Analysis of elements in Cocoa seeds (*Theobroma cacao* L.) using Laser-Induced Breakdown Spectroscopy (LIBS)

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**Abstract.** Cocoa seeds well known contains many antioxidant, thus it is really useful to human health. The elemental content of cocoa (*Theobroma cacao* L.) was examined using LIBS. The Cocoa seed was collected from Pidie Jaya Regency in the special autonomy region of Aceh, Indonesia. The examination was carried out using LIBS using an Nd-YAG laser (Q-Smart 850 model, 1064 nm, 5.5 ns, 10 Hz). The laser energy was varied from 12 mJ to 70 mJ. The tested cocoa is dried first, mashed and shaped into pellets with a radius of 3 cm and a thickness of 0.5 cm. The laser beam was focused on the pellet surface under air surrounding gas. The surrounding gas pressure was also varied. The emission spectrum was acquired for various experimental conditions. It was found in the recorded emission spectrum that many inorganic elements can clearly be detected such as Al, Mg, Mn, Ca, K, P, Fe, Cu and also main organic elements such as H, C, N, and O. The emission spectrum is dominated by the organic elements of C, H, O and N. The emission spectrum features changes with energy and surrounding gas pressure. The plasma characteristics in term of temperature and electron number density was examined. This results shows that the minor and trace elements can detected be detected clearly along with main organic element in the cocoa seeds using the emerging analytical tool of LIBS.

1. **Introduction**

The Cocoa tree is a plant from Brazil and it has been extensively used by humans since seven centuries ago. In Indonesia, chocolate was first introduced as a hot drinks at Batavia (Jakarta) since the early 18th century. Indonesia is one of the most extensive cocoa growing countries in the world. Cocoa in Indonesia is known for two types, namely flavor cocoa and bulk cocoa. Flavor cocoa was derived from criollo varieties with red fruit, and bulk cocoa (cocoa lindak) was derived from forestero varieties and trinitario with green fruit colors. Bulk cocoa is the second quality cocoa and used as a complementary ingredient. This Cocoa dominates all cocoa plantations in Indonesia. Cocoa is a source of polyphenols, so it have beneficial to human health. Therefore, cacao can be used for health purposes such as pharmaceutical raw materials. The presence of cocoa butter and polyphenols make cocoa and chocolate as functional foods [1]. Not only consists of fat, cocoa seeds also contain carbohydrates, protein, and minerals such as iron, phosphorus, potassium, chrome, magnesium,
manganese, and others. Cocoa also contains theobromine and caffeine. It is compounds that work in the nerve center in a certain amount and can be better the mood [2]. Thus, elemental analysis of cocoa is important.

LIBS is an atomic emission spectroscopy technique that uses a laser as a source of energy ablation [3]. The laser is focused on the surface of the sample. So, a portion of the sample will be excited and formed plasma. The plasma contains electrons, neutral atoms, ions and excited atoms. These excited atoms cause electrons to return to the ground state while emitted photon emissions. When the electrons in an excited atom descend to a ground state, they release energy in the form of photons and captured by a spectrometer, which is displayed in the intensity of the wavelength function [4,5]. Since LIBS was discovered in around 1962, LIBS offers several advantages compared other conventional techniques such as multi-element measurement, real-time data, little or no sample preparation, cost effectiveness, small sampling requirements, and quick and easy in situ methods [6,8]. Thus, it has found applications to many fields including direct elemental analysis of food materials such as cocoa seeds [9]. Present work is a first step of our work for a detailed elemental study of cocoa seeds from different origins in Indonesia.

2. Method
The experimental setup used in this work illustrated in Fig. 1. The experimental works was conducted in Laser Laboratory of the Center for Physics Research (P2F) at the Indonesian Institute of Sciences (LIPI) PUSPIPTEK Serpong, South Tangerang. Main LIBS system used consist of an Nd-YAG Laser (Q-Smart 850 model) and a compact spectrometer (MAYA 2000 PRO). The laser beam of fundamental wavelength of 1064 nm with a pulsed duration of 5.5 ns and a repetition rate of 10 Hz was focused using a positive lens (f =+15 cm) onto the surface of the tested sample. The emission from the consequent plasma then was delivered by an optical fiber to the spectrometer for spectrum acquisition.

![Image](image_url)

**Figure 1.** LIBS setup used in this work.

The cocoa seeds sample was taken from Pidie Jaya Regency, Aceh, Indonesia. Pidie Jaya Regency is a well-known region producing cocoa in Aceh. There is also some small scale industry for processing cocoa producing several cocoa based products. For this experiment, the cocoa seeds samples were dried openly under sunlight. The samples then were further dried using an oven at temperature of 40°C for 30 minutes. The cocoa seeds were grinded into fine powder. The fine powder was pressed into pellet with a pressure of 487.85 bar for 5 to 10 minutes. The dimension of the pellets
is 3 cm in diameter and 0.5 cm in thickness, respectively. The emission spectra were displayed using software of OriginPro 8.5.

3. Results and Discussion

Figure 2 shows a photograph of plasma produced on cocoa seeds in the form of pellet. It can be seen strong, luminous plasma can be generated on the cocoa seeds pellet upon focused laser irradiation. Thus, it is expected the cocoa seeds is excited well, resulting into strong plasma emission. Emission spectrum was taken from the cocoa seeds sample under different experimental conditions in term of energy and surrounding gas. Three cases of the laser pulse energy was adopted, namely namely 12 mJ, 45 mJ and 70 mJ. The plasma was produced under air surrounding at pressure of 10 Torr, 20 Torr, 30 Torr, and 40 Torr, respectively. As the results, Figure 3 shows spectrum taken from the cocoa seeds sample using the pulse energy of 70 mJ and the pressure of the surrounding gas at 40 Torr, for wavelength regions of (a) 340 nm-500 nm and (b) 500 nm-700 nm. Figure 4 displays spectrum taken under the same experimental condition in wavelength range of 700 nm-900 nm, consecutively. It can be seen in the three spectra, Figure 3 and Figure 4, many emission lines due to constituent of cocoa seeds detected, ranging from host element of organics (C, H, O, N) and other minor and trace. The spectra show that main carbon emission line in the ultraviolet region, namely C I 247.8 nm, cannot be detected because it is out of coverage of spectrometer used in this study. However, other lines of carbon can be found in the emission spectrum. Although the background level is very high for the emission spectrum in the wavelength range from 340 nm-500 nm, however the emission lines can be identified. Appearance of the emission lines due to Mg, Fe, O, C, P, H and N in the wavelength is confirmed. The background level of the emission spectrum in the wavelength regions of 500 nm-700 nm, Figure 3(b), and 700 nm-900 nm, Figure 4, is relatively low, especially compared to the wavelength region of 340 nm-500 nm, Figure 3(a). Thus, the quality of the spectrum is much better. The emission lines due to several elements including major, minor and trace occur in the wavelength range is confirmed. The background emission is mainly due to inverse bremsstrahlung (free–free) and recombination (free–bound) transition process. This process occurs strongly at the beginning of the plasma formation and also at later of plasma formation in case of a high temperature and high density plasma.

The LIBS spectra above readily shows that cocoa bean samples contain elements of Mg, K, P, Fe, and Cu and of course the main organic elements namely H, C, N, and O. The features of the emission spectrum basically can be improved. The characteristics of the formed plasma depends on many parameters of the experiment including characteristics of laser source, sample, surrounding gas and optical detector. It is well known that the features of the emission spectrum in terms of occurrence of specific lines, intensity, background and spectral width depend on the characteristics of the produced plasma. Therefore, in this study the characteristics of the produced plasma will be studied further.
Figure 3. Spectrum detected from the cocoa seeds plasma in a wavelength of (a) 340 nm-500 nm and (b) 500 nm-700 nm. The emission spectrum was taken when the Nd-YAG laser of 70 mJ was focused on cocoa seeds pellet under air atmosphere at a pressure of 40 Torr.

Figure 4. Spectrum detected from the cocoa seeds plasma in a wavelength of 700 nm-900 nm.
4. Conclusion
LIBS was successfully used to detect the atomic content of cocoa seeds (*Theobroma cacao* L.). The optimum experimental condition should be search for obtaining better features of LIBS spectra from cocoa beans. This technique is very practical, cocoa samples do not need complicated preparation, involving environmentally unfriendly chemical reagents. The analysis of cocoa seeds can be made simultaneously in a short time. The results showed that content of cocoa seeds were dominated by the organic elements C, H, O, N followed by several salts and metal.

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