Estimation of temperature and electron density of laser-induced breakdown spectroscopy (LIBS) on river clam shell using hydrogen emission lines

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Abstract. The physical characteristic in term of temperature and electron density of the laser-induced plasma produced on a river shell sample has been investigated. The plasma was produced by an Nd: YAG laser beam (1064 nm) at low pressure (5 Torr) of air surrounding gas. Multi-elemental panoramic line spectra (200-900 nm) have been analysed at different delay times (0.1-5 µs) and gate width of 50 µs. The hydrogen emission lines namely Hα at 656.27, Hβ at 486.13 and Hγ at 434.04 nm were identified and utilized to evaluate the plasma parameters. The temperature and electron density of the produced plasma were estimated by means of Boltzmann Plot and Saha-Boltzmann method using the hydrogen emission lines. The result shows that the plasma temperature and electron density vary from about 5633 K to 8810 K and 3.7 x 10²⁰ cm⁻³ to 9.7 x 10²⁰ cm⁻³, respectively. The temperature and electron density of the plasma produced on the river shell sample conform the Maxwell distribution and Me Whriter criteria for the laser induced plasma in local thermal equilibrium (LTE) condition.

1. Introduction
Waste of gold processing that flows into the river will cause pollution to the biota in the river. A River clam is one potential candidate sample for tracing pollution in a river because the species live sessile on the river bottom, obtaining food from surrounding organic matter. If the river polluted by heavy metal, it possibly causes an accumulation of the heavy metals in the clam organs, such as in muscle or shell. Accumulation in the muscle occurs due to feeding mechanism, while accumulation in the shell occurs is not only due to feeding mechanism but it is also possibly due to the absorption process since the shell is made mainly from porous media of calcium carbonate (CaCO₃). Therefore, in order to trace the possibility of heavy metal pollution in the river, it is important to study the clam shell sample.

Laser-induced breakdown spectroscopy (LIBS) technique is much more versatile than conventional methods and is ideal for on site analysis. LIBS is an emerging technique for determining elemental composition in real-time and able to analyse and identify materials in solids, liquids, and gas forms with little or no sample preparation. This technique is based on the analysis of the emission spectral lines of the elements present in the sample by focusing high power laser beam on the sample [1-2].
The performance of LIBS techniques is influenced significantly by characteristics of the plasma generated. The plasma characteristics are complex dependent on many parameters including the laser properties used as the excitation source, the experimental conditions, and the sample kind. Actually, the application of LIBS technique to a given sample generally starts with the observation and understanding of plasma characteristics and then identification and confirmation of the spectral emission line and finally making quantitative analysis. As mentioned above, the river clam sample is one possible sample that can be used for detecting pollution in the surrounding environment. However, the physical characteristic of the plasma produced on the river clamshell sample are not understood well yet. In previous work, it has been conducted a preliminary panoramic study of the profile of the plasma emission spectrum on the muscle part of the river clam sample. The obtained emission spectra are largely dominated by emission lines due to organic element such as carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) [3].

Therefore, in this work we studied the physical characteristic of the plasma produced on the river shell sample in term of temperature and electron density. The clam sample taken from Panga River, Aceh Jaya Regency, Aceh, Indonesia, a location where the traditional gold mining activities was intensively carried out. On the other hand, LIBS techniques have been used to analyse the physical characteristics of plasma in the clam muscle by means of Boltzmann plot and Saha Boltzmann method using Fe emission lines. The result shows that the temperature and electron density of the plasma is about 4211 K and 4.67 x 10^15, respectively [4]. The plasma temperature and electron density are important thermodynamic properties due to their ability to describe and predict the ionization state of the plasma and the complex processes of the plasma generation [5-6]. On the other hand, hydrogen emission lines was used for estimating temperature of plasma produced on water sample using a Nd:YAG laser at wavelength of 1064 nm. The plasma temperature was determined from the Boltzmann Plot of H_α at 656.27, H_β at 486.13 and H_γ at 434.04 nm emission lines and were found about 7550 K [7]. The energy level of hydrogen emission lines are spaced well, resulting in better estimation of the plasma temperature. Thus, the hydrogen emission lines are used for estimating the temperature and electron density of the plasma produced on the river clam shell sample. Actually, there are several methods can be used to estimate the plasma temperature using spectral emission lines, such as Boltzman Plot, Saha-Boltzmann, line-to-continuum, syntetic spectra method [8]. Therefore in this study, estimation of the plasma temperature is conducted by means of Boltzmann plot method as expressed in the following equations (1) [1-2]. Boltzmann plot method has been used in many works to determine plasma temperature [4,9-10].

\[
\ln \left( \frac{l_\lambda k Z}{g_{k Z} \lambda k Z} \right) = - \frac{1}{k_B T} E_{k Z} + \ln \left( \frac{\hbar c \lambda n Z}{4 \pi P} \right)
\]

where in \( I_\lambda \) is the intensity of the ionization state \( Z, \lambda \) is wavelength, \( g_k \) is the degeneration of the upper energy level \( k \), \( A_{kZ} \) is the transition probability, \( k_B \) is the Boltzmann constant, \( T \) is the plasma temperature, \( E_k \) is the upper level energy \( k \), \( h \) is Planck’s constant, \( c \) the speed of light, and \( L \) is the characteristic length of the plasma, \( n Z \) and \( P \) are the density and function of the partition of the species, respectively.

The plasma temperature is obtained from the slope of the Boltzmann plot curve. While the electron density of the plasma is measured using Saha-Boltzmann method [4,11-12] using the following Saha-Boltzmann equations [1-2].

\[
N_e = 6.04 \times 10^{21} (T)^{3/2} \left( \frac{l_\lambda}{g_{A_i} \lambda_{i A}} \right) \times \exp \left( - \frac{(V_{i A} - E_{i A})}{T} \right)
\]

\( N_e \) is electron density, \( A_i \) is subscript for neutral atom, \( i \) is subscript for ionized atom, \( E_i \) and \( E_{A_i} \) the energy levels of neutral atoms and ionic transitions, respectively. \( V \) is ionization energy of neutral atoms (eV).

The obtained data is evaluated to know fulfilment of local thermal equilibrium (LTE) condition using temperature and electron density. The temperature and electron density shows that the plasma in the
2. Experimental Procedure

The experimental set-up used in the present measurement is basically similar to that used in the previous studies [3-4]. Laser-induced plasma produced using a Nd:YAG laser (Quanta Ray, LAB SERIES) delivering 8 ns laser pulses at λ=1064 nm, maximum pulse energy of 500 mJ with adjustable repetition rate up to 10 Hz. The plasma emission was collected and transmitted through an optical fibers to OMA system. The accuracy of the OMA system is better than ± 0.05 nm, and it is equipped with an eschelle spectrograph and intensified charged couple device (ICCD) detector (Andor Mechelle ME5000). The laser beam was focused using a lens with a focal length of f =+150 mm onto the surface of the sample in a metal circular chamber.

In this study, the river clam shell is analyzed in fresh and pellet conditions. The river clam was taken from Panga river, Aceh Jaya regency, Aceh, Indonesia, where at the location once intensive traditional gold mining activities was made and still continues till now of a smaller scale. The river clamshell in fresh condition was cut into slices with dimension of 25 mm x 25 mm. The thickness of the fresh shell is about 2 mm. While sample in pellet form is prepared as follow. After three days of drying, the sample futher were crushed into powder and pressed into pellet with dimension 1 cm x 1 cm and 4 mm thick by a hydraulic press machine under pressure of 30 atmosphere.

In this work, the plasma emission generated by focusing Nd:YAG laser beam of 60 mJ under air surrounding gas at low pressure of 5 Torr at gate width of 50 µs with different delay times (0.1-5 µs). Optical fiber probe is used to collect the emission of produced plasma then carrying out into the entrance slit of the spectrograph of the OMA system. One end of optical fiber is placed at a distance about 5 cm from centre of plasma and the other end side is connected to the spectrograph of the OMA system. OMA system is run using AndoriStar software and detected emission spectrum is displayed on the computer screen. The emission spectrum obtained was identified and confirmed using the National Institute of Standards and Technology (NIST) atomic spectra database [13]. Spectroscopic data for the emission line was taken from the reference data base. The intensity of the hydrogen emission line the obtained from the measured spectrum was used for estimation of the plasma temperature and electron density. Plasma temperature was measured using equations (1), while the electron density measurement was estimated using equations (2).

3. Results and Discussion

In this study, the plasma was generated from river clam shell in fresh and pellet conditions. Figure 1 shows the emission spectrum detected from plasma generated from river clam shell in fresh condition using laser pulse energy of 60 mJ under air surrounding gas at low pressure of 5 Torr. The plasma emission are acquired with a delay time 100 ns and gate width of 50 µs. NIST atomic spectra database is used to identify the spectrum emission lines [13]. The emission lines of Calcium (Ca), Natrium (Na), Magnesium (Mg), Ferrum (Fe), Carbon (C), Oxygen (O) and Hydrogen (H) elements have been identified with strong emission lines, some strong lines for each element were also labelled by their chemical symbols. Based on Figure 1, it can be seen that the emission spectra is dominated by Ca emission lines. This is due to host element of the river clam shell is calisum carbonate (CaCO3). In addition to Ca emission line appears with very strong intensity, hydrogen emission line also appear with strong intensity so that can be seen clearly, especially Hα as shown in Figure 1. This can be understand due to the shell sample in fresh condition still contains a lot of water. In order to examine whether the river clam shell in pellet conditions contain hydrogen emission line or not, the similar experiment was conducted for pellet sample.
Figure 1 Emission spectrum of the fresh river clam shell by focusing Nd:YAG laser beam of 60 mJ under air surrounding gas at low pressure (5 Torr). The plasma emission was acquired with a delay time 100 ns, and gate width of 50 µs of the OMA system.

Figure 2 Emission spectrum of the plasma produced on the pelletized river clam shell under the same experimental parameters as in Figure 1

Figure 2 shows the emission spectrum detected from the plasma was generated from the pellet shell sample with same experimental parameters as in the fresh shell sample. Generally the profile of the emission spectrum detected from plasma produced on the pelletized clam shell sample are relatively similar to the fresh sample, namely dominated by Ca emission lines. However, in case of the pellet shell sample, the overall emission intensity increased drastically, especially for salt emission. This is due to increment of vaporized atoms as compared in the case of fresh sample. Although the profile is relatively similar, however the hydrogen emission line in this case decreased in intensity compared to the fresh
shell condition. This is because the pellet shell sample has been dried thus the water content reduced. Nevertheless, the intensity of hydrogen emission line is still clearly observed. Therefore hydrogen emission lines is good candidate of analytical lines used for estimating the plasma temperature due to its concurrent appearance in the wide coverage spectrum, well-spaced upper levels, relative high strength compared with other emission lines.

In order to confirm the hydrogen lines $H_\alpha$, $H_\beta$ and $H_\gamma$ for the two conditions, the spectrum has been especially expanded in this region. The strong $H_\alpha$ emission line at a wavelength of 656.27 nm in the red region, $H_\beta$ emission line at wavelength of 486.13 nm in the blue region and $H_\gamma$ emission line at a wavelength of 434.04 nm in the violet region can clearly be found. Thus, it can be confirmed firmly that all three lines of the hydrogen emission lines can be detected clearly, even though hydrogen is actually not major element in this sample. As mentioned above, this sample is mainly composed of calcium carbonate (CaCO$_3$). However, this sample as a biological sample inherently contains the main organics element including hydrogen and nitrogen at a certain level of concentration either as minor or trace elements. This results is very interesting since in previous studies, it was found that it is difficult to detect hydrogen as an impurity in solid samples using LIBS technique due to mismatching effect and detection was made with improved strategies [13-16]. Figure 3 shows the emission spectrum detected from plasma produced on the river clam shell as displayed in Figure 1 and Figure 2, specifically enlarged on the wavelength of the hydrogen emission lines of $H_\alpha$, $H_\beta$ and $H_\gamma$. As shown in Figure 3 the intensity of each hydrogen emission lines is strong, in particular $H_\alpha$ and $H_\beta$ emission lines show very strong emission intensities. In addition, based on Figure 3, the profile of the emission line from the fresh sample and the pelletized sample is relative similar, however the intensity of hydrogen emission lines from the fresh sample is higher than that of the pelletized sample. The intensity of $H_\alpha$ emission line decrease about twenty percent in case of the pelletized sample, while the $H_\beta$ emission line intensity is relative similar for the two sample conditions. The intensity of $H_\gamma$ emission line decreases about forty percent in case of the pelletized sample compared to the fresh sample. In general, these results mean either in the fresh sample or in the pelletized sample, hydrogen emission lines can convincingly be detected. This result indicates that hydrogen emission lines can be selected as a suitable analytical line for measuring the temperature and electron density of the plasma produced on the river clam shell sample. Since hydrogen in plasma is low due to their low concentration in the samples, self-absorption effect may be neglected within the experimental uncertainty.

From the intensity of the hydrogen emission line identified, Boltzmann plot has been made for different experimental conditions, according to equation (1). In this work, all spectroscopic data of the energy levels taken from atomic spectra database of NIST, United States of America (USA) [17]. The Boltzmann plot method was used to determine the temperature of plasma. Typical Boltzmann plots of the hydrogen lines are shown in Figure 4 for the fresh clam sample and the pelletized clam sample with the same experimental parameters. The emission spectrum detected from plasma generated on the river clamshell in fresh and pelletized conditions using lower laser pulse energy of 60 mJ under air surrounding gas at a low pressure of 5 Torr with the gating of the OMA system was set a delay time of 100 ns, and gate width of 50 µs. The curve slope yields to the plasma temperature. Based on Figure 4, the plot are fitted to straight lines with different slopes, showing the difference of the plasma temperature. Slope of the curve obtained from the fresh sample and the pellet sample is -1.41 and -1.31, respectively. From the slopes of the Boltzmann plot curve the temperature plasma was estimated to be about 8288 K for the fresh sample and 8810 K for the pelletized sample, respectively.
Figure 3 The atomic emission of the hydrogen lines Hα, Hβ and Hγ of the plasma was generated from the river clam (a) fresh shell conditions (b) pellet shell conditions

The physical characteristic of plasma produced on the shell sample have been analysed at different delay times (0.1–5 µs) and gate width of 50 µs of the OMA system. Figure 5 shows Boltzmann plot for
hydrogen emission lines of H\(_\alpha\), H\(_\beta\) and H\(_\gamma\) at 5 \(\mu\)s delay time and a 50 \(\mu\)s gate width of the OMA system. Based on the figure, it can be seen the slope of the Boltzmann plot curve sharper than that in case 0.1 \(\mu\)s delay. Slope of the curve obtained for the fresh sample and the pellet sample is -2.06 and -1.87, respectively corresponding to a temperature of 5633 K and 6197 K, respectively. Decrease of the plasma temperature is reasonable since the plasma cools down with time and the intensity of the lines decrease due to recombination process reaching its maximum. Overall the result of temperature plasma for all conditions shows that the plasma conform the Maxwell distribution criteria for plasma to achieve local thermal equilibrium (LTE).

**Figure 4** Typical Boltzmann plot of hydrogen lines of H\(_\alpha\), H\(_\beta\) and H\(_\gamma\) at 0,1\(\mu\)s delay time and 50 \(\mu\)s gate width of the OMA system detected from the river clamshell sample in (a) the fresh condition (b) the pellet condition

**Figure 5** Typical Boltzmann plot of hydrogen lines of H\(_\alpha\), H\(_\beta\) and H\(_\gamma\) at 5 \(\mu\)s delay time and 50 \(\mu\)s gate width of the OMA system detected from the river clam shell sample in (a) the fresh condition (b) the pellet condition
Table 1. Emission lines used and their spectroscopic parameters

| Element | \( \lambda \) (nm) | \( g_s/A_u \) \( (10^8 \text{ s}^{-1}) \) | \( E_i \) (eV) | \( E_k \) (eV) | \( g_1 \) | \( g_2 \) |
|---------|-------------------|-----------------|--------|--------|--------|--------|
| \( \text{H}_\alpha \) | 656.27            | 0.41            | 10.15  | 12.09  | 4      | 6      |
| \( \text{H}_\beta \) | 486.13            | 0.084           | 10.15  | 12.75  | 4      | 6      |
| \( \text{H}_\gamma \) | 434.04            | 0.0025          | 10.15  | 13.06  | 4      | 6      |

The estimation of the temperature and electron density of the plasma produced on the river clamshell sample was conducted using the emission intensity of the hydrogen emission obtained in the measurement results and the spectroscopic parameter data obtained from available atomic spectrum database. The spectroscopic parameter data of the emission spectrum hydrogen used this work is taken from National Institute of Standards and Technology (NIST) atomic spectra database as shown in Table 1.

The time evolution of the plasma temperature and electron density is shown in Figure 6. The plasma was produced from the river clam shell in fresh and pelletized conditions. The emission spectrum was acquired with different delay times of the OMA system (0.1 \( \mu \)s – 5 \( \mu \)s). The plasma temperature was estimated using the Boltzmann plot method for various delay times of the OMA system (0.1 \( \mu \)s – 5 \( \mu \)s). The estimated plasma temperature for various delay times starting from 0.1 \( \mu \)s to 5 \( \mu \)s vary with time from 5633 K to 8810 K. The estimated electron density of the plasma utilizing the Saha-Boltzmann method, also vary with time ranging from \( 3.7 \times 10^{20} \text{ cm}^{-3} \) to \( 9.7 \times 10^{20} \text{ cm}^{-3} \).

![Figure 6](image-url) Temporal behaviour of the plasma generated on the river clamshell sample in fresh and pellet conditions of (a) temperature (b) electron density

The result shows that the temperature and electron density of the plasma produced on the river clamshell in pelletized conditions is higher than that in case of fresh conditions under the same experimental parameters. This is due to the difference in the hardness of the sample, since the hardness of sample is crucial for generating strong plasma [18-19]. Nevertheless, the temperature and electron density of the produced plasma obtained for the river shell sample in both conditions of fresh and pellet conform the Maxwell and McWhirter criteria for a laser induced plasma to achieve local thermal equilibrium (LTE) condition. Maxwell criteria requires that the lower limit of electron density is \( N_e > 10^{16} \text{ cm}^{-3} \) and
temperature is \( kT < 5\text{eV} \) or \( kT < 50000 \text{ K} \) while McWhirter requires density of electron is \( N_e > 1.6 \times 10^{12} T^{3/2} (\Delta E)^3 \) which are well fulfilled by the considered plasma.

4. Conclusion

LIBS techniques can clearly detect emission lines of hydrogen produced from the river clam shell in fresh and pellet conditions using the Nd:YAG laser energy of 60 mJ under air surrounding gas at low pressure of 5 Torr and a gate width of 50 µs with different delay times (0.1 µs – 5 µs). The emission lines of hydrogen, namely \( H_\alpha \) at 656.27 nm, \( H_\beta \) at 486.13 nm and \( H_\gamma \) at 434.04 nm can be identified unambiguously. The hydrogen emission line were used for estimating the temperature and electron density of plasma. Estimation of temperature and electron density of plasma was carried out by means of Boltzmann Plot and Saha-Boltzmann method using the atomic emission lines of hydrogen. The result shows that the plasma temperature and electron density vary from about 5633 K to 8810 K and \( 3.7 \times 10^{20} \) cm\(^{-3}\) to \( 9.7 \times 10^{19} \) cm\(^{-3}\). The plasma temperature and electron density obtained from the river clam shell sample conform the Maxwell distribution and McWhirter criterion for plasma to achieve local thermal equilibrium (LTE) condition.

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