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Laser-Induced Breakdown Spectroscopy (LIBS) for Spectral Characterization of Regular Coffee Beans and Luwak Coffee Beans

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ABSTRACT

Luwak *(civet)* coffee refers to a type of coffee, where the cherries have been priorly digested and then defecated by a civet *(Paradoxurus Hermaphroditus)*, a catlike animals typically habited in Indonesia. Luwak will only selectively select ripe cherries, and digesting them by enzymatic fermentation in its digestive system. The defecated beans is then removed and cleaned from the feces. It is regarded as the world's most expensive coffee, Traditionally the quality of the coffee is subjectively determined by a tester. This research is motivated by the needs to study and develop a method to determining the quality of coffee products. LIBS technique was used to identify the elemental contents of coffee beans based on its spectral characteristics in the range 200-980 nm. Samples of green beans from variant of arabica and robusta, either regular and luwak, were collected from 5 plantations in East Java. From the recorded spectra, intensity ratio of nitrogen (N), hydrogen (H), and oxygen (O) as essential elements in coffee is applied. In general, values extracted from luwak coffee bean is higher with increases 0.03% - 79.93%. A Discriminant Function Analysis (DFA) also applied to identify marker elements that characterize the regular and luwak beans. Elements of Ca, W, Sr, Mg, and H are the ones used to differentiate the regular and luwak beans from arabica variant, while Ca and W are the ones used to differentiate the regular and luwak beans of robusta variant.

Keywords: Laser-Induced Breakdown Spectroscopy (LIBS), civet coffee, spectral characterization

I. INTRODUCTION

Coffee is one of most widely consumed beverages in the world. Based on data from the International Coffee Organization (ICO), coffee consumption increased by an average of 2.4 % since 2011. This shows that coffee is one of the important commodity in the world trade, i.e. second largest trading commodity in the world after oil. Indonesia is the fourth largest coffee producing country in the world after Brazil, Vietnam, and Columbia[1].

Coffea arabica (arabica coffee) and *Coffea canepora* (robusta coffee) are coffee variants of most consumed in the world. In Indonesia also there other type of coffee, which is regarded as the most expensive coffee in the world (with price up to $500 per kg), i.e. known as luwak (civet) coffee. Luwak (civet) coffee refers to a type of coffee, where the cherries have been priorly digested and then defecated by a civet *(Paradoxurus Hermaphroditus)*, a catlike animals typically found to be habited in Indonesia. Luwak will only selectively select ripe cherries, and digesting them by enzymatic fermentation in its digestive system. The defecated beans is then removed and cleaned from the feces in the form of hard skin seeds[2].

During the digestion process in the civet's digestive system, there are certain enzymes that contribute to enzymatic process to breakdown proteins into free amino acid that will affect to reduce the bitter taste, more fragrant smell, as well as increasing of free amino acids[3], and also believed to shorten the fermentation process on coffee beans. This will affect the content and composition of the elements to produce a unique taste and aroma. Some studies have indicated that luwak coffee have different characters from regular coffee, either physically[4], taste[5], as well as in its chemical composition and sensory value[6].

Coffee containing caffeine ($C_8H_{10}N_4O_2$), trigonelline ($C_7H_7NO_2$), chlorogenic acid ($C_{16}H_{18}O_9$), amino acid (COOH-R-NH_2), peptide (-CO-NH-), citric acid ($C_6H_8O_7$), malic acid ($C_4H_6O_5$), and other compounds that determine the taste and aroma of coffee[7]. The composition of coffee is very complex, so it is somewhat difficult to determine the contents that

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characterize the coffee. Traditionally, the quality of the coffee still relies on the subjective judgement of tester. Characterization based on spectroscopical techniques offer possibilities to develop objective parameters characterizing coffee's quality. Until now there is no standardized techniques available, hence it still opens plenty rooms for research for determining accurate set of parameters that characterizes the coffee's quality

Laser-Induced Breakdown Spectroscopy (LIBS) is an atomic emission spectroscopy that uses high-energy laser pulses to excite atoms from its lower energy levels to the high energy ones. Laser beam is focused to generate plasma that will make a tiny spark on the sample and atomize into small portions[7,8]. This plasma emission can provide "spectral signatures" of chemical composition from many different kinds of materials either in solid, liquid, or gas state[9]. LIBS has many advantages as analytical technique, highly sensitive, fast analysis process with only little sample[7,10]

In this study, LIBS was employed to identify the differentiation of regular coffee and luwak coffee qualitatively. The coffee samples used are dry processed green beans and will be compared to the ones that have been prior digested by the civet. Different processes will impact the quality of coffee in terms of its taste and aroma due to differences in compositional contents. Compositional contents of coffee are displayed in the form of graph of intensity vs wavelength from their atomic emissions. These emission intensities show the corresponding element's concentrations in coffee.

The recorded spectra graph are used to identify differences of elements which forming compounds in regular as well as luwak coffee beans. The analysis were mainly focused on the N, H, and O elements which are regarded as essential elements of the organic substances that make coffee beans. Spectral analysis based intensity ratio method compares main elements with Ca as host elements. A Discriminant Function Analysis (DFA) was also applied to determine the specific mineral elements that characterize differences of regular and luwak green coffee beans.

2. METHODOLOGY

2.1 Samples of Green Coffee Beans

Coffee beans samples were collected from five plantations in three regions in East Java (i.e. Pasuruan, Malang, and Bondowoso), all are from two different variants, i.e. the Arabica and Robusta , as can be seen in Table 1.

Table 1. Green Coffee Beans Sample

Coffee Variant		Plantation				
		#1	#2	#3	#4	#5
Arabica	Regular	√	√	√	√	
	Luwak	√	√	√	√	
Robusta	Regular				√	√
	Luwak				√	√

Each group of samples were plucked from the same plantation in the period of 2011 to 2015. The regular beans were obtained by dry-processing, while the luwak beans are taken from farmed civet. The moisture contents of the coffee beans are between 11 – 15%.

2.2 Experimental Setup

The LIBS experimental setup used in this work is shown in Fig. 1. The LIBS system consist of a laser source, i.e. a Nd:YAG laser (model CRF 200 mJ, 1,064 nm, 7 ns), and equipped with a spectrometer from Ocean Optic type HR2500+, a sample plate, and a dedicated software of OOILIBS. The laser, with frequency of 5 Hz, as focused on the coffee sample using a convex lens (focal length of 10 cm) for plasma formation. Radiation emission of elements in spectral range of 200-980 nm were recorded by detector CCDs (14.336 MP and spectral resolution 0.1 nm[11]. Experiments were fixed at laser energy of 120 mJ, delay time 1 µs, FWHM of 0.18, and average of 3 shots employed per sample beans. All experiment was conducted under air pressure of 1 atm. Coffee beans samples are randomly selected from each group, and was put on a sample plate in a light-tight chamber in order to prevent light contamination from outside that might affect the experiment's results.

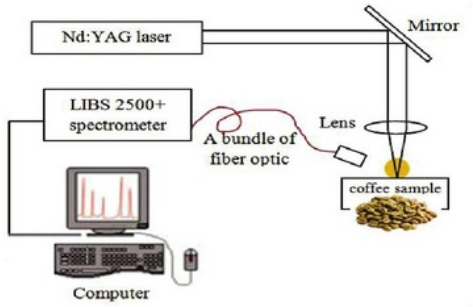


Figure 1. Schematic of the LIBS experimental setup

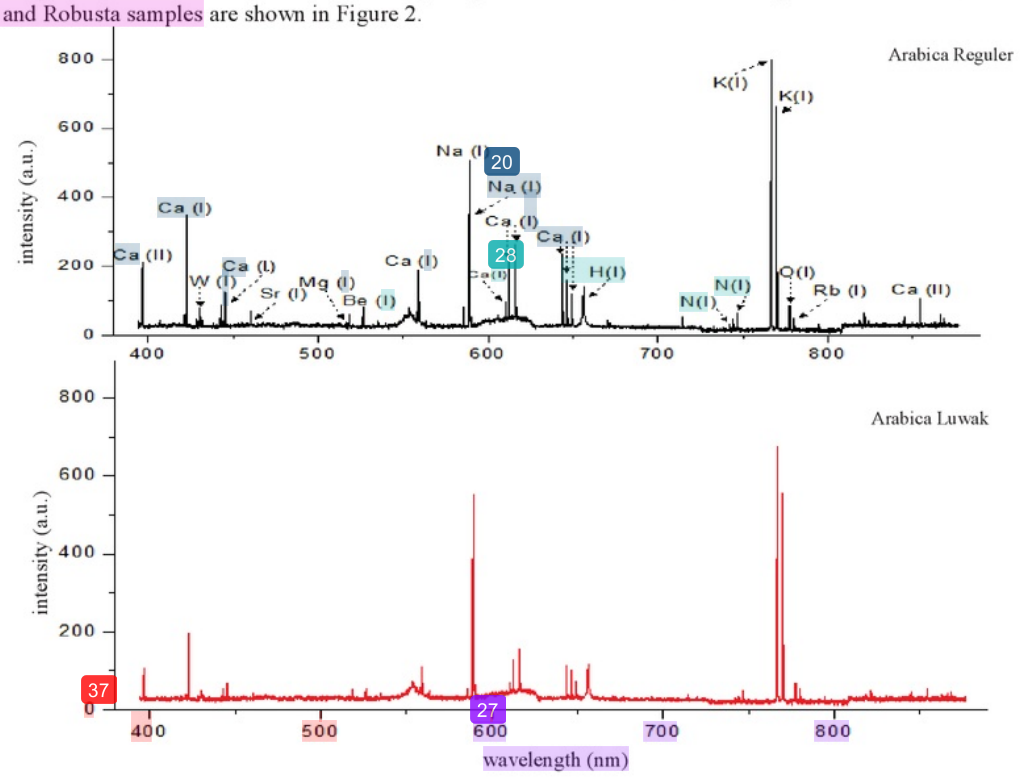
2.3 Data Processing

LIBS spectra in the form of intensity vs wavelength graph of emission were processed using OOILIBS software. Meanwhile the AddLIBS software was used to identify the constructing elements and data validation with the ones of NIST. The area under the curve of peak intensities were then calculated, and respective ratio intensity of N, H, O to host element of Ca element were determined. A Discriminant Function Analysis (DFA) was then applied to determine the fingerprint elements that characterized the differences of regular and luwak green coffee beans. The data from the experiment processed by OriginPro 8.5, and SPSS 17.

3. RESULTS AND DISCUSSION

3.1 Green Coffee Beans LIBS Spectra

The LIBS Spectra of elemental constituents in a regular green coffee beans and Luwak green coffee beans, for both of Arabica and Robusta samples are shown in Figure 2.



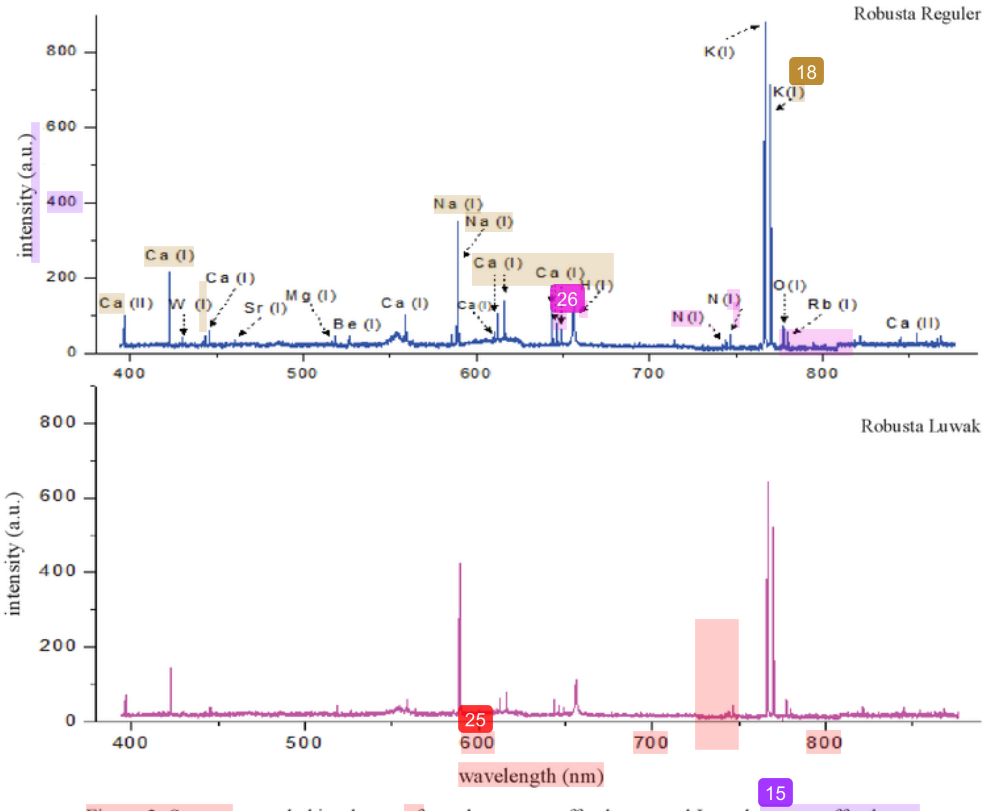


Figure 2. Spectra recorded in plasma of regular green coffee beans and Luwak green coffee beans for both Arabica and Robusta variants

The concerned elements in the LIBS spectra of coffee beans are Ca (calsium), W (tungsten), Sr (strontium), Be (beryllium), Mg (magnesium), Na (natrium), H (hyrogen), N (nitrogen), K (pottasium), O (oxygen), and Rb (rubidium). Figure 2 shows that no additional macro elements that appear in green coffee beans due to the digestive process by the civet. These differences are shown by the respected emission intensities, where intensities from the civet coffee tends to be lower than the ones of regular coffee beans, indicating lower content of these elements.

The majority elements contained in regular and luwak green coffee beans of Arabica and Robusta were recorded at wavelengths which corresponding to the energy levels of each element, i.e. for both neutral atoms or ions. These elements of coffee beans bonded to each other and form certain compounds that characterize the characteristics of coffee.

Elements of C, H, N, and O are essential elements that can be used for identification in this study. These elements are organic elements that often detected in biological samples[10], as in coffee beans. Further analysis were conducted on these N, H, and O elements, meanwhile the C elements were not detected with the LIBS without any special treatment. C is light element, fast moving, easily bound or recombined with other elements in air, such as N and O to form molecules of C—O and C—N.

The intensity values of the atomic emissions in the LIBS spectra of coffee beans show varying values, indicating a difference in the concentration of the constituent elements. Therefore, the variations of area under intensity curve of peaks was used to perform intensity ratio analysis. Spectral fingerprints that differentiate between regular coffee beans and luwak coffee beans were extracted through comparison among normalized intensity of the elements N, H and O. A statistical processing by Discriminant Function Analysis (DFA) was also applied in this study.

3.2 Ratio of IntensityAnalysis

In the ratio of intensity analysis, the peak intensity of N, H, and O elements are divided to the one of Ca as h elements. In general, the area under curve of peak intensity of luwak green coffee beans tend to lower than regular green coffee beans. The intensity of elements of N, H, and O are fluctuated, it might be due to abundance of these elements in nature which also easily to interact with other elements to form a molecule. Besides coffee is also a hygroscopic material which can easily absorb these elements in water molecules in the air. So the value of these elements in coffee beans which analyzed by LIBS are very dependent on humidity conditions in the environment. It means that the value of the elements is the sum of the impurity of N, H, O elements and constituent elements of coffee molecule. The intensity ratio of normalize elements of N, H, and O to Ca as host element of coffee beans detected shown in Fig. 3.

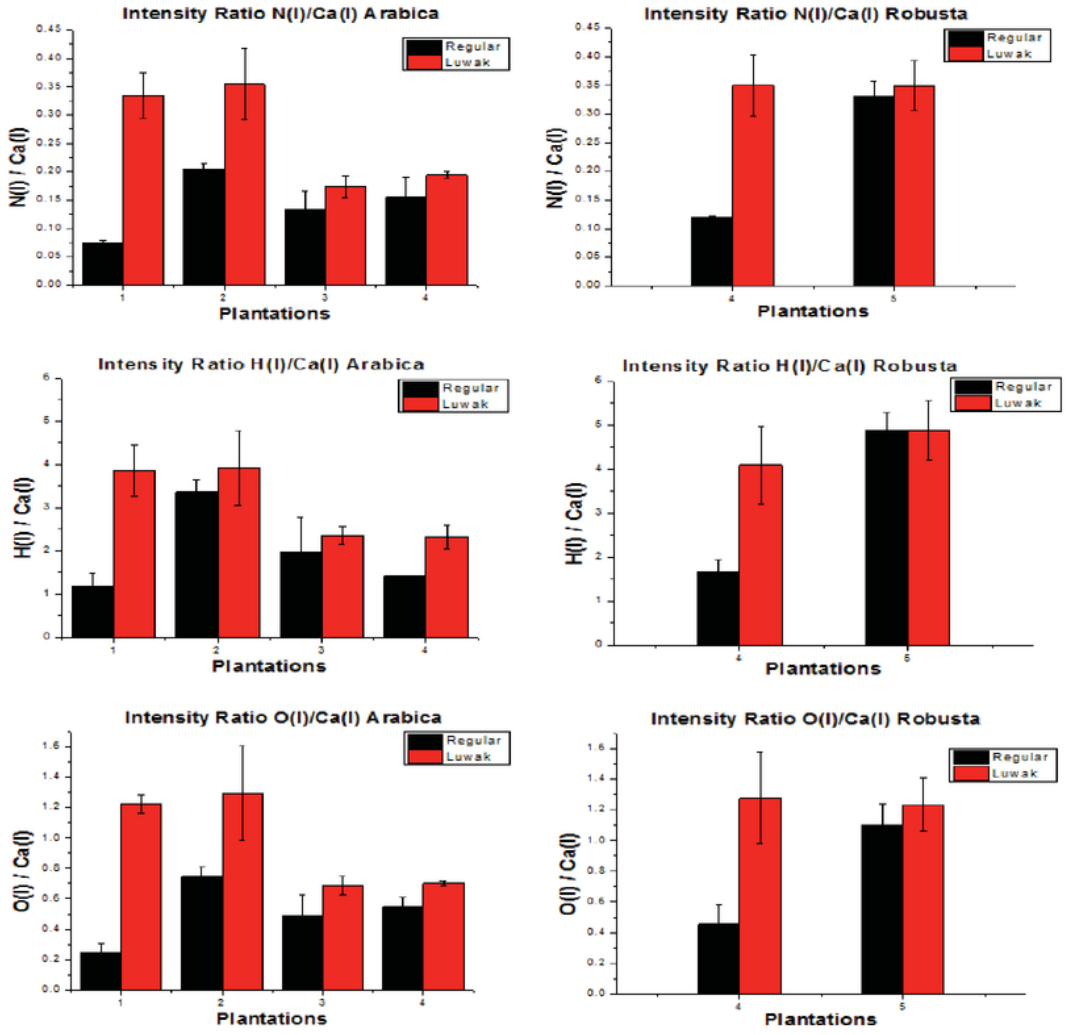


Figure 3. Intensity ratio of coffee element, Left: Arabica, Right: Robusta

The graphs shows that the intensity ratio of luwak coffee beans are higher than regular coffee beans. Changes in the values of normalized intensity ratio may indicate changes in the balance of elemental contents in coffee beans. Luwak coffee is claimed to have a better flavor and aroma. Enzymatic processes in the digestive tract of civet may penetrate

porous surface of the coffee beans which will affect the chemical compositions in coffee beans to be significantly altered. This process causes protein to be breaken down into amino acids. From the measured data, the intensity ratio of N to Ca ranges between 0.075 to 0.331 for regular beans and 0.174 to 0.354 for luwak beans. The intensity ratio of H to Ca ranges between 1.18 to 4.89 for regular beans and 2.32 to 4.891 for luwak beans. Meanwhile the intensity ratio of O to Ca varies between 0.25 to 1.1 for regular beans and 0.69 to 1.3 for luwak beans. These variations might due to differences in processing experienced by the samples collected from different producers / plantations.

Besides containing of N, H, and O elements, coffee beans also containing other elements such as Ca, K, Mg, Na which are major elements found in the environment[12]. These elements are found in the soils and the environments where the coffee trees are grown, so the contents is different for coffee beans collected from different plantations. Meanwhile, other elements such as W, Sr, Be and Rb are regarded as minor elements contained in coffee beans[12].

3.3 Comparative Analysis of Elements with DFA (Discriminant Function Analysis)

Discriminant Function Analysis (DFA) was used to characterize or sort out the regular and luwak green coffee beans viewed from all elements that exist on coffee beans. This method applied by selecting the independent variables which significantly affect and the ones which does not affect the dependent variable. The dependent variable is regular green coffee beans and luwak green coffee beans, while independent variables in this case are all elements detected in the experiment.

Data processing of intensity area of each element perform by SPSS, obtained the result shown in Table 2.

Table 2. Tests of Equality of Group Means

Elements	Arabica					Robusta				
	Wilks' Lambda	F	df1	df2	Sig.	Wilks' Lambda	F	df1	df2	Sig.
Ca	0.626	3.586	1	6	0.107	0.330	4.053	1	2	0.182
W	0.616	3.744	1	6	0.101	0.657	1.042	1	2	0.415
Sr	0.521	5.508	1	6	0.057	0.852	0.348	1	2	0.615
Mg	0.931	0.445	1	6	0.530	0.955	0.095	1	2	0.787
Be	0.843	1.114	1	6	0.332	0.596	1.356	1	2	0.364
Na	0.993	0.040	1	6	0.849	0.997	0.007	1	2	0.942
H	0.760	1.899	1	6	0.217	0.941	0.125	1	2	0.758
N	0.915	0.554	1	6	0.485	0.997	0.007	1	2	0.942
K	0.820	1.314	1	6	0.295	0.704	0.842	1	2	0.456
O	0.942	0.371	1	6	0.565	0.999	0.001	1	2	0.975
Rb	0.869	0.907	1	6	0.378	0.664	1.012	1	2	0.420

The Wilk's Lambda values tend to close to 1, means that the data of each group tends to similar. This is also evidenced by the value of the F test obtained sig. > 0.05, which means almost no difference between groups of regular green coffee beans and luwak green coffee beans. Table 3, *Canonical Discriminant Function Coefficients*, consist of function to find the correlation between the independent variable. Ca, W, Sr, Mg, and H were used to differentiate the regular and luwak

Table 3. Canonical Discriminant Function Coefficients

Elements	Function	
	Arabica	Robusta
Ca	-0.993	0.317
W	5.030	-0.811
Sr	2.923	
Mg	-0.380	
H	0.017	
constant	0.996	-5.929

green coffee beans of arabica, while Ca and W are used to differentiate the regular and luwak green coffee beans of robusta.

Table 4. Functions at Group Centroids

Type of coffee samples	Code	Function	
		Arabica	Robusta
Regular	0.00	2.816	1.364
Luwak	1.00	-2.816	-1.364

In the application, if random coffee beans samples analyzed with LIBS and the value of intensity area from elements multiplied with the function in Table 3, the value obtained is positive, means the coffee beans is regular. But, if the value obtained is negative, it means that the beans is luwak coffee.

4. CONCLUSION

This preliminary study demonstrates a successful application of a LIBS to differentiate between regular green coffee beans and luwak green coffee beans. The elements detected in coffee beans are Ca, W, Sr, Mg, Na, H, N, C, O, and Rb. However, overall there are no additional elements in regular coffee beans due to the digestive process by the civet. Intensity ratio method were applied by comparing normalize elements of N, H, and O to Ca. The results showed that the luwak green coffee beans have higher intensity ratio values in comparison to regular green coffee beans. Discriminant Function Analysis (DFA) was also successful in characterizing the difference between regular and luwak green coffee beans. Ca, W, Sr, Mg, and H are the discriminant elemental markers to identify the regular and luwak green coffee beans from arabica variant, whilst Ca and W are the discriminant elemental markers to identify the regular and luwak green coffee beans from robusta variant.

REFERENCES

[1] European Coffee Federation, "Coffee producing countries", http://www.ecf-coffee.org/about-coffee/coffee-facts

[2] Jumhawan, U, Putri, S.P., Yusianto, et al.. "Selection of Discriminant Markers for Authentication of Asian Palm Civet Coffee (Kopi Luwak): A metabolomics Approach," Journal of Agriculture Food Chemistry, 61, 7994-8001 (2013).

[3] Marcone, M.F., "Composition and Properties of Indonesian Palm Civet Coffee (Kopi Luwak) and Ethiopian Civet Coffee", Journal of Food Research International 37, 901–912 (2004).

[4] Asyah, M., Fuferti, Z., Syakbaniah, and Ratnawulan, "Comparison of Physical Characteristics of Arabica Civet Coffee beans to the regular ones (in Indonesian), " Pillar of Physics, 2, 68-75 (2013).

[5] Yusiyanto, Mawardi, S.. 2010. "Physical Characteristics and Taste of Civet Coffee (in Indonesian)". Prosiding Simposium Kopi, 2010.

[6] Mahendradatta, M., Zainal, Israyanti, Tawali, A. B., "Comparison of Chemical Characteristics and sensory Value between Luwak coffee and Original Coffee from Arabica (Cafeea arabica. L) and Robusta (Cafeea canephora. L)", 2013, http://repository.unhas.ac.id/handle/123456789/2560

[7] Kim, T. dan Lin, C.. 2012.: [Advanced Aspects of Spectroscopy, Chapter 5: Laser–Induced Breakdown Spectrosc], InTech, 131-164 (2012).

[8] Cremers, D. A. dan L.J. Radziemski, [Handbook of Laser-Induced Plasma and Applications], 2nd Ed., John Wiley & Sons, Ltd. (20130.

[9] Miziolek, A.W. Palleschi, V., Schechter, I., [Laser-Induced Breakdown Spectroscopy (LIBS) : Fundamental and Applications], Cambridge University Pers (2006).

[10] Rai, V.N.. 2014. Laser-Induced Breakdown Spectroscopy : A Versatile Technique of Elemental Analysis and Its Applications. <URL:https://arxiv.org/ftp/arxiv/papers/ 1407/1407.0132.pdf> (July 2014)

[11] Insight™, [Laser Induced Breakdown Spectroscopy: Manual and User Guide], 2009

[12] Pohl, P., Stelmach, E., Welna, M., "Determination of the Elemental Composition of Coffee Using Instrumental Methods". Journal of Food Anal. Methods (2013) 6:598–613 (2013).

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