Predicting Lipid, Caffeine And Chlorogenic Acid Contents Of Arabica Coffee Using NIRS

Safrizal, Sutrisno, Lilik Pujantoro EN, Usman Ahmad, Samsudin

Abstract: Coffee is one the most increasingly propular baverage in the world community because it's very distinctive taste for each region of origin of coffee, which is closely related with the special chemical composition of coffee such as caffeine, lipid and chlorogenic acid components. A Component analysis of coffee in the bean form needs to be done in order to easily classifying the quality of coffee based on its chemical composition. Some studies resulted that NIR able to predict the chemical components in some agricultural materials, such as coffee that can also be predicted its composition using NIRS that should be combined by applying several data treatments on the spectrum including Multiplicative Scatter Correction (MSC), Standard Normal Variate (SNV), Mean Normalization (MN) and the transformation group represented by Orthogonal Signal Correlation (OSC), as well as De-Trending (DT). The purpose of this study was to analyze the correlation between the NIR spectrum and the chemical composition of grinded coffee. Coffee samples were taken from the Indonesian Gayo highland, which 50 samples with 100 grams for each sample were harvested from various height of the planting and species. The samples were then prepared according to the method of Specialty Coffee Association of America (SCAA) protocol. NIRS measurements were done by using a Buchi NIRFlex N-500 spectrophotometer, while chemical components analysis were conducted using a UV-VIS spectrophotometer. The reseach analysis showed that the calibration using Partial Least Square (PLS) that combined with MN and OSC data pretreatment were found to be the best results for predict caffeine content with r value of above 0.7 and the Relative Percent Difference (RPD) value of above 2. The similar results were also found in prediticing of lipid and chlorogenic acid content with RPD values of above 2. The research concluded that NIRS can be used to predict the lipid, caffeine and chlorogenic acid content in the coffee.

Keywords: Arabica, Coffee, NIRS, Caffeine, Chlorogenic Acid, Lipid, Gayo.

1 INTRODUCTION

Coffee has become a popular agricultural commodity in the world because some people have made coffee as a regular daily drink, therefore the demand for coffee in the world continues to increase along with increasing interest in the world coffee consumption. Besides being a favorite drink, the coffee also has a good chemical composition for the healthy if it is not consumed excessively. The chemical compositions of coffee are also affect the quality of coffee taste, especially its macro components such as lipid, caffeine and chlorogenic acid. Before coffee is used as a beverage, roasting is first treatment that should be done, because "flavor" of coffee will be produced during the roasting process, depends on the type of green coffee used, the method of processing coffee beans, roasting, grinding, storage and brewing methods. The taste of coffee will be determined eventually by processing in factories. Roasting will chemically change the content in the coffee beans, accompanied by their weight loss, increasing the size of the coffee beans and changing the color of the seeds. Coffee beans after roasting will experience chemical changes which are very important elements of flavor [4]. Coffee beans naturally contain various types of compounds including caffeine, chlorogenic acid, trigonelin, carbohydrates, lipids, amino acids, organic acids, volatile aromas, and minerals. Caffeine is one of the most important alkaloid compounds found in coffee beans, where the caffeine content contained in a cup of tea is about 40-50 mg, and depend on the variety it can reach 80-100 mg.

- *Safrizal is Postgraduate Student of Bogor Agricultural University (IPB) and lecturer of Syiah Kuala University, Indonesia, PH+6281362893616. E-mail: ri-zal_oct@yahoo.com*
- *Sutrisno, Lilik Pujantoro EN, Usman Ahmad are Lecturers of Bogor Agricultural University (IPB), Indonesia.*
- *Samsudin is Researcher of BALITTRI Bogor, Indonesia*

The chemical content in coffee is obtained by using laboratory analysis by dissolving it in a solvent first, and recently known that through a long temporary process of research [7] getting result that NIR can detect chemical bonds that occur in solid materials. In was succefull testing using cocoa beans as research material, and also with the same test is also expected for grinded coffee beans, so that the composition of coffee can be detected easily without complicated laboratory analysis. Chemical components besides affecting the healthness of coffee drinkers, moreover has also affect the quality of coffee taste, so that analyzing the chemical composition becomes a necessity for coffee processing companies. The use of NIRS is recently wellknown as a tool for more effective detects the concentration of coffee component, where generally if NIR rays are emitted on a material then some of the light will be transfered, some others are absorbed and the others will be reflected. The amount of NIR light that absorbed depends on the chemical atomic bond in the material to be tested, where the correlation between NIRS and its chemical composition can be done using PLS with correlation coefficient (r) and The Ratio of Performance to Deviation (RPD) as indicators. The objective of this research was to analyze correlation between NIR spectra and chemical components of grinded coffee beans, especially caffeine, total lipid and chlorogenic acid.

2 PROCEDURE

2.1 Instrument and Materials

Coffee beans were taken directly from the Gayo highland by 50 random samples in 50 locations by homogenizing the height of the planting and varieties so that they would get more variety of cupping qualities. The samples were prepared following the procedures issued by SCAA [5], he coffee samples must be roasted within 24 hours of cupping test and left to rest for at least 8 hours, then roasted on the light flame profile measured by M-Basic (Gournet) in an estimate of 58 Agron scales for all seeds and 63 Agron scales at the bottom, roasting was carried out not less than 8 minutes and no later than 12 minutes, then cooled immediately. When the sample has reached room temperature, the sample must be stored in an

impermeable package until testing and stored in a cold room but not in the refrigerator. All samples were then analyzed for chemical components using UV-VIS spectrophotometer, and paralely cupping test have also done.

2.2 NIRS measurement

The measurement of the coffee spectrum was carried out by using a spectrophotometer Buchi NIRFlex N-500 by placing the sample in petridisk then scanned it

2.3 Analysis of coffee chemical components

Coffee which were analyzed for its chemical components were first refined in order to facilitate extracting certain chemical components. Before being analyzed using a UV-VIS spectrophotometer, the fine coffee was first extracted. Components to be analyzed in this research were include caffeine, chlochlorogenic acid, and lipid.

Caffeine Content

One gram of grinded coffee beans were put into a beaker and then 150 mL distilled hot water were added while continuously stirred. Hot coffee solution were filtered through a funnel with filter paper into Erlenmeyer, then 1.5 g of Calcium Carbonate ($CaCO_3$) and the coffee solution were put into a separating funnel then extracted 4 times, each with the addition of 25 mL of chloroform. The bottom layer were taken, then the extract (chloroform phase) were evaporated with a rotary evaporator until completely evaporated. The solvent-free caffeine extract was put into a 100 mL measuring flask, diluted with distilled water until the mark line, and homogenized, then determined by UV-Vis spectrophotometry at a wavelength of 275 nm, and concentration data were obtained after calibrated with standard caffeine solution.

Chlorogenic Acid Content

The 25 grams of coffee beans were weighed, then macerated in a glass container with 500 ml of methanol 70% for 48 hours and filtered through Whatman No. 1 filter paper with a vacuum filter and accommodated. Maseration and filtration were repeated 3 times in the same way so that 1.5 liters of maseration were obtained. The obtained maceration were evaporated with rotavapour temperature of 40^{o}C to obtain a thick extract. This extract was stored in a refrigerator at 4^{o}C for further analysis. Before determining the levels of chlorogenic acid of coffee bean extracts, the analysis method was validated first. Validation of analytical methods includes linearity parameters, detection limits and limits of quantitation, precision and accuracy. The method of analyzing chlorogenic acid using thin-layer (TLC)-densitometry comatography were done as follows: Created several concentrations of standard chlorogenic acid solution that would be used for the standard curve. Weighed a certain number of samples, then dissolved in 95% ethanol. After that the standard solution and the sample solution were sprayed on the TLC plate. The plate was then removed. The results of the elution were then analyzed using densitometry. Measurement of chlorogenic acid concentration in the sample by plotting the area of the chlorogenic acid sample on the standard curve.

Lipid Content

Lipid content measurement was done using the Soxhlet Method [6]. The measurement were began with drying the flask with several flints for 1 hour at 105^{O}C, then cooled in the exicator, weighed it, and the results were recorded as L. The sample of 10 grams were inserted in the extration thimble and then covered with cotton and placed in a soxhlet device, and added 100-150 ml of n-hexana into a measuring flask, then the extraction process can be began. Extraction was carried out for 6 hours at 95^{0}C until n-hexana was completely cleaned. N-hexane was evaporated with a rotary evaporator until remained lipid liquid only, dried a lipid-containing in measuring flask in an oven at 105^{0}C for 30 minutes. Finally, the measuring flask was cooled in the exicator. After cooling, the flask was re-weighed and recorded as LA value. Calculation of lipid content (FC) follows the equation:

$$FC(\%) = \frac{(LA - L)10000}{10x dry\ matter}\%$$

2.4 Spectrum Processing Method

Spectrum Processing of NIRS was done by using the application The Unscrambler® X version 10.3. The spectrums was corrected with 2 types of pretreatment, namely normalization represented by Multiplicative Scatter Correction (MSC), Standard Normal Variate (SNV), and Mean Normalization (MN), and transformation groups represented by Orthogonal Signal Correlation (OSC) and De-Trending (DT), and Spectral data processing using Partial Least Square (PLC). The correlation between NIR spectrum and cupping test value was made using PLS which would be compared with the results of laboratory tests. PLS is one of the most popular methods for multivariate calibration of NIR spectra data. PLS takes (NIR spectral data) X and Y (desired quality attributes) the matrix considers when developing a model to find the latent variable in X that best predicts the latent variable at Y. PLS maximizes the covariance between X and Y. In this case, system convergence for minimum residual errors often achieved in fewer factors. PLS also leads to a reduction in the number of latent variables [2][1].

3 Results and Discussion

After measuring NIRS and processing them, then carried out the introduction of each peak of the curve by estimating what components affect the peak as shown in Fig. 1 and then set the NIR spectrum calibration with its chemical components as shown in the figure below.

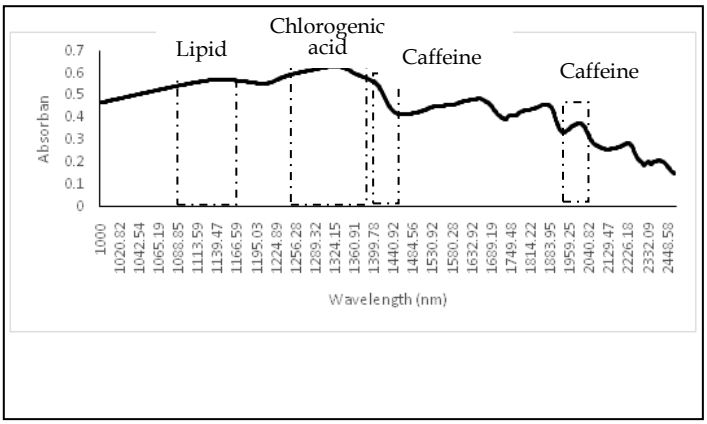

Fig.1. *NIR spectrum of grinded coffee which was measured and several peaks for chemical components*

3.1 Caffeine

One of the most imprtant compounds that make a specific taste of coffee is caffeine, specifically the content is more dominant than other baverages. Caffeine in coffee will also strongly affect the taste quality of coffee, where the concentration of caffeine is around 1.1%. The caffeine concentration data is calibrated with NIRS data as shown in the Fig.2

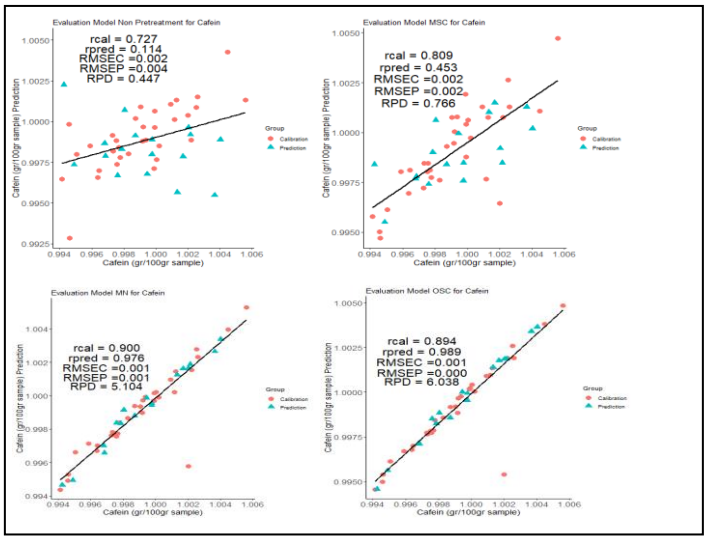

Fig.2. *Calibration curve of caffeine component of coffee with NIRS: without pretreatment (a), pretreatment using MSC (b), using MN (c), and using OSC (d)*

The results above are PLS analysis used in caffeine data, and the results show that not all treatments resulted the best value of calibration. It is clearly shown that non-retreatment, MC, MSC, SNV, and Dt were found not sufficiently good in estimating the caffeine value by using NIRS. The pretreatment using MN and OSC were found to be the best prediction parameter's values, have the relatively high r value with the low values of RMSEC, RMSECV, RMSEP. Furthermore, the value of RPD obtained can also be said to be a good model as shown in Table 1

TABLE 1

Result of calibration and prediction of caffeine concentration with NIRS

Treatment	Laten Variable	Calibration			Prediction	
		r	RMSEC	RMSECV	RMSEP	RPD
Non Pretreat treatment	1	0.08213	0.00000008	0.005637	0.003094	0.131205
MC	1	0.13937	0.00000002	0.005600	0.003140	0.276287
MSC	3	0.70611	0.00000019	0.004005	0.002035	1.330786
SNV	3	0.68513	0.00000017	0.004120	0.002336	0.998641
MN	2	0.71692	0.00000125	0.003943	0.001360	2.957044
DT	3	0.66181	0.00000004	0.004240	0.002980	0.893473
OSC	2	0.71692	0.00000119	0.003943	0.001360	2.957044

3.2. Lipid

As the same with other organic components, lipid is known as substances with variety of formulas their chemical bonds, where the constituent elements of C, H and O in the chemical formula bond will make these nutrients can be used as energy sources. Lipids can dissolve in organic solvents but are not soluble in water or solvents containing water. The concentration of lipid in coffee was found to about 12.5%, and the total lipid concentration of the analysis results was then calibrated with NIRS data as shown in Figure 3.

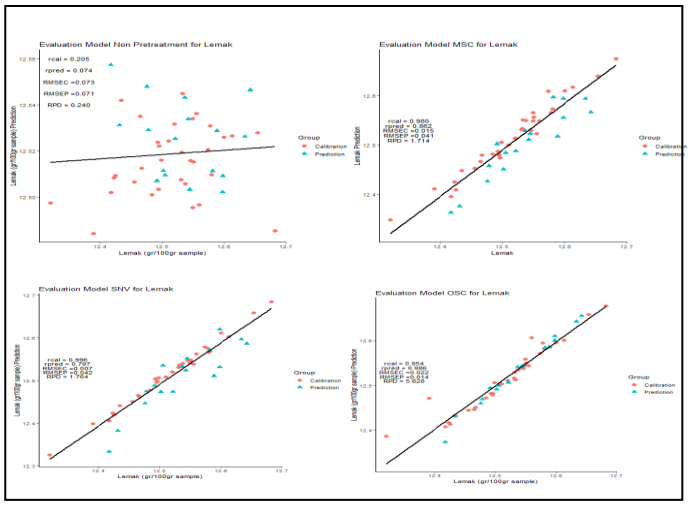

Fig.3. *Calibration curve of total lipid component of coffee with NIRS: without pretreatment (a), pretreatment using MSC (b), using SNV (c), and using OSC (d)*

The results above are PLS analysis used for lipid data, and it was resulted that not all treatments can be used for calibration for lipid content. It was found that non-pretreatmen, MC, and Dt were not good enough for estimating the value of lipid, while data pretreated by using MSC, SBV, MN, and OSC were found to be good in estimating the value of lipid. The analysis were resulted the r value were quite high (> 0.9), with fhe values of RMSEC, RMSECV, and RMSEP were quite low, and the RPD value at the pretreatment of MSC and SNV were of 1.5 - 2.0. By this data, it was resulted that the model is sufficiently good enough to be used for predicting the lipid value of the coffee. The general data analysis can shown in table 2.

TABLE 2

Result of calibration and prediction of lipid concentration with NIRS

Treatment	Laten Variable	Calibration			Prediction	
		r	RMSEC	RMSECV	RMSEP	RPD
Non Prtreatment	1	0.20516	0.00000059	0.072858	0.071152	0.240181
MC	1	0.21302	0.00000045	0.072733	0.069381	0.252004
MSC	9	0.98006	0.00000409	0.014793	0.041493	1.713773
SNV	11	0.99589	0.00000349	0.006741	0.042120	1.764143
MN	3	0.95138	0.00000057	0.022930	0.011483	6.557163
DT	10	0.98741	0.00000076	0.011774	0.049375	0.946461
OSC	4	0.95375	0.00000306	0.022377	0.013623	5.628009

3.3. Chlorogenic Acid

Chlorogenic acid and other related components are the main phenolic components found in coffee beans. The content of chlorogenic acid in coffee beans were found to be about 14% (dry weight). This component has beneficial potential for health related to antioxidant activity as hepatoprotector, hypoglycemic and antiviral (Farah et al. 2006). Chlorogenic acid is an important component affecting a specific coffee flavor. Furthermore Farah et al. (2006) said that chlorogenic acid contributes to the total or final acidity, astringency and bitterness of the coffee. Calibratiion analysis using PSL between NIRS and chlorogenic acid are shown in Figure 4.

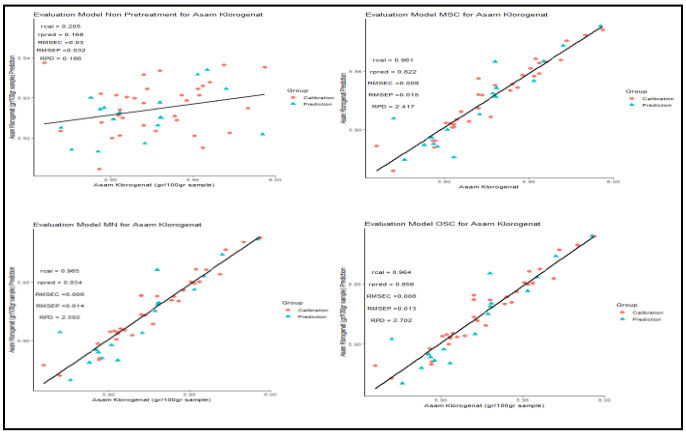

Fig.4. *Calibration curve of chlorogenic acid component of coffee with NIRS: without pretreatment (a), pretreatment using MSC (b), using MN (c), and using OSC (d)*

As can be seen in Figure 4, the analysis show that not all treatments are resulted the best parameters value for predition of the chlorogenic acid content. The best results were found by using the NIRS data treated by MSC, SNV, MN, DT, and OSC. All of these treatments produced a high r value (above 0.9), with the RMSEC, RMSCEV, and RMSEP values were quite small. The analysisi of RPD was found to be enough good model to be used for prediction of chlorogenic acid content. In general, the analysis with pretreatment data of NIRS would resulted a better parameters value than of without pretreatment, however not all pretreatments can be used for this predition model as like MC since their less good values of parameters needed, as shown in table 3.

TABLE 3

Result of calibration and prediction of Chlorogenic acid concentration with NIRS

Treatment	Laten Variable	Calibration			Prediction	
		r	RMSEC	RMSECV	RMSEP	RPD
Non Pretreat treatment	1	0.20470	0.00000019	0.030351	0.031780	0.185854
MC	1	0.28246	0.00000269	0.029745	0.037633	0.254905
MSC	4	0.96089	0.00000214	0.008587	0.014597	2.417041
SNV	4	0.95787	0.00000224	0.008905	0.011860	2.893452
MN	5	0.96505	0.00000119	0.008126	0.014385	2.502301
DT	3	0.95809	0.00000060	0.008883	0.013841	2.498451
OSC	4	0.96393	0.00000070	0.008252	0.013396	2.702401

In general it can be seen that the chemical compositions of coffee, especially caffeine, total lipid and chlorogenic acid content can be detected using NIRS since in pricipally the NIR spectrum is influenced by the chemical content of the coffee ingredients.

4 Conclution

In general general, this research concluded that the chemical compositions caffeine, total lipid and chlorogenic acid content of coffee can be predicted using NIRS with specific data treatments as bellows:

1. The content of caffeine can be determined using NIRS with quite good calibration model with a large r value above 0.7 and the RPD value above 2, this result is obtained if NIRS spectrum were pretreated using MN and OSC.
2. NIR spectrum calibration with the best total lipid concentration was obtained when NIRS were pretreated using MN and OSC with with RPD values above 2.
3. Chlorogenic acid concentration was predicted by PSL calibration using pretreated NIRS producing good results using almost all pretreatments except Mean Centering that was marked by RPD value of above 2.

References

[1] CAMO. 2012. Method Reference The Unscrambler® X 10.2

[2] Felizardo P, Baptista P, Menezes JC, Correia MJN. 2007. Multivariate Near Infrared Spectroscopy Models for Predicting Methanol and Water Content in Biodiesel. Analytica Chimica Acta. 595: 107-113

[3] Kummer, Corby. 2003. Caffeine and Decaf. The Joy of Coffee. Houghton Mifflin Cookbooks.;. 160-165

[4] Ridwansyah. (2003). Pengolahan Kopi. Departemen Teknologi Pertanian. Fakultas Pertanian. Universitas Sumatera Utara. Medan

[5] SCAA (2014). SCAA Protocol Cupping Specialty Coffee. https://www.scaa.org/?page=resources&d=cupping-protocols accesed November 15Th 2015

[6] Vesela A, Barros AS, Synytsya A, Delgadillo I, Copikova J, Coimbra MA. 2007. Infrared Spectroscopy and Outer Product Analysis for Quantification of Fat. Nitrogen. and Moisture of Cocoa Powder. J Analytica Chimica Acta 601: 77–86. www.elsevier.com/locate/aca

[7] Zulfahrizal (2014). Pengembangan Metode Pengukuran Nondestruktif Untuk Menentukan Mutu Dan Fermentasi Biji Kakao Utuh Menggunakan Nir Spectroscopy. Disertasi. Sekolah Pascasarjana-IPB.Bogor.