for qualitative and quantitative). In this spectral window, several peaks were identified at 260 nm (corresponding with the absorbance of vanillic acid) [25], 283 nm (related to absorbance of caffeine), 300 nm and 322 nm (corresponding with the absorbance of caffeic acid) [13].



(a) (b)

FIGURE 1. The plot of averaged spectral data of Lampung coffee samples with different adulteration level in the range of 190-1100 nm and 250-450 nm. Original spectra (a) Preprocessed spectra (b).

The Classification of Lampung Coffee Using Principal Component Analysis

To establish the relationship of Tanggamus Lampung coffee samples with different adulteration level, PCA was employed with twenty principal components (PCs) on preprocessed spectral data in the range of 250-450 nm. The

result was shown in Figure 2. It can be seen that using PC1 (85% explained variance) and PC2 (11% explained variance), a clear separation between low (10-20% w/w), middle (30-40% w/w) and high (50-60% w/w) level of adulteration can be achieved. Especially using PC2, most of low groups (10-20% w/w) were located at PC2 negative while all high groups were located at PC2 positive.

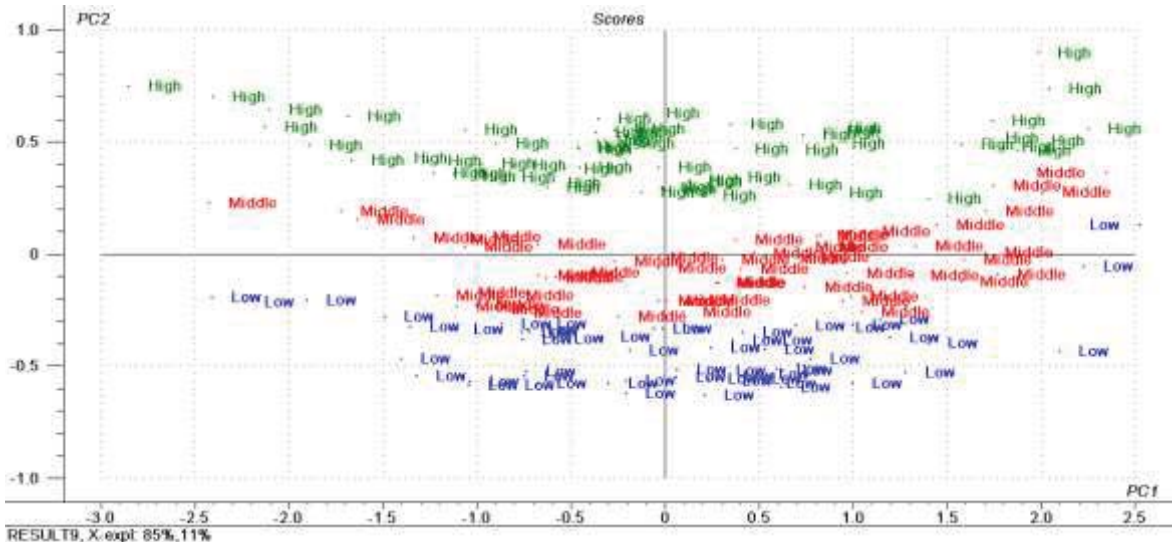


FIGURE 2. Score plots of Lampung coffee samples with different adulteration level calculated based on preprocessed spectral data (MA 3s+MSC+Normalize) in the range of 250-450 nm.

The Calculation of Adulteration Level using PLSR Method

The PLS calibration model was developed using the t-test validation method on preprocessed spectral data in the wavelength of 250-450 nm. The calibration and validation plots were shown in Figures 3 and 4, respectively. The coefficient of determination (R^2_{cal} and R^2_{val}) is near 1 as regression line is very close to target line. The obtained root mean square of error of calibration (RMSEC) was 1.598% and RMSEV was 2.083%.

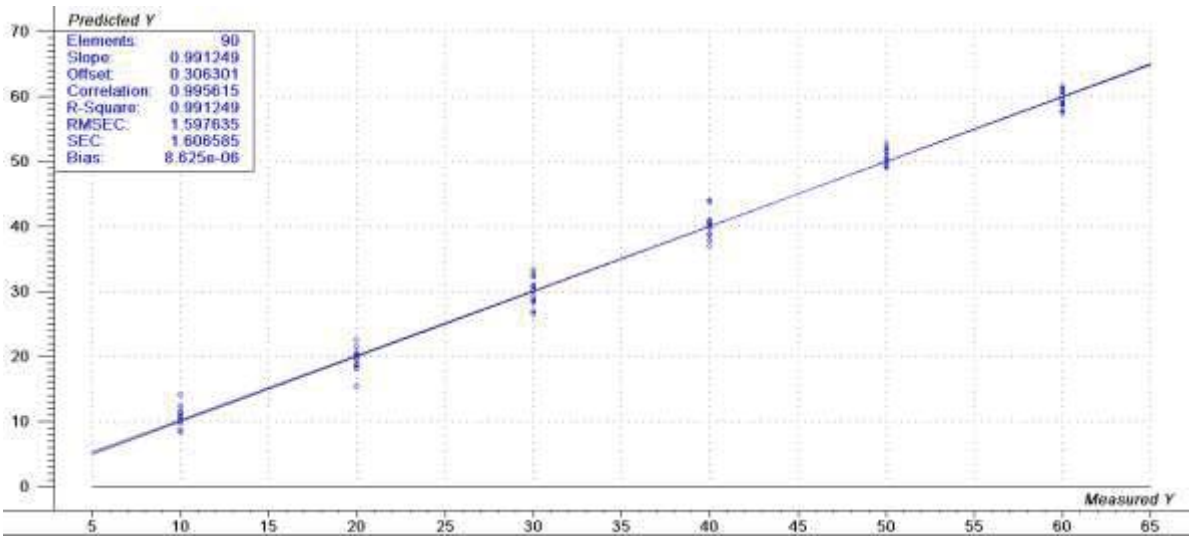


FIGURE 3. PLSR calibration model developed using preprocessed spectra in the wavelength of 250-450 nm.

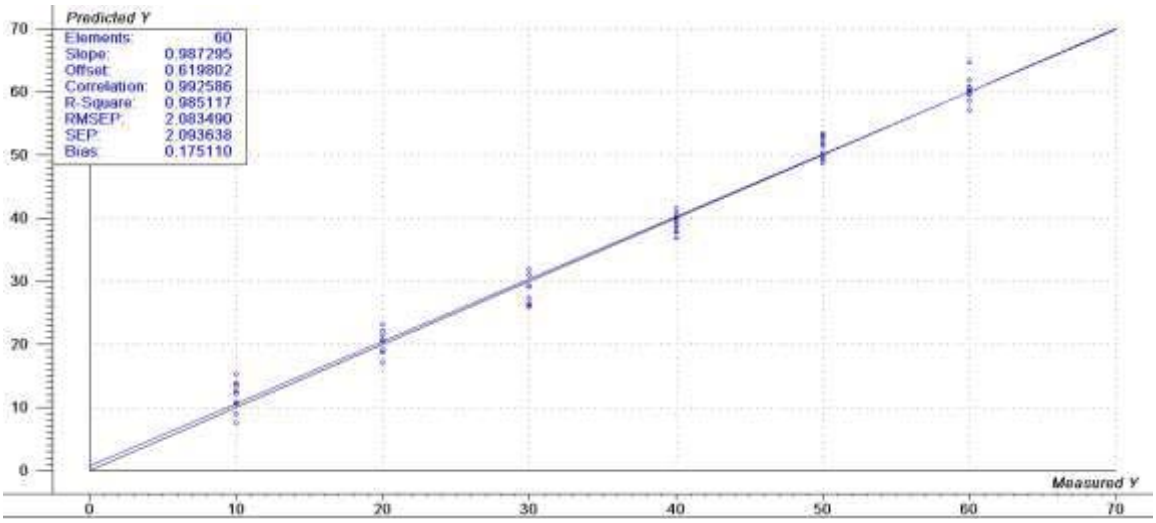


FIGURE 4. Validation result of PLSR calibration model developed using preprocessed spectra in the wavelength of 250-450 nm.

The result of prediction was presented in Figure 5. The coefficient of determination in prediction (R^2_{pred}) was 0.98 with very low bias of -0.812% and low SEP of 2.382%. The ratio to prediction (RPD) was calculated based on previous reported studies [12-13]. The RPD of 7.292 was obtained and it was acceptable for quantification purposes. This result confirms us that UV-visible spectroscopy along with PLSR method can be used to quantify the level of adulteration in Lampung coffee samples.

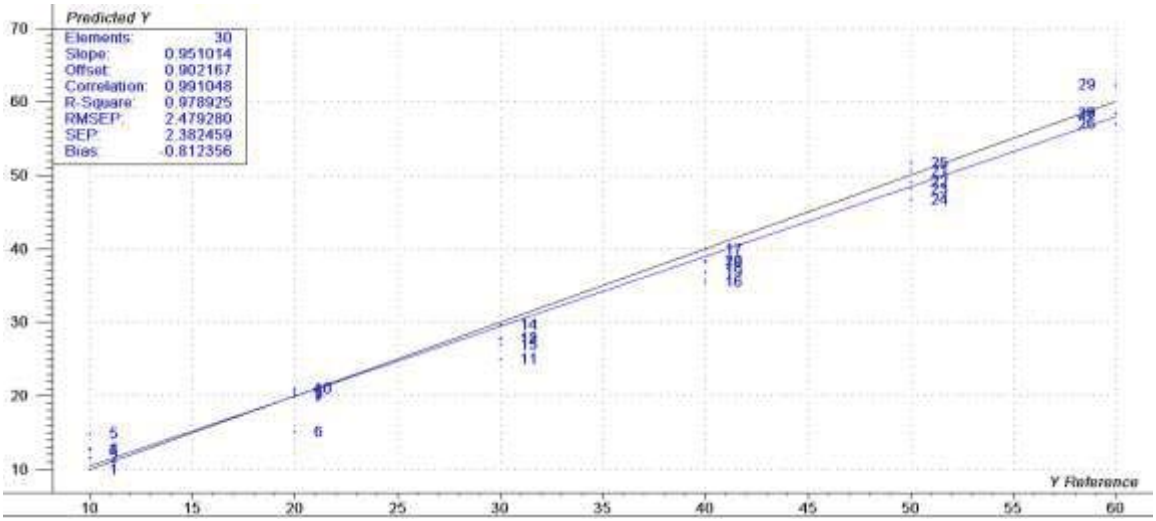


FIGURE 5. Prediction plot between actual and predicted level of adulteration predicted using PLSR calibration model developed using preprocessed spectra in the range of 250-450 nm.

SUMMARY

The UV-visible spectroscopy associated with PCA and PLSR methods is effective in the classification and calculation of adulteration level in ground roasted Tanggamus Lampung Robusta coffee. The results obtained was acceptable both for qualitative and quantitative analysis. The RPD of 7.292 was obtained and it was acceptable for quantification purposes. Analysis based on UV-visible spectroscopy is simple, low cost and easy to follow thus it can be used in the coffee industry or commercial sectors for routines analysis of coffee quality control.

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REFERENCES

1. H.Y. Song, H.W. Jang, T. Debnath and K.-G. Lee, Int. J. Food Sci. Technol. 54, 256–262 (2019).
2. M. Yulia and D. Suhandy, MATEC Web Conf. **197**, 1–5 (2018).
3. V. Belchior, B.G. Botelho, S. Casal, L.S. Oliveira and A.S. Franca, Food Anal. Methods, **13**, 275–283 (2020).
4. DGIP. http://e-book.dgip.go.id/indikasi-geografis/filemedia/robusta-lampung/.(2020).
5. N. Reis, A.S. Franca and L.S. Oliveira, LWT - Food Sci. Technol. **50**, 715–722 (2013).
6. D. Suhandy and M. Yulia, MATEC Web Conf. **197**, 1–4 (2018).
7. D. Thorburn Burns, L. Tweed and M.J. Walker, Food Anal. Methods, **10**, 2302–2310 (2017).
8. E.D. Pauli, F. Barbieri, P.S. Garcia, T. B. Madeira, V.R.A. Junior, I. S. Scarminio, C. A. P. Camara and S. L. Nixdorf, Food Res. Int. **61**, 112–119 (2014).
9. R.M. Correia, F. Tosato, E. Domingos, R.R.T. Rodrigues, L.F.M. Aquino, P.R. Filgueiras, V. Lacerda Jr and W. Romão, Talanta, **176**, 59–68 (2018).
10. M.V. De Moura Ribeiro, N. Boralle, H. Redigolo Pezza, L. Pezza and A.T. Toci, J. Food Compos. Anal. **57**, 24–30 (2017).
11. T.C.B. De Morais, D.R. Rodrigues, U.T. de Carvalho Polari Souto and S.G. Lemos, Food Chem. **273**, 31–38 (2019).
12. D. Suhandy and M. Yulia, Int. J. Food Sci. 1-7 (2017).
13. D. Suhandy and M. Yulia, Int. J. Food Prop. **20**, S331–S339 (2017).
14. D. Suhandy and M. Yulia, AIP Conf. Proc. **2021**, 040001 (2018).
15. M. Yulia and D. Suhandy, IOP Conf. Ser.: Earth Environ. Sci. **258** 012044 (2019).
16. M. Yulia and D. Suhandy, MATEC Web of Conf. **197**, 09003 (2018).
17. M. Yulia and D. Suhandy, J. Phys.: Conf. Ser. **1341**, 022006 (2019).
18. M. Yulia, A. R. Asnaning and D. Suhandy, IOP Conf. Ser.: Earth Environ. Sci. **147**, 012010 (2018).
19. D.S. Himmelsbach, F.E. Barton, A.M. McClung and E.T. Champagne, Cereal Chem. **78**, 488–492 (2001).
20. L.S. Wang, R.J. Wang, C.P. Lu, J. Wang, W. Huang, Q. Jian, Y.B. Wang, L.Z. Lin and L.T. Song, J. Appl. Spectrosc. **86**, 465–469 (2019).
21. J. Guezenoc, A. Gallet-Budynek and B Bousquet, Spectrochim. Acta B, **160**, 105688 (2019).
22. D. Suhandy, M. Yulia, Y. Ogawa and N. Kondo, Eng. Agric. Environ. Food, **6**, 111–117 (2013).
23. M. Yulia, D. Suhandy, Y. Ogawa and N. Kondo, Eng. Agric. Environ. Food, **7**, 148–154 (2014).
24. D. Suhandy, T. Suzuki, Y. Ogawa, N. Kondo, H. Naito, T. Ishihara, Y. Takemoto and W. Liu, Eng. Agric. Environ. Food, **5**, 90–95 (2012).
25. D. Suhandy and M. Yulia, IOP Conf. Ser.: Earth Environ. Sci. **258**, 012029 (2019).