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# THE USE OF ULTRAVIOLET (UV) SPECTROSCOPY AND CHEMOMETRICS TO QUANTIFY THE PERCENTAGES OF ADULTERATION IN KALOSI GROUND ROASTED SPECIALTY COFFEE

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## Abstract

The purpose of this study is to analyse the use of ultraviolet (UV) spectroscopy with chemometrics to quantify the percentages of adulteration of Kalosi ground roasted specialty coffee. A total of 220 mixtures of coffee samples adulterated with different percentages of skins ranging from 0 to 90% were prepared at low (0-20% w/w), middle (30-50% w/w), and high adulteration (60-90% w/w). Each sample was extracted and diluted using hot, distilled water. All spectral data were measured in transmittance mode employing a UV-Visible benchtop spectrometer called Genesys™ 10S manufactured by Thermo Scientific, USA, and assembled with a monochromator as well as a xenon flash lamp, in the range of 200-450 nm with a 1 nm resolution. The principal component analysis (PCA) was applied to the preprocessed and original spectral data, with the percentages of adulteration quantified by using a multivariate calibration model in accordance with the partial least square (PLS) regression method. The preprocessed spectral data was used to determine 98% data variance of PCA score plot of PC1 and PC2 with the samples separated into three clusters, namely low, middle, and high percentages of adulteration. The best calibration model was achieved using the preprocessed spectral data with an $R^2$ value of 0.995 for calibration and validation, respectively. The prediction result showed that the percentages of adulteration are accurately calculated using $R^2$=0.977, bias = -1.415%, and SEP=3.892%.

Keywords: Authentication, Adulteration, PCA, PLS regression, Ultraviolet spectroscopy.

## 1. Introduction

In 2018, Indonesia produced approximately 13.5% of the world's robusta coffee [1]. This production was mainly carried out in Java, Sumatera, Bali, Sulawesi, and Papua Islands, using special techniques, which lead to unique characteristics such as different flavour complex, aroma, acidity, body, and mouth feel. Approximately 314,400 tons of coffee are consumed by Indonesian [2]. Recently, due to the increase in customer demand for coffee diversification, there is a rise in differentiation based on geographical origin, also known as specialty coffee, which significantly influences cup profile. Therefore, in 2008 the Indonesian government initiated the law of intellectual property in accordance with geographic indications of origin (GIs) as legal protection, which allows producers to explain the link between a product's quality and origin to clients and consumers [3].

The continuous increase of consumer demand for authentic single-origin specialty coffees and its limited supply are the main reason associated with the risk of fraud adulteration [4]. For this reason, GIs has significant points to protect Indonesian specialty coffee from fraud adulteration. In terms of producers and customers, the policy contributes to establishing fair trading, customer royalty, and increased international market competitiveness [3]. By March 2020, there were a total of 91 types of Indonesian products with GIs certification, and this included the Arabica Kalosi Enrekang (Kalosi) coffee from South Sulawesi. The product was awarded GIs with certificate number ID G 000 000 018 since 15 February 2013 [5]. Kalosi coffee is regarded as a specialty with superior taste and aroma available in both domestic and international markets. This coffee seed is planted in podzolic soil in a highland area of approximately 1000-2000 meters above sea level on the slopes of the Latimojong Mountains, which covers the five districts of Bungin, Baraka, Buntu Batu, Baroko and Masalle in the Enrekang regency [5].

The adulteration is both frequent and diversified in the form of ground roasted coffee [6]. Coffee adulteration may be performed by changing the quality of beans or adding other low-cost coffee and non-coffee materials as described by previous reported studies: robusta coffee [7], inferior quality of arabica coffee [8], mixed of four materials (coffee husks, spent coffee ground, barley, and corn) [9], wheat, corn, and chickpea [10], soybeans, green mung beans and spent coffee grounds [11] and coffee husks, soybean, corn, barley, rice, and wheat [12]. Mostly Kalosi green bean coffee was processed using dry method resulted in huge amounts of coffee skins as one of coffee by-products. For this reason, in real situation the adulteration of ground roasted Kalosi involved the intentional addition of fine grinded coffee skins.

In addition, ground roasted coffee is the most difficult form of coffee adulteration, and visually, very hard to discriminate the specialty, GIs, and normal coffee (non-GIs) with samples of roasted and ground coffee [13-16]. Similarly, the conventional method using visual assessment (VA) to discriminate between roasted fine grinded coffee skin and ground roasted coffee is difficult and easily exposed to human error due to the dependency of the technique on human visual skill [16-18]. Therefore, the microscopy method is commonly used to evaluate the adulteration in ground roasted coffee. However, the dark colour and small particle size make it difficult to detect the roasted adulterants in the original sample. Several advance analytical methods are available for coffee authentication, which includes the quantification of adulterant in ground roasted coffee blends [6, 19]. High-performance liquid chromatography (HPLC) and its derivative have been used to

detect and quantify coffee adulterated by roasted soybean and wheat as sources of fraud [20, 21]. Furthermore, HPLC with fluorescence detection, ultraviolet adsorption (UV), diode array and mass spectrometry were also used to determine the coffee adulteration [16, 22]. Although chromatographic techniques are very accurate, they are time-consuming, and use expensive devices, with the extensive preparation of chemical-based samples [23].

NIR spectroscopy was used with PLS regression to quantify corn adulteration in Brazilian coffee [24]. Assis et al. [25] used mid-infrared spectroscopy and PLS regression to determine 40 meshes of robusta-arabica coffee blends in the analytical range of 0.0 to 33.0% w/w. Nuclear magnetic resonance (NMR) spectroscopy was used to monitor robusta coffee adulteration in Brazilian arabica coffee and to quantify 16-O-methylcafestol (16-OMC) [26]. Fourier transform infrared (FTIR) is one of the important analytical techniques and quite popular for characterizing samples [27]. FTIR has been used for quantification of robusta coffee in arabica coffee blends in ground roasted coffee [28]. Furthermore, there were reports on the quantification of arabica and robusta concentration in coffee blends using synchronous fluorescence spectroscopy [29]. These spectroscopic methods are attractive, provide accurate quantification, fast measurement with very little or no sample preparation. However, those spectroscopic methods involved the use of expensive devices (spectrometers).

Comparing to other spectroscopic methods (NIR, mid-infrared, NMR and fluorescence spectroscopy) or conventional methods (HPLC and its derivative), spectroscopy in UV region has several advantages: spectrometer in this region is relatively low cost and it is available to most standard laboratories, a green technology without chemical waste during sample extraction and simple in sample preparation. Several qualitative studies have been reported using UV spectroscopy for authentication of Indonesian specialty coffee [14, 30]. However, authentication of Indonesian specialty coffee in the term of quantification of adulterant or degree of adulteration is very limited. Therefore, this research aims to determine the possible application of UV spectroscopy and chemometrics method for ground roasted Kalosi coffee authentication both in qualitative (classify the samples into low, middle and high degree of adulteration) and quantitative studies (quantify the percentage of adulteration in Kalosi ground roasted coffee). This proposed method can be used as a routine analysis for final quality inspection of ground roasted Kalosi coffee before packing.

## 2. Materials and Methods

### 2.1. Kalosi coffee samples

Kalosi coffee green bean samples were directly collected from trusted farmers in Enrekang, South Sulawesi, Indonesia, as shown in Fig. 1. The coffee samples were subjected to medium roasting at 200°C for 10 minutes using a home machine. Approximately 500 grams of roasted coffee beans were mechanically grounded using a home grinder. This study utilized a particle size of 420 $\mu$m to sieve all ground roasted coffee samples with mesh number of 40 on a Meinzer II sieve shaker (CSC Scientific Company, Inc., USA) for 10 minutes. Approximately 220 mixtures of Kalosi coffee samples adulterated with different percentages of coffee skins were prepared. In this study, to provide a wide range of adulteration, the ratio between ground roasted Kalosi coffee and coffee skins is 0 to 90% (w/w) in increment of 10% from low (0-20% w/w), middle (30-50% w/w) and high degree of adulteration (60-90% w/w) for calibration, validation and prediction. 1 gram of each sample was

weighed and placed in a glass beaker. It was extracted, distilled and diluted using hot distilled water based on sample preparation procedure described in previous works [13-15]. For multivariate analysis, the samples were divided into three sets, namely calibration (111 samples), validation (73 samples), and prediction sets (36 samples) using the random sample method. Table 1 shows the descriptive statistic of the samples used in this research, which are statistically similar.

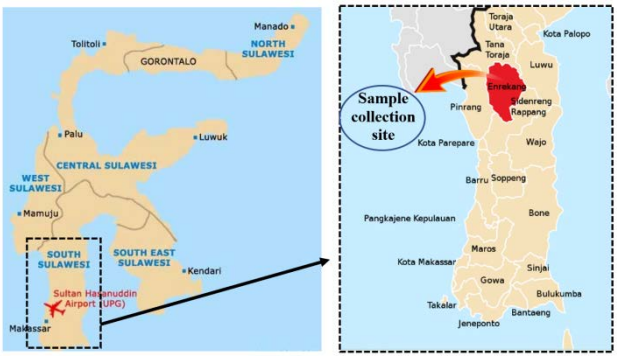


**Fig. 1. Site for sample collection in Enrekang, South Sulawesi, Indonesia.**

**Table 1. The descriptive statistic of calibration, validation, and prediction sample set used in this study.**

| | Calibration set | Validation set | Prediction set |
|---|---|---|---|
| **Number of samples** | 111 | 73 | 36 |
| **Minimum** | 0 | 0 | 0 |
| **Maximum** | 90 | 90 | 90 |
| **Mean** | 45.225 | 45.753 | 45.556 |
| **SD** | 27.793 | 27.483 | 27.302 |
| **Unit** | % (w/w) | % (w/w) | % (w/w) |

## 2.2. Extraction of coffee samples

The extraction of each coffee sample was performed according to previously reported works [13-15], with the procedure shown in Fig. 2.

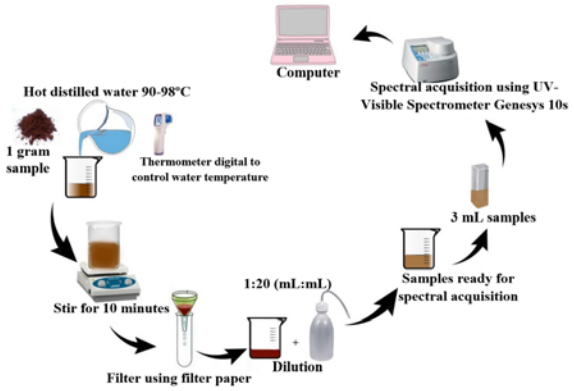


**Fig. 2. Extraction procedure of Kalosi coffee samples for UV spectral acquisition [13-15].**

## 2.3. Spectral data acquisition

A 3 mL of aqueous coffee samples were placed in the 10 mm of quartz cell. All the UV spectral data were acquired by means of a dual-beam UV-Visible benchtop spectrometer (Genesys 10s UV-Vis, Thermo Scientific Inc., Madison, WI), equipped with a high-intensity xenon lamp and dual Silicon photodiodes as a detector. Spectra were measured between 200 and 450 nm with a resolution of 1 nm. The absorbance of samples (A) was calculated using Eq. (1), with two spectral measurements and averaged for each sample. The original spectra were modified by applying three preprocessing algorithms, namely, moving average smoothing with 5 segments, standard normal variate (SNV), and Savitzky-Golay (SG) 1st derivative with segments and polynomial order value of 5 and 2. In general, smoothing was used to reduce the noise and improve the signal-to-noise ratio (SNR). SNV and derivative are frequently used mathematical preprocessing methods for scatter correction, linear baseline drifts removal, and enhancing the resolution of overlapped peaks [31].

$$A(\lambda) = -\log_{10}\left(\frac{I_S(\lambda)}{I_o(\lambda)}\right) \quad (1)$$

where, $A(\lambda)$ is the absorbance of the sample at wavelength $\lambda$, $I_s(\lambda)$ is the intensity of light passed through the sample at wavelength $\lambda$ and $I_o(\lambda)$ is the intensity of light passed through the reference at wavelength $\lambda$.

## 2.4. Statistical analysis of multivariate

PCA was used as unsupervised pattern recognition to reduce data dimensionality and transform the original highly correlated data into new uncorrelated variables (called principal components or PCs) [32]. The two-dimensional scores plot of the first two PCs (PC1xPC2) were used to present the sample distribution clustering and outlier detection. The quantification percentages of adulteration were predicted through the development of a calibration model using partial least square (PLS) regression using original and preprocessed spectra over the range of 200-400 nm. The optimum number of PLS components was analysed by the lowest root mean square error of cross-validation (RMSECV). The quality of the final PLS model was also evaluated by using the determining coefficient of calibration and validation ($R^2_{cal}$ and $R^2_{val}$), root mean square error of calibration and validation (RMSEC and RMSEV), and bias [33, 34]. The structure of developed PLS regression model was evaluated by plotting X-loadings versus wavelengths [35]. The wavelengths with a higher value in the X-loadings of a latent variable (LV) (local maxima or minima) could be considered more important than other wavelengths. Four parameters were used, to evaluate the performance of prediction, namely coefficient of determination of prediction (close to 1), bias (close to 0), ratio prediction to deviation (RPD) (higher than 3.0), RER (ratio error range) (higher than 10.0), standard error of prediction (SEP), and low root mean square error of prediction (RMSEP) [36, 37]. The calculation method of RPD and RER was performed based on Suhandy et al. [37]:

$$RPD = \frac{SD}{SEP} \quad (2)$$

$$RER = \frac{(maximum - minimum)_{reference\ value\ at\ prediction\ set}}{SEP} \quad (3)$$

Limit of detection (LOD) and limit of quantification (LOQ) were calculated to evaluate the smallest concentration reliably measured by the developed calibration model [38]. In general, LOD is described as the lowest concentration of an analyte that is detectable from a sample [39]. Meanwhile, LOQ is the smallest concentration of an analyte quantifiable with acceptable precision and accuracy. The LOD and LOQ in multivariate calibration are the most questioned and not adequately defined concentration. However, several works have proposed more precise calculations for this parameter [39]. In this work, the LOD and LOQ were computed using standard deviations of the residual between actual and predicted or standard error of prediction (SEP), and slopes of the regression line (*s*) based on the following formulas [40, 41].

$$LOD = \frac{3.3 \times SEP}{s} \tag{4}$$

$$LOQ = \frac{10 \times SEP}{s} \tag{5}$$

All chemometrics calculations, including spectral preprocessing, PCA, and PLS regression, were performed by using The Unscrambler X version 10.4 (64-bit) (Camo Software AS, Oslo, Norway).

## 3. Results and Discussion

### 3.1. Spectral analysis of Kalosi coffee with different degree of adulteration

Figures 3 and 4 show the original average and preprocessed spectral data of Kalosi coffee samples with three degrees of adulteration, namely low, middle, and high in the range of 200-450 nm. Figure 4 shows a clear intensity of absorbance decrease in line with an increase in the degree of adulteration. This result is in line with the previous study on coffee authentication [19]. Several peaks were observed both in original and preprocessed spectra. The peak at approximately 275 nm was related to the maximum absorption of caffeine [7, 19]. At 290 nm and 320 nm, the peaks were associated with the presence of chlorogenic acids and trigonelline [7, 19]. The intensity at the spectral window of 400-450 nm was very low therefore, at 200-400 nm, it was selected for further analysis.

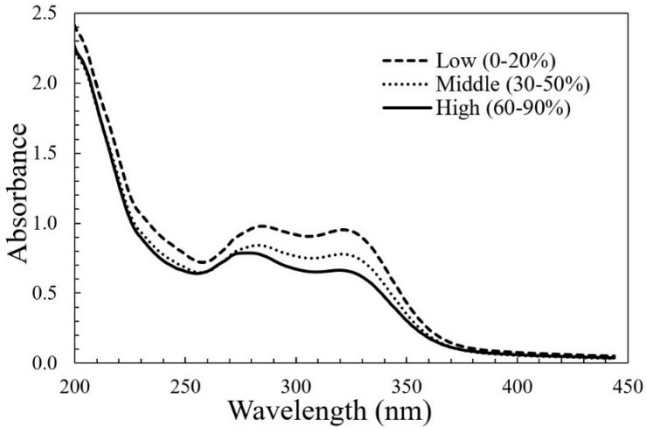


**Fig. 3. The average original Kalosi spectral data with different percentage of adulteration in the range of 200-450 nm.**

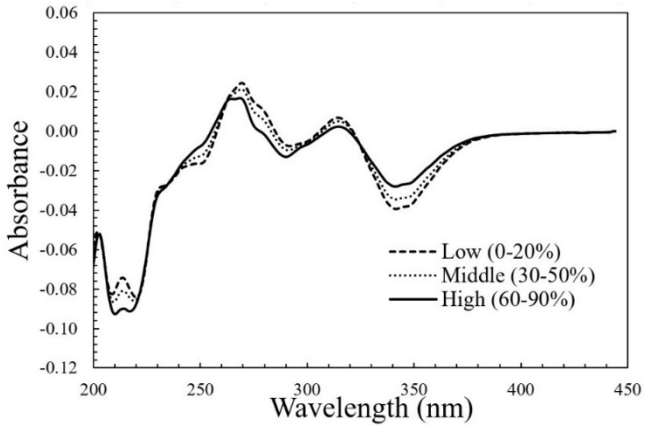


**Fig. 4. The average pre-processed Kalosi spectral data with different percentage of adulteration in the range of 200-450 nm.**

## 3.2. PCA results

First, PCA was calculated using original spectral data in ranges of 200-400 nm with the result plotted in Fig. 5. The variance obtained 89% for PC1 and 10% for PC2. Furthermore, Fig. 5 shows that the separation of Kalosi coffee samples with different percentages of adulteration were not established, especially along the PC1 axis (x-axis). Therefore, a new PCA calculation was performed using preprocessed spectral data, and the result was demonstrated in Fig. 6. The first two PCs obtained a total explained variance of 98% (PC1 94% and PC2 4%). Figure 6 shows a clear separation of Kalosi coffee samples with different percentages of adulteration achieved along the PC1 axis. All samples with a low percentage of adulteration were in the positive PC1 (PC1>0), while those with high percentages were located at negative PC1 (PC1<0). It means that the selected spectral preprocessing method effectively enhanced the spectral difference due to the percentage of adulteration. Previous studies performed by Suhandy and Yulia [14], showed that UV-visible spectroscopy, coupled with PCA, allowed the estimation of authenticity in Indonesian peaberry coffee.

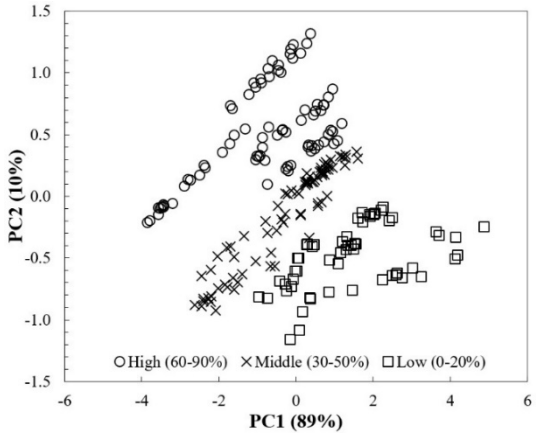


**Fig. 5. PCA score plot of Kalosi coffee samples with different percentages of adulteration calculated using original spectra in the range of 200-400 nm.**

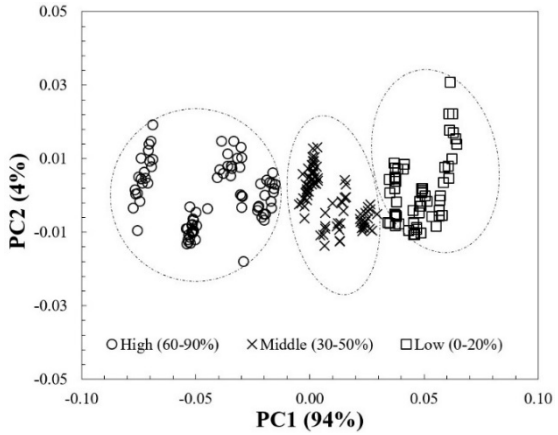


**Fig. 6. PCA score plot of Kalosi coffee samples with different percentages of adulteration calculated using pre-processed spectra in the range of 200-400 nm.**

Another important plot from PCA was Hotelling's $T^2$ versus Q-residual plot used to check the possible occurrence of an outlier in the data set. The Hotelling's $T^2$ is the variation within the PCA model, while Q-residual is used to measure the dimensional data in the model [42]. For guidance, a sample was considered as an outlier assuming the Hotelling's $T^2$ and Q-residual values are greater than the 95% confidence interval (red dotted line). Figure 7 shows that all samples were located in the left lower part of the plot, and the Hotelling's $T^2$ and Q-residual values were lower than the 95% confidence interval (red dotted line). Therefore, no outlier was detected, and this led to the use of all 220 samples for further analysis.

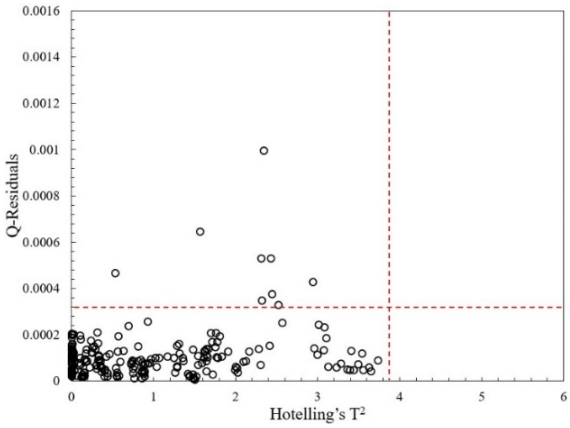


**Fig. 7. Hotelling's $T^2$ versus Q-residual plot of coffee samples from PCA calculated using preprocessed spectral data in the range of 200-400 nm. The red dotted line (---) represents a 95% confidence interval.**

## 3.3. The quantification of adulteration percentage using PLS regression

The calibration model was developed for original and pre-processed spectral data, as shown in Table 2. The number of factors was 11 and 6 in the original and pre-

processed calibration model, which led to the lowest RMSEV. The developed calibration models were good at $R^2_{cal}$ and $R^2_{val}$ and close to 1 with low RMSEC and RMSEV for the original and pre-processed calibration model. The pre-processed calibration model fitted correctly with RMSEC close to RMSEV. Figure 8 shows a plot of wavelengths versus X-loadings for the first latent variables (LV1) used to identify important wavelengths that are responsible for the quantification of degree of adulteration in ground roasted Kalosi coffee samples. Wavelengths with high X-loadings were observed at 215 nm, 230 nm, 250 nm, 278 nm, 315 nm, and 350 nm. These wavelengths had a great contribution to quantification of the percentage of adulteration and are related to the absorbance of some important chemical components of ground roasted coffee [14, 22]. The peak at 250 nm is closely related to the absorbance of vanillic acid. The peak at 278 nm is related to the absorbance of caffeine and the peak at 315 nm is closely related to the absorbance of caffeic acid [14].

**Table 2. The calibration model development using original and preprocessed spectral data.**

| | Original | Preprocessed |
|---|---|---|
| $R^2_{cal}$ | 0.995 | 0.995 |
| $R^2_{val}$ | 0.987 | 0.995 |
| $Slope_{cal}$ | 0.995 | 0.995 |
| $Slope_{val}$ | 1.000 | 0.994 |
| **SEC** | 1.872 | 1.959 |
| **RMSEC** | 1.864 | 1.950 |
| **SEV** | 3.085 | 1.900 |
| **RMSEV** | 3.065 | 1.888 |
| **Bias** | -0.080 | 0.066 |
| **Factor** | 11 | 6 |

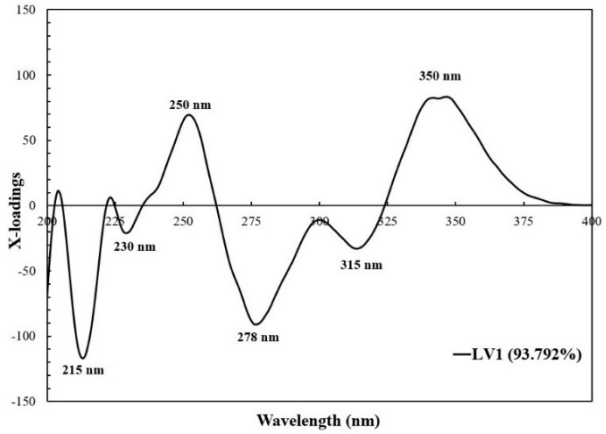


**Fig. 8. X-loadings plot of the first latent variables (LV1) calculated using pre-processed spectral data in the range of 200-400 nm.**

The prediction was applied using 36 samples for original and preprocessed calibration models, as shown in Figs. 9 and 10. Both prediction results were acceptable in terms of high $R^2_{pred}$, with bias close to 0 and low to RMSEP with the RPD high in both models. The standard deviation of the prediction samples set (SD)

is 27.302% (w/w), as shown in Table 1. Figures 9 and 10 show that the SEP was 4.079% (w/w) for original and 3.892% (w/w) for preprocessed calibration model, respectively. As calculated using Eq. (2), the values of RPD were 6.693 for original and 7.015 for preprocessed calibration models. Similarly, Eq. (3) was used to obtain RER of 22.064 and 23.124 for the original and preprocessed spectra.

### 3.4. The calculation of LOD and LOQ

Figures 9 and 10 show that the standard deviation of the difference between actual and predicted percentage of adulteration or SEP was 4.079% (w/w) for original and 3.892% (w/w) for preprocessed calibration model. The slope of prediction plot (s) was 0.972 for the original and 0.985 for preprocessed. Using Equations (4) and (5) the percentages of LOD and LOQ were obtained at 13.848% (w/w) and 41.965% (w/w) for the original calibration model. Similarly, the LOD and LOQ for the preprocessed calibration model were 13.039% (w/w) and 39.513% (w/w). This result was less accurate compared to previous work by Correia et al. [28] which stated that the quantification of robusta in arabica coffee blends using ATR-FTIR spectroscopy with LOD and LOQ of 1.3 (wt%) and 4.3 (wt%). Daniel et al. [43] stated that a simple voltametric electronic tongue for the analysis of coffee adulterations obtained LOD and LOQ percentages of 0.9% and 2.7%. However, the use of UV spectroscopy showed that an effective quantification is performed for percentages above 41.965% (w/w), which is sufficient for economically motivated adulteration in Indonesian specialty coffee. The affordable cost of a UV spectrometer is also another advantage for the development of an analytical method used for the authentication of Indonesian specialty coffee. However, to realize a routine authentication analysis of ground roasted Kalosi coffee using UV spectroscopy, several improvements should be considered. For example, it is highly desired to develop a more rapid analysis by cancelling the laborious sample preparation of sieving. It can be achieved by developing robust PLS regression model which is less sensitive to the influence of particle size variation on the authentication of ground roasted Kalosi coffee. It is also recommended to develop robust PLS regression model using selected spectrum with several fewer important wavelengths instead of using full spectrum.

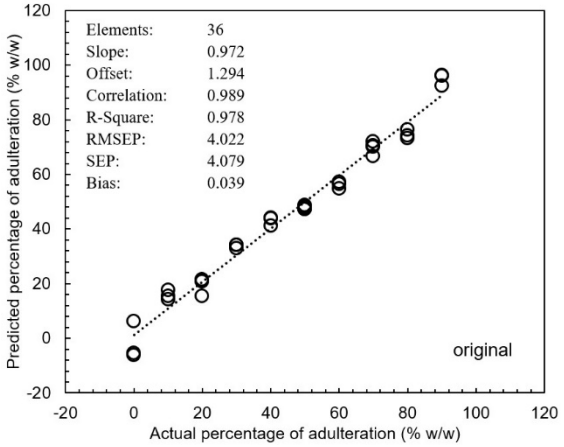


**Fig. 9. Score plot between actual and predicted percentage of adulteration calculated using original spectral data in the range of 200-400 nm.**

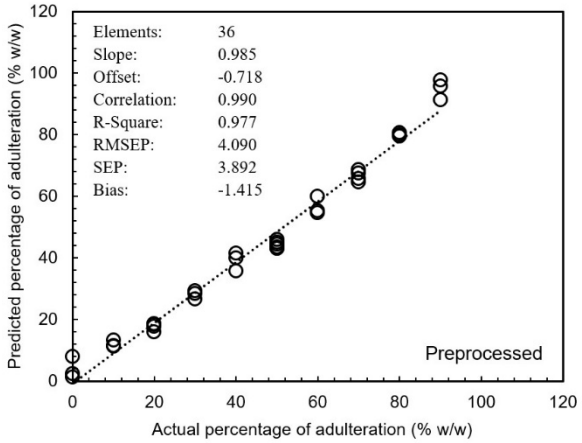


**Fig. 10. Score plot between actual and predicted percentage of adulteration calculated using pre-processed spectral data in the range of 200-400 nm.**

## 4. Conclusions

This study demonstrated the potential use of UV spectroscopy with chemometrics to perform simple and affordable authentication of Indonesian Kalosi ground roasted coffee. The samples were separated using preprocessed spectra over the range of 200-400 nm to determine their various adulteration percentages. Furthermore, the quantification percentages of adulteration were achieved using the original and preprocessed spectra with a high coefficient of calibration and validation. The prediction was satisfactory with high RPD and RER for preprocessed spectra, which led to acceptable LOD and LOQ that are sufficient for economically motivated adulteration in Indonesian specialty coffee.

## Acknowledgments

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## Nomenclatures

| | |
|---|---|
| $A$ | Absorbance |
| $I_o(\lambda)$ | Intensity of light passed through the reference at wavelength, $\lambda$ |
| $I_s(\lambda)$ | Intensity of light passed through the sample at wavelength, $\lambda$ |
| $s$ | Slopes of the regression line |

***Greek Symbols***

| | |
|---|---|
| $\lambda$ | Wavelength |

**Abbreviations**

| | |
|---|---|
| GIs | Geographic Indication |
| HPLC | High-Performance Liquid Chromatography |
| LOD | Limit of Detection |

| | |
|---|---|
| LOQ | Limit of Quantification |
| NIR | Near Infrared |
| NMR | Nuclear Magnetic Resonance |
| PC | Principal Component |
| PCA | Principal Component Analysis |
| PLS | Partial Least Square |
| RER | Ratio Error Range |
| RMSEC | Root Mean Square Error of Calibration |
| RMSECV | Root Mean Square Error of Cross-Validation |
| RMSEV | Root Mean Square Error of Validation |
| RPD | Ratio Prediction to Deviation |
| SD | Standard Deviation |
| SEP | Standard Error of Prediction |
| SG | Savitzky-Golay |
| SNR | Signal-to-Noise Ratio |
| SNV | Standard Normal Variate |
| UV-VIS | Ultraviolet-Visible |

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