Assessing the temperature of plasma produced in carbon dioxide (CO$_2$) Laser-Induced Breakdown Spectroscopy (LIBS) from soil sample prepared by two different methods of metal mesh and silicone grease

A M Sari$^1$, K Lahna$^2$, N Idris$^{2,*}$, M Ramli$^3$, K Kurihara$^4$, and Marwan$^5$

$^1$Graduate School of Mathematics and Applied Sciences, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia
$^2$Department of Physics, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jl. Syech Abdurrauf No. 3 Darussalam, 23111 Banda Aceh, Aceh, Indonesia
$^3$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jl. Syech Abdurrauf No. 3 Darussalam, 23111 Banda Aceh, Aceh, Indonesia
$^4$Department of Physics, Faculty of Education, University of Fukui 3-9-1, Bunkyo, Fukui 910-8507, Japan
$^5$Department of Chemical Engineering, Faculty of Engineering, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia

*E-mail: nasrullah.idris@unsyiah.ac.id

Abstract. Temperature of plasma generated by CO$_2$ laser from soil sample prepared by the two different methods, namely metal mesh, and silicone grease methods, was examined. The plasma was produced by focusing the laser beam on the sample at 1 atmospheric pressure. The plasma characteristics namely temperature was estimated by the Boltzmann plot method. The detection was made in region of 300 nm-400 nm. In the case sample prepared using the metal mesh method, the estimated temperature was about 11605 K for the metal mesh no. 50 and 12440 K for mesh no. 40, respectively when helium was used as surrounding gas. When air was used as surrounding gas, plasma temperature was about 10315 K and 10990 K, respectively. In case the soil sample prepared by soil mixed with silicon grease (SMS) smeared on a surface of metal sub target, plasma temperature was about 8913 K and 9218 K for air and helium as a surrounding gas, respectively. It can be concluded that plasma temperature is not significantly different although the sample was prepared with different methods.

1. Introduction

Simple and fast analysis of environmental samples for monitoring purposes is very important. Some conventional techniques have been used to analyse environmental samples, but these techniques need a long analysis time. Laser-induced breakdown spectroscopy (LIBS) is an emerging analytical tool. It has many superior advantages such as capability for multi element detection in one measurement, independence from tiring sample treatment, flexible applicability to various kinds of samples including solid, liquid, even gas and allows for qualitative and quantitative analysis [1-2]. Due to these advantages, it has popularly been employed for analysis of various environmental samples, including soil samples [3].
Analytical performance LIBS technique is strongly influenced by several factors such as experimental conditions, laser parameters, and sample matrix. For soil sample analysis, LIBS commonly uses an Nd-YAG laser to generate plasma, and soil sample generally is made in the form of pellet for analysis [4-6]. However, utilizing unique characteristics of a pulsed CO\textsubscript{2} laser in plasma generation, in addition to the pellet method, other sample preparation method has been developed to reduce the blowing effect on soil samples analysis namely soil mixed silicone grease (SMS) metal sub target and metal mesh [7-8]. In research using these preparation methods, LIBS analysis of soil samples has been made using the CO\textsubscript{2} laser and measurements was carried out under 1 atmospheric pressure. However, to make qualitative and quantitative analysis using LIBS including CO\textsubscript{2} LIBS adopting various different sample preparation methods, the characteristics of plasma generated need to be studied carefully to assure the local thermodynamic equilibrium (LTE) condition is achieved.

Light emitted by laser induced plasma contains important information for analytical purposes and on physical characteristics of the consequent plasma. One very important characteristics of the laser induced plasma affecting inherently plasma emission is temperature [9]. Knowing plasma temperature is very important to understand various processes taking during plasma formation including dissociation, atomization, ionization, and excitation [10-11]. Therefore, the focus of this work is to study the one important characteristics of plasma generated by CO\textsubscript{2} laser in soil samples prepared employing two different preparation methods, namely silicone grease with metal sub target and metal mesh.

2. Experimental Procedure

The experiment set-up that employed is the same as used in the previous studies [7-8]. A transversely excited at atmosphere (TEA) CO\textsubscript{2} laser emitting 10.6 µm wavelength was used as excitation source. The laser beam was directed onto surface of the sample by means of a focusing lens (zinc selenide, f = +200 mm) for generating a plasma. Energy of laser pulse used in this study was set at 2.5 J. The measurement was made at atmospheric pressure under two different ambient gas of air and helium, separately. A standard soil (Japan Industrial Standard Test Powders 1 Class 7) was used in present experiment [7].

For sample preparation using the soil mixed silicone grease (SMS) method, as in previous studies, the mixture of soil and silicone grease has a ratio of 50%: 50% and then smeared uniformly on a nickel plate surface. Nickel plates with dimensions of 2.5 mm x 3 mm serve as sub-target. Samples have been smeared on a plate surface with a thickness of 1 mm and placed in the sample holder in the chamber. While, for the metal mesh method, two nickel metal meshes with different filter sizes have been used, namely no. 40 and no. 50 (equivalent to 0.420 mm and 0.297 mm particle size, respectively). Metal hole inside a round metal chamber is filled 3 mg of soil sample, then covered using a nickel-metal mesh.

Identification and confirmation emission lines have been made using available atomic database [12]. Similarly, spectroscopic data of interested emission lines for estimating plasma temperature were also deduced from the database. Using the emission measured emission intensity and respective spectroscopic data, plasma temperatures have been calculated using several Ca emission lines appearing in a region of 350-450 nm using the Boltzmann plot, according to the equation:

\[ \ln \left( \frac{I_\lambda}{gA} \right) = - \frac{E_k}{kT} - \ln \left( \frac{4\pi Z}{hcN_0} \right) \]

I is measured intensity of the emission line, \( \lambda \) is the wavelength of the element, \( g \) is the statistical weight, \( A \) is transition probability, \( E_k \) is the upper energy level, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( Z \) is the partition function, \( h \) is the Planck constant, \( c \) is the speed of light and \( N_0 \) is the total population. From the equation, the left side plot vs the energy level \( E_k \), the temperature \( T \) can be calculated from the curve slope.
3. Result and discussion

Soil sample using in this work contains 0-3 % Ca. Spectrum emission from the soil plasma taken in 350 nm-450 nm region is displayed in Figure 1. Several emission lines due to Ca were identified. Actually, emission lines due to other constituent of soil sample were also found in spectrum. However, the other emission lines are out of interest in present work. Overall, Ca emission lines detected from the two different sample preparation methods are equal. The spectroscopic data of Ca line obtained from the NIST atomic spectra database are tabulated in Table 1.

![Figure 1. Ca emission lines in the range of 350 nm - 450 nm detected from the soil sample prepared by SMS method](image)

| Wavelength (nm) | gk Aki (s^-1) | Ei (eV) | Ek (eV) |
|-----------------|---------------|---------|---------|
| 393,36          | 5.88 x 10^8   | 0       | 3.150984|
| 396,84          | 2.80 x 10^8   | 0       | 3.123349|
| 422,67          | 1.7 x 10^7    | 0       | 2.932512|
| 428,3           | 2.17 x 10^8   | 1.8858075| 4.779784|
| 428,93          | 1.80 x 10^8   | 1.8793402| 4.769028|

From equation 1, if the values of ln (Iλ/gk Aki) versus Ek are plotted, the slope of the curve (m = -1 / kT) can be obtained. The temperature of the plasma can be calculated from the slope without need to know the total atomic species and the partition function. Figure 2 displays plot of Boltzmann distribution function for Ca emission lines. The intensity of emission lines was extracted from the spectrum obtained from the LIBS measurement. There are several Boltzmann plot was made for different soil sample preparation methods and different ambient gas used of air and helium, respectively.
Figure 2. The Boltzmann graphs for Ca element from samples prepared by (a-b) metal mesh no 40, (c-d) metal mesh no 50, (e-f) SMS in air and helium as a surrounding gas

From Figure 2, it can be seen that the slope for each type of sample preparation method is different resulting in different plasma temperature. For soil samples prepared by the metal mesh method, the use of mesh no 50 makes temperature of the plasma tends to be higher than that of using mesh no. 40. In case of mesh no. 50, it is assumed that the effect of blowing-off of the soil sample can be minimized.
more effectively since the sieving grid of the mesh is smaller than mesh no. 40. For soil samples prepared using SMS method, plasma temperature is found lower than that of metal mesh method. It is related to complex processes in sample ablation and plasma formation. The addition of silicone grease material to the soil sample is likely to cause a longer ablation process because the energy of laser pulse is also absorbed by the silicone grease constituent, in turn affecting the process of plasma formation.

Figure 3. Comparison of plasma temperature measured in air and helium environment for each type of sample preparation method

The plasma temperature generated under two different surrounding gas, namely air and helium at a pressure of 1 atm has been calculated. Figure 3 shows a comparison of the plasma temperature generated under air and helium environments. Overall, plasma temperature is higher when helium was used instead of air. For sample prepared by metal mesh no 40, temperature of the plasma is about 10315 K (air case) and 11605 K (helium case). When metal mesh no 50 was used, the plasma temperature increases to 10990 K in air and 12440 K in helium. The same pattern is obtained for soil sample prepared by SMS method which is the plasma temperature higher in case of using helium namely 9218 K, while in case of air environment it is about 8913 K. It is considered that fewer electrons are produced in helium where the inverse bremsstrahlung (IB) process is less efficient and more energy conveyed to the sample, thus the higher temperature plasma is generated [13]

4. Conclusion
Estimation temperature of soil plasma produced by means of CO2 laser-induced plasma was carried out using Boltzmann plot. The soil sample was prepared by two different sample treatment methods, namely the metal mesh and the soil mixed silicone grease (SMS) methods. Temperature of the laser induced plasma was calculated from Boltzmann plot of Ca lines in a range of 350-450 nm. It was found that temperature of plasma generated from the soil sample prepared by the mesh no 50 is higher than of the SMS method, namely 10990 K and 12440 K under environment of air and helium, respectively. While the case of mesh no 40, temperature of the laser induced plasma is about 10315 K and 11605 K under helium and air, respectively. While in case of the SMS method temperature of the plasma is about 9218 K and 8913 K under air and helium, respectively. It was found in all cases that plasma temperature is higher when helium is used as surrounding gas than air case. Based on the obtained temperatures, plasma generated using the CO2 laser from soil sample prepared by two different methods, namely the metal mesh and SMS methods fulfils LTE criteria.

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