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Elemental analysis and hardness characterization of fermented green arabica coffee bean using Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract. By applying fermentation, the value of Gayo Arabica coffee can increase nearly fourfold. This study aims to differentiate green bean coffee of ordinary (unfermented) and wine (fermented) types using Laser-Induced Breakdown Spectroscopy (LIBS). Visual distinction between the two is challenging, but LIBS enables element identification through spectral characteristics. Green bean samples were analyzed using LIBS under optimized conditions of 120 mJ laser energy and 1,000 ns delay time. Elements such as C, H, N, O, Ca, Mg, Na, K, W, and Rb were detected in both types. The spectral intensity of Ca was notably higher in ordinary coffee, with the Ca (II)/Ca (I) ratio 2.2 times that of fermented coffee, indicating a softer structure in fermented beans. This study demonstrates the potential of LIBS for distinguishing spectral characteristics of Gayo Arabica green beans.

1 Introduction

Gayo coffee is a coffee produced in Bener Meriah District, Central Aceh and Gayo Lues. Those areas are in the region of Aceh, Sumatra, Indonesia. In regular condition, without post-harvest treatment, the price offered for one kilogram of gayo arabica coffee is 100,000 IDR. On the other hand, using post-harvest treatment such as fermentation, the coffee price can soar almost 4 times. The name of the fermented coffee is known as wine gayo arabica coffee [1].

Different types of samples have different elemental characteristics representing the composition in them. Thus, although ordinary (unfermented) and wine (fermented) gayo arabica coffee beans (GACB) type is visually similar, addition of fermentation process certainly makes the characteristics of the elements in the fermented coffee different compared to ordinary coffee. In order to present the elemental composition of sample, analytical method is something that need to be prepared [2].

Identification using coffee samples has been carried out using Flame Atomic Absorbtion Spectrometry (AAS) techniques [3], Inductively Coupled Plasma–Mass Spectroscopy (ICP-

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MS) [4], and Laser Induced Breakdown Spectroscopy (LIBS) [5]. Although provide detection with high accuracy and sensitivity, both AAS [6] and ICP-MS [6,7], they require laborious sample pretreatment (Iqhrammullah, 2021) [8]. Meanwhile, LIBS which was used as an elemental analysis technique in this study was assessed as little or no sample pretreatment [8–10].

This study aims to determine the differences in samples of ordinary and fermented GACB based on differences in post-harvest handling. The type of coffee will be identified based on the atomic emission spectral lines produced from the two green beans. With the increase in the fermentation process for arabica gayo wine, it is hoped that LIBS will be able to show the spectral differences between fermented and ordinary GACB.

2 Research Method

2.1 Sample Preparation

2.1.1 Gayo Arabica Coffee Bean

Samples of red coffee beans were taken from Mekar Ayu Village, Timang Gajah district, Bener Meriah Regency. Samples in the form of coffee cherries were sorted according to the perfect level of maturity by naked eye. The coffee cherries are hulled to separate the red skin on the coffee cherries using a machine while running water is added. Then the coffee beans are dried under the sun for seven days. After being dried, the horn shells attached to the coffee beans were separated and green beans were obtained.

2.1.2 Fermented Gayo Arabica Coffee Bean

Flawless coffee cherries are taken as samples. Fermentation process of coffee beans was carried out for 13 days of ripening period. The coffee beans are placed in a dark, closed place, and ensure that no light and air from outside can enter the fermentation place. After that, the coffee beans are dried under the sun for 20 days while being turned over. The process continued with the milling process using a machine to separate the shell, horn skin and epidermis on the coffee cherries. Finally, fermented GACB sample can be obtained.

2.1.3 Sample Selection

Green beans that would be used as samples were first selected to maintain sample homogeneity. The selected coffee beans were not deformed, flawless, and had almost uniform sizes for each sample. Furthermore, the samples were stored in plastic and aluminum foil to avoid contamination from the outside due to the hygroscopic nature of coffee and easy to absorb odor.

2.2 Instrumentation

The LIBS components consisted of a light source in the form of a Neodymium Yttrium Aluminum Garnet (Nd:YAG) laser with λ = 1,064 nm, 500 mJ total energy, 8 ns pulse width, and frequency of 10 Hz as a plasma excitation source. A focusing lens, F = 155 mm and an optical detector (Optical Multichannel Analyzer, OMA system) consisting of an Echelle spectrograph and an Intensified Charged Couple Device (ICCD), a detector (Andor Mechelle

ME5000) in the wavelength range 200-980 nm and 0.5 nm resolution were used. The arrangement of the components was in accordance with Figure 1.

The coffee bean sample was attached to the surface of the copper plate and placed in the sample holder to be irradiated by a laser beam for the plasma generation. Plasma was generated at a pressure of 1 atm, while the energy and delay time were adjust as mentioned in the optimum condition characterization step. The generated plasma emissions were collected by optical fiber and then transferred to the OMA system to obtain atomic emission wavelengths and lines or spectra. Spectral emission lines that have been obtained and recorded were displayed on the computer using ANDOR SOLIS software.

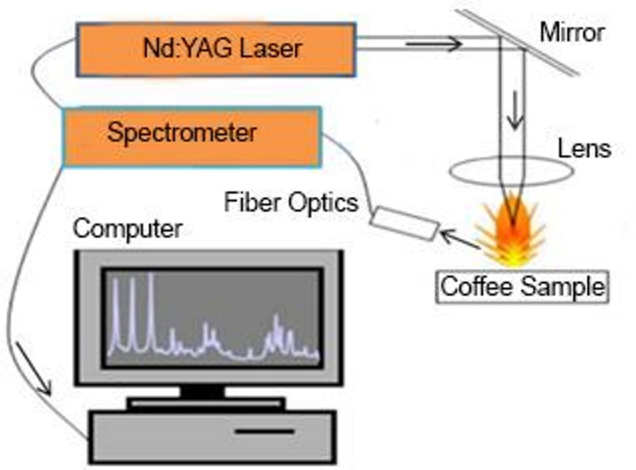


Fig. 1. Experimental Set-up.

2.3 Optimum Condition Characterization

The characterization of the optimum test conditions was carried out by determining the detection delay time and laser energy. Optimum conditions are expected to produce a low background and a high emission intensity signal. Low background indicates low density while high emission intensity indicates high element concentration. In this coffee bean sample test, the optimum conditions were determined by varying the energy of 80, 100, and 120 mJ, and delay time of 0.2, 0.5, and 1 µs.

2.4 Spectrum Evaluation

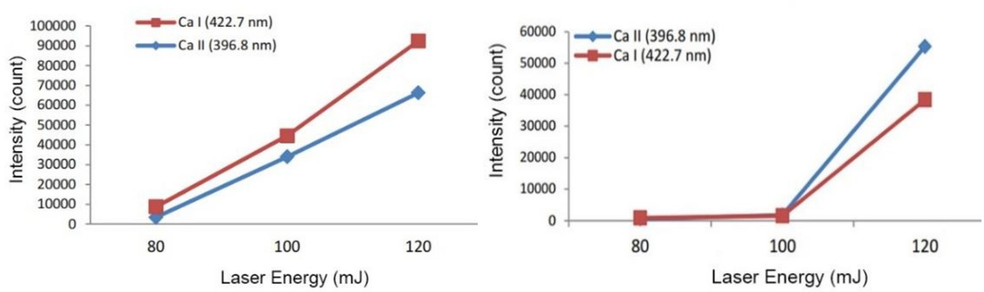
The spectral lines that have been obtained by capturing the emission from the laser plasma were then confirmed or matched with the database at the National Institute of Standards and Technology (NIST), which archives spectroscopic data and reference materials that can be accessed online. Since direct analysis of the intensity measurements of experimental results was quite difficult to obtain significant changes, different ratio of emission intensity spectra could also be used to obtain information about plasma. In this study, the ionic Ca (II) 396.8 nm line and atomic Ca (I) 422.6 nm line intensity would be compared. Some of its applications can be done by comparing the elements detected in the sample with neutral elements, as well as with the main elements. Comparison of the main elements was needed to maintain the stability of a system and to know the composition ratio between elements in the sample.

3 Result and Discussion

3.1 Optimum Condition of LIBS Emission Spectrum

3.1.1 Laser Energy

Figure 2 represent Ca (I) and Ca (II) intensities of the ordinary (Fig. 2a) and fermented GACB (Fig. 2b) for energies of 80, 100, and 120 mJ. Based on the graph, it can be seen that the laser energy of 120 mJ shows the highest emission intensity of Ca (I) and Ca (II) from the two coffees compared to the other two energies, 80 mJ and 100 mJ. This increasing intensity phenomenon occurs because the quantity of ablated materials can significantly increase due to higher laser energy [11]. Therefore, in this study the spectral identification of GACB used the optimum laser energy of 120 mJ.



(a) (b)

Fig. 2. The effect of energy variation on emission intensity of Ca (II) 396.8 nm and Ca (I) 422.7 nm in (a) ordinary and (b) fermented GACB.

3.1.2 Delay Time

Figure 3 shows the emission lines of Ca (I) and Ca (II) elements in fermented coffee samples using three variations of delay time taken from 200, 500, and 1000 ns. It can be seen that the delay time of 1000 ns has the smallest background value than the others, 500 ns and 200 ns. In the beginning of plasma formation (10 ns), the density of particles (electrons, neutral atoms, ions, and excited atoms) is very high [12]. In this stage, continuum background emissions dominate. Recombination (free-bound) and Bremsstrahlung (free-free) event are the cause of background emission. Plasma continues to expand over time. Thus, the electron density and temperature drop in the plasma (1 μs). and consequently the background signal has also decreased [13]. So based on the Figure 3, the optimum spectrum can be obtained using 1,000 ns delay time.

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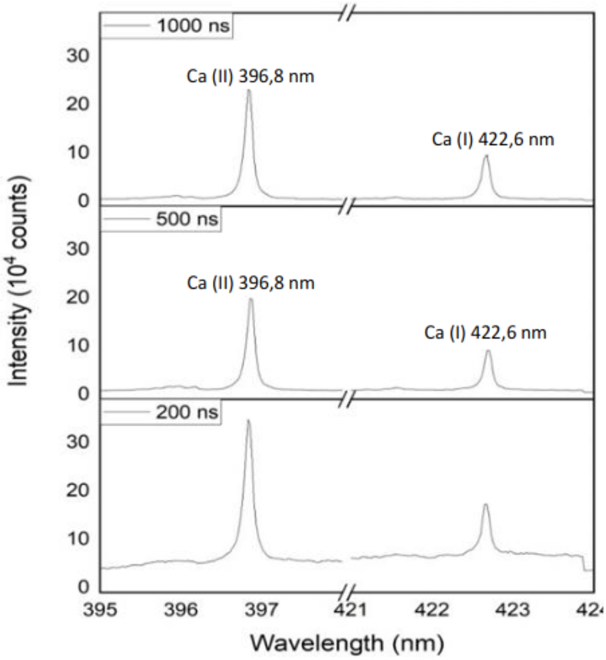
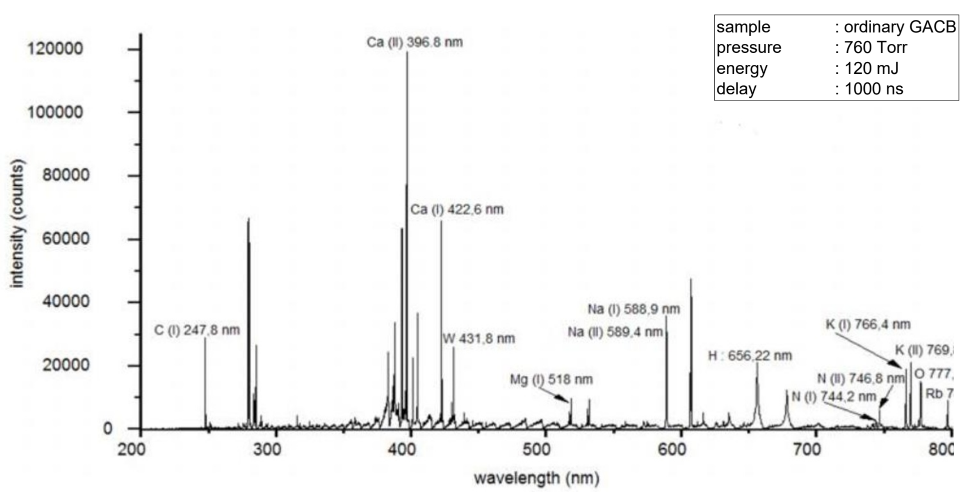


Fig. 3. Effect of delay time on spectral signal and background.

3.2 Coffee Bean Spectrum Identification

Identification on samples have been conducted and the results can be seen on Figure 4. According to that graphic, both ordinary and wine have the same constituent elements such as C, H, O, N, Ca, K, Mg, Na, and Mo which are described in detail in the Table 1.



(a)

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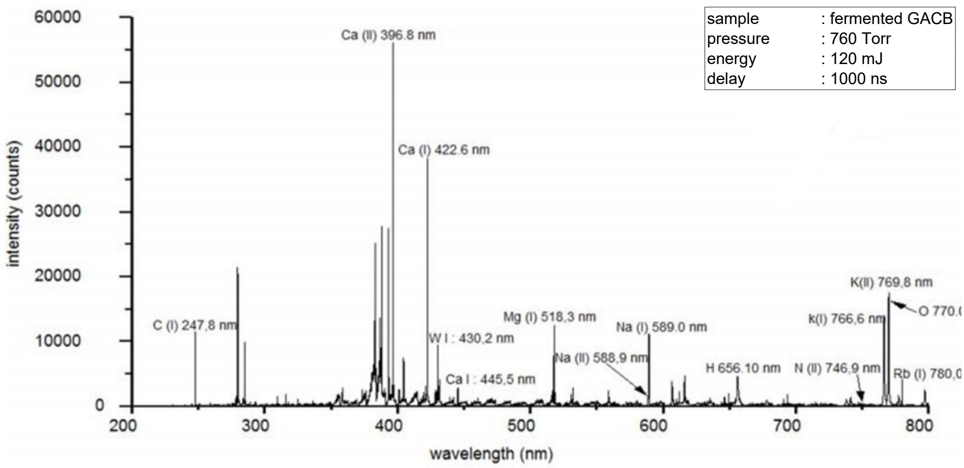

(b)

Fig. 4. LIBS characteristic spectrum of (a) ordinary and (b) fermented GACB.

Coffee beans include organic materials, therefore they were dominated by the elements C, H, N, and O [14]. Elements such as Ca, K, Mg, and Na which easily found in the environment are also detected. Mo is also detected because it belongs to minor element in coffee [15]. The existence of these elements in the coffee bean was influenced by the soil or the given post-harvest treatment [16]. Ca appears as a dominant element either in fermented or in ordinary coffee. That is indicated by the highest intensity value of Ca against other elements. Ca plays an important role in plant growth, it does not only contribute to the cell wall and membrane stability but also to the physiological processes [17]. Thus, it is true that Ca should be present in large quantity in plant organs.

Table 1. Identified elements from the peaks appeared on both ordinary and fermented GACB LIBS spectrum

Detected element	Wavelength (nm)	Detected element	Wavelength(nm)
C (I)	247.9	Mo (I)	431.8
Mg (II)	279.6	Mg (I)	518.3
Mg (II)	280.3	Na (I)	588.9
Mg (I)	285.2	Na (II)	589.4
Ca (II)	315.9	H (I)	656.2
Ca (II)	317.9	N (I)	742.4
Ca (II)	373.7	N (I)	744.2
Ca (II)	393.4	N (I)	746.8
Ca (II)	396.8	K (I)	766.4
Ca (I)	422.6	K (II)	769.8
		O (I)	777.1

Samples of ordinary and fermented GACB contain the same elements from each spectral form. The only difference is the intensity of each element of both samples. Therefore, further analysis is needed by determining the characteristics or differentiators between these two GACB samples.

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3.3 Hardness Characterization

An analysis of LIBS spectral characteristics from green beans samples of ordinary and fermented GACB has been done by comparing the intensities of the main constituents of coffee beans. The comparison is obtained using the ratio of the emission intensity of Ca (II) 396.8 nm to the emission intensity of Ca (I) 422.6 nm [18].

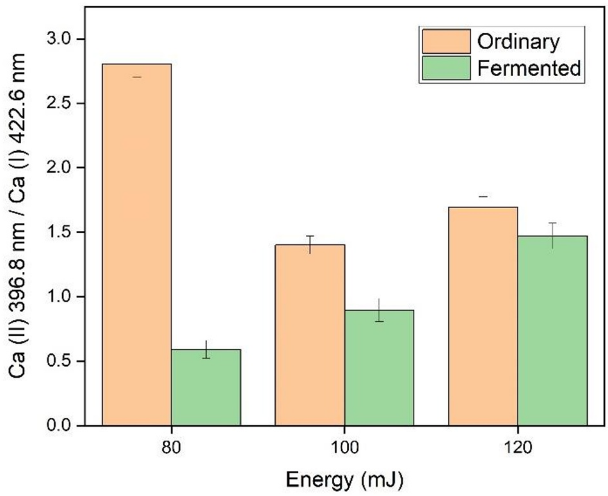

Fig. 5. Intensity ratio of Ca (II) to Ca (I) using various laser energy.

Figure 5 displayed the comparison of the average emission intensity after normalized of Ca (II) to Ca (I) in the samples of ordinary and fermented GACB. When the laser energy was 80 mJ, intensity ratio value of ordinary coffee was 2.80, while in fermented coffee it decreased to 0.59. At 100 mJ laser energy, the intensity ratio of ordinary and fermented coffee was 1.40 and 0.89, respectively. Furthermore, the intensity ratio of ordinary coffee was 1.70, while that of fermented coffee was 1.47 at a laser energy of 120 mJ. Using the three energies, the intensity ratio of ordinary coffee samples was always higher than that of fermented coffee. Thus, it could be expressed that the fermented green bean coffee was softer than the ordinary coffee. The higher the ratio of emission intensity of Ca (II) to Ca (I) elements, the greater the ionization that occurs in the plasma. Ionization caused by the high plasma temperature of the sample, results in a greater electron push as well [18]. That's what causes the emission intensity ratio of Ca (II)/ Ca (I) to determine the hardness of the sample and can be used as a marker for samples of green beans for ordinary and fermented gayo arabica coffee. This study proves that the LIBS analytical method can be used as a GACB spectral identification and to find out the hardness characteristics of different type of coffee beans.

4 Conclusion

Elemental analysis has been carried out on GACB using LIBS. The optimum LIBS spectrum occurs at 120 mJ energy laser and 1,000 ns delay time of detection. The elements such as C, H, O, N, Ca, K, Mg, Na, and Mo have been identified either in ordinary or in fermented GACB, while Ca is the most abundant element in the coffee sample. By doing the intensity ratio of Ca (II) 396.8 nm against Ca (I) 422.6 nm, the ordinary coffee samples always had higher intensity ratio than that of fermented coffee or in other words the fermented GACB is softer than the ordinary GACB.

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