Emission Spectral Profile of Salt in Laser-Induced Breakdown Spectroscopy (LIBS) on River Clamshell Sample

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Abstract. Since the river clamshell is commonly used as one of the raw materials for making lime betel widely consumed, inspection of its salt content is very important. This work is to study the profile of salt emission spectrum from the river clamshell sample in laser-induced breakdown spectroscopy (LIBS). The observation of the general emission profile is possible thanks to the availability of the optical multichannel analyzer (OMA) system with a wide wavelength coverage from 200 nm-950 nm. LIBS apparatus used in this work consist of Nd-YAG (neodymium-doped yttrium aluminum garnet) laser and an OMA system equipped with an echelle spectrograph system. The river clamshell samples were collected from Panga River, Panga, Aceh Jaya, Aceh, Indonesia. The Panga river up streams to mountain of Gunong Ujeun, used to an intensive traditional mining location. The plasma generation was made by focusing the Nd-YAG laser beam on the clamshell sample under air surrounding gas at atmospheric pressure. There are two kinds of sample used, namely fresh sample without any treatment and pelletized sample. The result shows the emission spectrum in general consist of a large number of Ca emission lines, both atomic and ionic lines. However, several other salt emission lines such as Mg, Na, K, and Al also can be clearly observed at various wavelengths. This result suggests the emission spectrum of salt detected from the river clam sample are predominantly dominated by Ca emission lines.

1. Introduction
The river clamshell normally contains salt elements at a natural level of concentration which safe for eating. The salt concentration may change due to changes of the environment surrounding the clamshell. The changes of the salt concentration in the river can be caused by natural factors or human activities. The clamshell living on the riverbed causes it to easily be impacted by mineral decomposition in the river. The other, the clamshell got food by sucking river water reinforcing the notion that they are vulnerable to be affected by their environment. The composition or structure varies of clamshell developed as the habitat change [1]. Therefore, the clamshell can be a natural history recorder of environmental events throughout its lifetime [2]. One of those is such pollution [3].
Betel lime, made from the river clamshell, has been widely used in foods and medicines in Aceh, Indonesia. Basically, mineral (salt element) such as Ca, Na, and Mg is several nutrients that play an important role in the maintenance of body functions. Mineral deficiency can cause health problems such as anemia, mumps, osteoporosis and osteomalacia [4]. On the other hand, one of the main factors increasing cardiovascular and blood pressure diseases is consuming excessively the salts. Cardiovascular is noted as one of the leading causes of death and disability worldwide [5]. Those facts cause the salt in the river clamshell being important to be studied as valuable further information to the community especially in Aceh.

Currently, there are many analytical techniques used to identify the content of salt in materials such as electrical conductivity (EC) and atomic absorption spectrophotometry (AAS). Those techniques are generally a chemical technique requiring strong acids in the process [6]. Laser-induced breakdown spectroscopy (LIBS) is a type of the atomic emission spectroscopy involving the production of hot plasma by laser ablation and excitation of the atoms present in studied sample [7]. Nowadays, LIBS is considered as a versatile tool for direct elemental analysis of solids. It offers several advantages compared to other conventional techniques such as multi-element measurements, the data in real time, little or no sample preparation, cost effectiveness, small sampling requirements, and in situ methods which fast and easy [8,9,10]. On the other hand, this technique is capable for analysing spectrochemically various sample in any phases including solid, liquid and gas. A TEA CO2 LIBS utilizing a unique subtarget effect was used for detection and identification of salt emission lines in soils samples. There are several emission lines of salt detected clearly such as Ca II 393.36 nm, Ca II 396.84 nm and Ca I 422.67 nm. Other salt emission lines that have detected are Na and Mg [11]. Thus, LIBS technique in general is spectrochemical analytical technique that has many unique advantages compared other conventional techniques [12]. Several studies of shells has conducted as well such as used LIBS for studying seashell analysed by an assistant process called graphite enrichment [13], showed potentially LIBS in mapping of element distribution in the shell [14], and analysed shells using LIBS for in situ identification [15].

Previously, a preliminary study of the muscle of the river clam using Nd-YAG LIBS has conducted. The study examined general features of the emission spectrum of plasma detected from the muscle of the river clam, finding emission lines due to the organic elements such as Carbon (C), Hydrogen (H), Oxygen (O), and Nitrogen (N) mainly dominated the emission spectrum [16]. Also known that the harder the shell is used, the more calcium oxide content in which CaO is obtained from the calcination process of clamshell containing CaCo3 [17]. Further study has been performed for characterizing the physical properties in term of temperature and electron density of the plasma produced on the river clam muscle. The result shows temperature and electron density of the plasma are well above the Maxwell and McWhirter criteria [18]. This work is to evaluate in general the profile of the salt emission spectrum detected from plasma produced on the river clamshell sample using the Nd-YAG LIBS.

2. Experimental Procedure

The LIBS equipment used in this present work consists of a Nd-YAG laser (Quanta Ray, LAB SERIES, 1,064 nm) and an optical multichannel analyzer (OMA) system (Andor Mechelle ME5000) equipped with an echelle spectrograph and a iStar intensified charge coupled device (ICCD) camera. The OMA system covers a wide wavelength region, ranging from 200 nm to 975 nm for each acquisition. The basic LIBS equipment arrangement used in this work is shown in Figure 1. The laser pulse energy was reduced using a set of filters and fixed at 60 mJ. The plasma was produced by focusing the laser beam on the sample by a convex lens of 150 mm focal length. The sample was placed on the sample holder in the sample chamber. The environment of the plasma generation chamber was air at various pressure variations, starting from 5Torr to 760 Torr. The surrounding gas pressure was controlled by means of a vacuum pump.

The river clamshell samples used in the present study were collected from Panga River, Panga District, Aceh Jaya Regency, Aceh, Indonesia. The upstream of the Panga River is in mountain of
Gunong Ujeun located also in Aceh Jaya regency and it is a location of the traditional gold mining activities. The activities was used to very intensity, however it now reduces at a much smaller scale. The river clamshell samples are prepared in two conditions, namely in fresh condition without any chemical and physical treatment and pelletized form. For fresh condition, the clamshell was cut into slides with a dimension of 25 mm x 25 mm. While the pelletized samples, the river clamshell was crushed using a hammer into small parts and further into finer powder sizes using mortar and pestle. The fine powder was sieved and then was made into pellet form using a hydraulic press machine at a pressure of 30 MPa.

The Nd-YAG laser beam was focused the sample surface for plasma generation. The clamshell plasma emission was collected using an optical fiber and forwarded to the OMA system input section (Mechelle ME5000). The OMA system was run using Andor iStar software. The detected emission spectrum is displayed on a computer monitor. The time delay and pulse duration of the OMA system was fixed at 100 ns and 50 µs, respectively. The emission spectra obtained were identified and confirmed using an atomic spectrum database from the United States National Institute of Standards and Technology (NIST) [19-20] providing spectroscopic data of spectral emission lines for various elements.

![Figure 1 Schematic diagram of the LIBS experimental setup](image)

3. Results and Discussion

Figure 2 shows the emission spectrum detected from plasma produced when the Nd-YAG laser beam of 60mJ was focused on the slice of the fresh river clamshell sample under air as the surrounding gas at a high pressure of 760 Torr. The OMA system covers wide wavelength region, ranging from 200 nm to 950 nm. Although the plasma generation was made under air as the surrounding gas at atmospheric pressure, thus the back emission intensity is relatively high, however the emission lines in the spectrum can be clearly identified. It can be clearly seen there are many atomic and ionic emission lines due to calcium appearing at various wavelength in the spectrum. The emission intensity of the calcium emission lines is very strong, especially the ionic calcium emission lines of Ca II 393.36 nm and Ca II 396.85 nm. This is because the clamshell mainly consists of calcium carbonate (CaCO₃) as host. It is well known that Ca is relatively easily ionized due to low ionization energy. Along with the calcium emission lines, atomic and ionic emission lines due to other salts also appear clearly at various wavelength including magnesium (Mg), sodium (Na) and potassium (K).

In addition to the emission lines from salts, emission lines due to metals also occur, namely ferrum (Fe) and aluminum (Al), probably the river clamshell also contains the metals. However, it is not clear whether it comes from natural sources or anthropogenic origins and this now is under investigation and will be reported elsewhere in near future. Emission lines due to organic elements also arise in the wide ranging emission spectrum, namely carbon (C), hydrogen (H), nitrogen (N), and oxygen (O). Aside from host elements of C and O of calcium carbonate, it is considered that as biological samples the river clamshell sample also definitely contains organic elements at some extent, resulting in the observed emission lines of C, H, O, and N, namely CI 247. 86 nm, Hα 656.28 nm, OI 777.19 nm, OI 777.42 nm, OI 777.54 nm and NI 818.80 nm, NI 821.63 nm, NI 822.31 nm, NI 824.24 nm. Although the emission
intensity due to the organics elements are superficially seems very low, however the emission intensities are relatively high.

**Figure 2** Emission spectrum detected from plasma induced after focusing the Nd-YAG laser beam of 60 mJ on the fresh river clamshell sample under air surrounding gas at a high pressure of 760 Torr.

**Figure 3** Emission spectrum detected from plasma produced after irradiation the focused Nd-YAG laser beam of 60 mJ on the pelletized river clamshell sample under air surrounding gas at a high pressure of 760 Torr.

Figure 3 shows the emission spectrum taken when the clamshell was made in the form pellet under the same experimental conditions. It can be seen that the feature of the emission spectrum especially in term of the number emission lines and the wavelength region of its appearance are the same with the case of the fresh sample, namely there are many emission lines due to Ca distributed over wide ranging region, from 300 nm to 650 nm. The emission intensity of the calcium emission lines are also very strong, particularly the calcium ionic lines. In general the emission intensity of the emission lines
dramatically increased in comparison with the fresh sample case. It is considered that in case of pellet sample, the density of sample increases thus increasing largely the vaporized amount, resulting in remarkably strong emission intensity, about 11 times higher than in case of the fresh sample. Since the emission spectrum features are basically the same in the two cases, and the only difference is its intensity, thus for identification the emission lines in detail, several part of the spectrum of the fresh sample was enlarged as shown in the following figures.

Figure 4 The enlarged spectral emission lines of the emission spectrum detected from the plasma produced on the fresh clamshell (Figure 2) for ultraviolet wavelength region, starting from 220 nm to 410 nm.
Figure 5 The enlarged spectral emission lines of the emission spectrum detected from the plasma produced on the fresh clamshell (Figure 2) for visible and infrared wavelength regions, starting from 410 nm to 800 nm.
Figure 4 and Figure 5 show the enlarged spectrum detected from the plasma produced from the fresh river clamshell from ultraviolet to infrared regions. The emission lines were identified and confirmed using NIST atomic spectrum database [11-12]. It can clearly be observed many calcium emission lines appearing in ultraviolet, visible and infrared regions. The calcium emission lines including atomic (Ca I) and ionic (Ca II) emission lines appear almost throughout of the emission spectrum. Thus, by this closer view, it seems almost every high peak of the spectrum is dominated by Ca. The ionic emission lines of Ca II generally appears at the wavelength region below 400 nm, whereas the atomic emission lines of Ca I occurs at wavelength region upper 400 nm. As mentioned above the dominance of Ca emission lines is very reasonable, since the clamshell mainly contains is CaCO$_3$, yielding to predominant appearance of Ca emission lines at many wavelength with high intensity in the enlarged emission spectrum. Although it did not appear at many wavelengths in the spectrum, the other salt emission lines such as Mg I, Mg II, Na I, K I, and Al II also appear with relatively strong intensity. These clearly show that the river clamshell contains many salt including Ca, Mg, Na, K and Al.

The profiles of emission spectrum detected from the plasma produced on the fresh river clamshell samples at atmospheric pressure of 760 Torr shows the emission spectrum mostly consists of Ca emission lines together with much fewer lines of other salts of Mg, Na, K, and Al and the background emission intensity is relatively high. It is well known that the emission features especially in term of the background emission are significantly improved. Thus, the profile of the emission spectrum was also studied at under a low pressure of 5 Torr. Owning it is very possible to be used at the normal conditions without having to regulate air pressure at certain level. Beside of 760 Torr pressure, this research was also conducted at low pressure, namely 5 Torr. Figure 6 shows the emission spectra detected form the plasma produced on the fresh clamshell sample by focusing the Nd-YAG laser beam of 60 mJ under air at low pressure of 5 Torr. As it can be seen, at low pressure, the emission intensity of the emission lines is far higher than that in case at 760 Torr. There are also many emission lines appearing within high intensity. That is can be seen at wavelength ranges of 350 nm – 450 nm. It can be seen more clearly by enlarging the wavelength scale as shown in Figure 7 and Figure 8.
Figure 7 The enlarged spectral emission lines of the emission spectrum detected from the plasma produced on the fresh clamshell (Figure 6) for various wavelength regions, starting from 220 nm to 600 nm.
Figure 8 The enlarged spectral emission lines of the emission spectrum detected from the plasma produced on the fresh clamshell (Figure 6) for red and infrared regions, starting from 600 nm to 800 nm.

Figure 7 and Figure 8 shows the enlarged spectral emission lines of the emission spectrum detected from the plasma produced on the fresh clamshell (Figure 6) under air surrounding gas at a pressure of 5 Torr. The general profile of the emission spectrum is similar; however, the emission intensity is far larger in case of low pressure. Moreover, the background emission intensity is very low in low-pressure case. The summary of the observed emission lines is tabulate in Table 1.

| Salt Elements | Wavelength (nm) | Lower Level | Upper Level |
|---------------|----------------|-------------|-------------|
| Ca I          | 422.67         | 3p6 4s2     | 3p6 4s4p    |
| Ca I          | 428.30         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 428.93         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 429.89         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 430.25         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 430.77         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 431.86         | 3p6 4s 4p   | 3p6 4p2     |
| Ca I          | 442.54         | 3p6 4s 4p   | 3p6 4s 4d   |
| Ca I          | 443.56         | 3p6 4s 4p   | 3p6 4s 4d   |
| Ca I          | 445.48         | 3p6 4s 4p   | 3p6 4s 4d   |
| Ca I          | 518.88         | 3p6 4s 4p   | 3p6 4s 5d   |
| Ca I          | 526.22         | 3p6 3d 4s   | 3p6 4s 4p   |
| Ca I          | 526.56         | 3p6 3d 4s   | 3p6 4s 4d   |
| Ca I          | 527.03         | 3p6 3d 4s   | 3p6 4s 4d   |
| Ca I          | 558.78         | 3p6 3d 4s   | 3p6 4s 4d   |
| Ca I          | 559.45         | 3p6 3d 4s   | 3p6 4s 4d   |
| Ca I          | 559.85         | 3p6 3d 4s   | 3p6 4s 4d   |
| Ca I          | 610.27         | 3p6 4s 4p   | 3p6 4s 5s   |
| Ca I          | 612.23         | 3p6 4s 4p   | 3p6 4s 4d   |
| Ca I          | 616.20         | 3p6 3d 4s   | 3p6 3d 4d   |
| Ca I          | 643.91         | 3p6 3d 4s   | 3p6 3d 4p   |
| Ca I          | 646.26         | 3p6 3d 4s   | 3p6 3d 4p   |

| Salt Elements | Wavelength (nm) | Lower Level | Upper Level |
|---------------|----------------|-------------|-------------|
| Ca I          | 649.38         | 3p6 3d 4s   | 3p6 3d 4p   |
| Ca I          | 315.89         | 3p6 4p      | 3p6 4d      |
| Ca I          | 317.93         | 3p6 4p      | 3p6 4d      |
| Ca I          | 370.60         | 3p6 4p      | 3p6 5s      |
| Ca I          | 373.70         | 3p6 4p      | 3p6 5s      |
| Ca I          | 393.36         | 3p6 4s      | 3p6 4s      |
| Ca I          | 396.85         | 3p6 4s      | 3p6 4s      |
| Mg I          | 285.21         | 2p6 3s2     | 3s 3p       |
| Mg I          | 516.73         | 3s 3p       | 3s 4s       |
| Mg I          | 517.27         | 3s 3p       | 3s 4s       |
| Mg I          | 518.36         | 3s 3p       | 3s 4s       |
| Mg I          | 279.55         | 2p6 3s      | 2p6 3p      |
| Mg I          | 279.80         | 2p6 3p      | 3p6 3d      |
| Mg I          | 280.27         | 2p6 3s      | 2p6 3p      |
| Na I          | 588.99         | 2p6 3s      | 2p6 3p      |
| Na I          | 589.59         | 3p6 3s      | 2p6 3p      |
| Na I          | 309.28         | 2s2 2p6 3s  | 2s2 2p6 3p  |
| K I           | 766.64         | 3p6 4s      | 3p6 4p      |
| K I           | 770.06         | 3p6 4s      | 3p6 4p      |
| Al II         | 394.40         | 3s2 3p      | 3s2 4s      |
| Al II         | 396.15         | 3s2 3p      | 3s2 4s      |
4. Conclusion
A strong plasma can be induced from the river clam sample using the Nd-YAG laser beam under air surrounding gas both a higher pressure of 760 Torr or a lower pressure of 5 Torr. The plasma emission generated at lower pressure yield to a far higher emission intensity and lower background emission intensity in comparison with the case of high pressure. Either under low pressure surrounding gas or high pressure surrounding gas, the emission spectrums are predominantly dominated by the calcium emission lines including atomic and ionic emission lines. This is explained by the fact that the river calm shell mainly contains calcium carbonate (CaCO$_3$) as host. Along with the calcium emission lines, other salts such as magnesium (Mg), sodium (Na), potassium (K), and aluminum (Al) also clearly appeared. In addition, emission lines due to ferrum (Fe), carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). The emission profile obtained promises a possibility for carrying out qualitative and quantitative analysis.

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