Temperature estimation using Boltzmann plot method of many calcium emission lines in laser plasma produced on river clamshell sample

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Abstract. Temperature as one very important characteristics of a laser-induced plasma was estimated using many calcium emission spectral lines. This was possible due to the availability of a wide coverage and high resolution optical multichannel analyser (OMA) system allowing a simultaneous detection of many emission spectral lines from one element. The plasma emission was produced after focusing an Nd-YAG (neodymium-doped yttrium aluminium garnet) laser onto a river clamshell samples under air as surrounding gas at low and high pressures. The emission spectrum was acquired using the OMA system equipped with an echelle spectrograph system. The clamshell sample was collected from Panga River, Panga, Aceh Jaya, Aceh, Indonesia. The plasma temperature estimation was carried out by Boltzmann plot method. All calcium spectral lines either atomic and ionic emission were identified including resonant emission spectral lines in the recorded spectrum. Boltzmann distribution function firstly was plotted for all identified calcium spectral lines either atomic and ionic emission including their respective resonant emission spectral lines. In the further stage, the resonant emission lines then were excluded from the Boltzmann plot. As the results, the estimated temperature changes significantly with the number emission lines included and also with inclusion of the resonant spectral lines. The plasma temperature heavily influenced by inclusion the resonant emission lines. Thus, this work demonstrated clearly the influence of number emission lines used in Boltzmann plot to the plasma temperature estimation. The results also demonstrated explicitly the apparent effect of self-absorption of the resonant spectral line in estimation the plasma temperature.

1. Introduction
As one of the famous techniques in spectroscopy which has many unique advantages, LIBS has been used in a lot of applications which is not only limited to inorganic samples such as solid and metal but also begun to be applied in organic and biological sample such as wide variety of plants, woods, trees and alga. There are several very important advantages of LIBS uniquely useful for analysis of the complex samples such as multi-elemental detection, suitable to remote measurement and minimal
sample preparation [1-3]. In spite of having all that advantages, LIBS technique experimentally as well as theoretically depends on many influential parameters used affecting the obtained spectrum. Those influences are generally grouped as laser parameters, ambient surrounding and sample characteristics. The laser parameters influencing LIBS analytical performance are wavelength, pulse width, energy and pulse laser mode. While other parameter is the ambient surrounding including the type of gas species and the pressure of the surrounding gas. Other very important parameter is composition and physical features of the sample [4]. Thus, plasma generation is a complex process governed by many parameters of laser, sample, surrounding gas and optical detector. All influential factors are embraced by the plasma characteristics informing the feasibility of plasma conditions to be used in identifying qualitatively and quantitatively the content of elements in a target sample.

In order to perform an analytical study on a sample using LIBS, characteristics of plasma produced on the sample must be studied well since the plasma characteristics essentially determines the analytical performance of LIBS. The plasma characteristics, especially plasma temperature, are the most important knowledge in LIBS technique [5]. The information of plasma temperature can be used as primary data to do the further identification, then understanding the physical processes involved in the whole complex processes of the laser induced plasma generation, including dissociation, atomization, ionization, and excitation [6]. In the other hand, plasma temperature represents other characteristics of the plasma including the relative population of energy levels and the speed distribution of particles. A common way of estimation plasma temperature is plotting Boltzmann distribution function assuming the fulfilment of local thermodynamic equilibrium (LTE) in the laser induced plasma, called as Boltzmann plot method [7]. Actually, there are several other methods normally used for estimating plasma temperature in LIBS namely Saha Boltzmann method, line-to-continuum method and synthetic spectra method [4]. Nevertheless, the proper choice of the measurement method is crucial depending on the plasma condition to the estimated temperature. For example, because of due to the ineffectiveness in energy difference, the uncertainties in the transition probabilities and also its statistical weight, it is not suggested to calculate the excitation temperature of brass plasma using the line-pair ratio method of Boltzmann two-line method [8].

Although the two methods based on Boltzmann distribution function, Boltzmann plot method (BP) is considered more accurate than the Boltzmann two-line method (BT) since BP uses many available emission spectral lines [6]. Furthermore, it was found Boltzmann plot method can be used for predicting the degree of matrix effect and also the ablation process in any sample mixing at various concentrations measuring temperature of the laser induced plasma [9]. Ahmed et al and Li suggested the minimum number of spectral lines to obtain representative plasma temperature estimated by Boltzmann distribution function plot [10, 11]. Ghazanfar et al have determined temperature and electron density of a laser plasma induced on rock sample. Boltzmann plot method was used for determining the plasma temperature and applying it to make qualitative and quantitative analysis of Ca and Si. The result shows the plasma temperature is greater than 10000 K and the electron density of the plasma is equivalent to $10^{16}$ cm$^{-3}$ [12]. The same experiment for estimating plasma temperature using Boltzmann plot method of calcium emission spectral lines has also been conducted for different samples namely lead-calcium and eggshell. The results obtained inform the temperature of plasma from the samples are 11400 K and 5956 K, respectively and the self-absorption for each spectral lines and the homogeneity of the plasma has been evaluated [13, 14]. It is important to confirm the lines used in estimating plasma temperature is the optically thin lines and free from self-absorption [15, 16]. The other work for estimating plasma temperature by means of Boltzmann plot method was made on aluminium alloy sample (Al 6063 alloy) and obtained a plasma temperature of about 7580 K [17]. Actually several previous works on application of LIBS to organic samples has been conducted. LIBS has been successfully used for studying shell sample including meat shell and calm shell [18-19]. The different method, namely Boltzmann two-line method, was used for estimating plasma temperature in
the same sample and spectral emission lines. The plasma temperature obtained for meat clam shell varies from 4020 K – 15195 K [19].

Principally, in LIBS experiments the self-absorption process normally occurs on the strong emission spectral lines such as the spectral lines due to the major constituents of the target material [20-21]. The self-absorption bring about reduction of the emission intensity of the spectral line and broaden its the full width at a half maximum (FWHM). This self-absorption effect is observed far serious in case of the intense spectral lines than in the case of the less intense spectral lines for species with higher concentrations [16, 22-24]. However, self-absorption also was used to obtain quantitative analytical information. This technique successfully shown that the strongly self-absorbed lines can be used in probing Cu concentration in the sample [25]. Alonso reported that the self-absorption effect of the emission spectral lines causes a systematic error in obtaining the intensities of the emission spectral lines [26]. Baig et al in their work shows the resonant lines of calcium, magnesium and also multiple structure of calcium emission spectral lines. They noticed the resonant transition line of calcium at 422.67 nm. They also found the triplet structure of magnesium spectral line at around 518 nm [17]. Another resonant spectral line is at 396.26 nm of neutral aluminium [27].

2. Experimental Procedure
The experimental system employed in this current work is similar to described in previous work [18-19, 20]. Clamshell, the organic sample used in this work, was collected from Panga River, Panga district, Aceh Jaya Regency, Aceh, Indonesia, where the upstream of that river is a place of traditional gold mining activities conducted by local society. Those samples were prepared in two separated conditions namely fresh and pelletized samples. The fresh sample is the clam shell sample without no any chemical and physical treatments. The pelletized sample was formed by drying up the fresh sample and then grinding the dried clam shell into fine powder. The sieved fine powder then was pressed using a hydraulic press machine at a pressure of 30 MPa pressure to make the pellet sample.

Laser pulses from a Q-Switched Nd:YAG laser (Quanta Ray, LAB SERIES) operated at the fundamental wavelength of 1064 nm was focused through a lens of 150 mm focal length onto the surface of clamshell sample. The energy and repetition rate of laser pulse was fixed at 60 mJ and 10 Hz, respectively. The sample was placed on a motorized sample holder. The sample holder together with the sample placed in the vacuum chamber was kept to rotate around on its axis during spectral data acquisition. The surrounding gas in the vacuum chamber is air environment. The pressure of the surrounding gas adopted in this experiment was 760 Torr and 5 Torr.

The plasma radiation was collected using an optical fibre and delivered into the optical multichannel analyser (OMA) system ((Andor Mechelle ME5000). The timing setup of the gating device of the OMA system was set at a delay of 100 ns and a width of 50 µs, respectively. The emitted spectra were acquired using the OMA system and recorded then processed using an iStar intensified charge coupled device (ICCD) camera. The OMA system is equipped with an echelle configured spectrograph enabling an ample coverage of detection wavelength, starting from 200 nm-975 nm. The spectra were stored in a computer for further analysis and treated by a software.

National Institute of Standards and Technology (NIST) United States of America was used for identification and confirmation of the spectral lines. The spectroscopic data also was used for estimating the temperature of the laser induced plasma. Estimation the plasma temperature was carried out using Boltzmann distribution function plot method using the following equation:

\[
ln\left(\frac{I_\lambda}{gA}\right) = -\frac{1}{k_BT}E + \ln\left(\frac{4\pi Z}{hcN_\theta}\right)
\]
I is intensity of the spectral line, λ is wavelength of spectral line, g is statistical weight of the energy level, A is transition probability, k_B is Boltzmann constant, T is temperature, E is energy level of the upper state for emission, h is Planck constant, Z is partition function, c is speed of light, and N_o is total species population. Assuming there is a Boltzmann distribution, it is simply a linear plot, thus observing the terms in the right part of Equation 1 will straightforwardly shows that the slope (m) of the Boltzmann distribution plot represent the plasma temperature [30-31]. Since accurate Boltzmann plot will be obtained by using accurate intensities of the measured spectral lines, accurate probabilities of the involved transitions, and well-spaced upper energy levels, and there are many spectral lines due to calcium available in the acquired emission spectra, the calcium emission spectral lines was used for estimating the temperature of the laser induced plasma using Equation 1. This was made possible because Ca is major element in the sample in form of CaCO_3 and the emission spectrum was acquired using a spectrometer with a capability for wide ranging wavelength coverage, starting from 200 nm to 975 nm. The spectral line intensity, I was obtained from the acquired emission spectra, while the other terms of Equation 1 including statistical weight of energy level, g and transition probability, A as well as energy level of the upper state for emission, E was taken from NIST atomic spectrum database.

3. Results and discussion

The complete emission spectrum of clamshell plasma has been shown in previous work [19]. Based on the emission spectra taken from the fresh sample of clamshell using Nd-YAG laser at various laser energies at a pressure of 1 atmosphere of air ambient, it was found that calcium emission spectral lines dominate the emission spectra. The fresh sample is clamshell sample without any pretreatment prior to laser irradiation. The fresh clamshell was just cut into slices for laser irradiation. Similar result was also found when plasma was produced under air surrounding at low pressure. The same experiment was also conducted for pelletized clamshell sample. As explained in the experimental procedure section, the pelletized sample was prepared by grinding the clam shell into fine powder and then was pressed. The same results were found either when plasma was produced at low or high pressure of air surrounding under the same experimental condition as adopted for the fresh sample, namely the emission spectra were heavily dominated by calcium emission spectral lines. These results confirm that the emission spectra are mainly due to Ca emission spectral lines. It is actually very reasonable considering that the host of clamshell is CaCO_3. The data elaborate in this work is for clamshell sample in a pelletized form. After careful observation, there are 29 emission lines of calcium consisting of 23 calcium atomic emission (Ca I) and 6 calcium ionic emission (Ca II) lines successfully identified. The spectral lines identification was mainly based on wavelength and relative emission intensity using NIST database. The spectral lines with strong relative intensity was selected and tabulated. The relative intensity of Ca atomic emission spectral lines ranging from weak intensity (20 for Ca I 428.30 nm and several other spectral lines) to the strongest emission intensity (50 for Ca I 422.67 nm). While the relative intensity of Ca ionic lines is ranging from weak (170 for Ca II 315.89 nm) to the strongest line (230 for Ca II 393.36 nm). The identification was relatively easy to make since the emission spectra mainly consists of Ca spectral lines. The selected Ca emission spectral lines and spectroscopic data obtained from NIST atomic spectra database for all identified calcium emission lines are tabulated in Table 1, Table 2 and Table 3. In the present work, the plasma temperature was estimated using Boltzmann plot method by means of the tabulated calcium emission spectral lines. The estimation was made by two schemes. In the first scheme, plotting Boltzmann function was carried out by using all identified spectral lines including resonant spectral lines while in the second scheme Boltzmann function was plotted without inclusion of the resonance emission spectral lines. Boltzmann function was plotted for the two groups of emission spectral lines including calcium atomic and ionic emission spectral lines. The obtained temperature in the two schemes then was evaluated.

Table 1 shows all calcium atomic emission spectral lines while calcium ionic spectral lines are shown in separated table, namely Table 2 including the resonance emission spectral lines. Table 3 shows only resonant spectral lines. Considering the main components of clamshell is CaCo_3, and the acquired plasma emission spectrum shows many calcium emission spectral lines occurring at various
wavelengths in the ample region (200 nm – 900 nm) as compared to other elements, determination the plasma temperature using calcium emission spectral lines poses a highest probability for obtaining the best estimation. However, as well known the resonant emission spectral lines influence significantly the plasma temperature estimation. Therefore, as shown in Tables 1, 2, and 3, the calcium emission spectral lines were classified into several groups, namely atomic, ionic and resonant emission spectral lines. It is important to avoid the resonant spectral lines due to possible self-absorption effect would be larger in that condition. Thus, in the present work will be shown the influence of several groups, namely atomic, ionic and resonant emission spectral lines to estimation of the plasma temperature.

**Table 1** Spectroscopic parameters of selected Ca I emission lines used to estimate plasma temperature using Boltzmann plot method.

| Wavelength (nm) | gA. Aua (s⁻¹) | Transition | Ei (eV) | Ea (eV) |
|-----------------|----------------|------------|---------|---------|
| 422.67          | 6.54 x 10⁸     | 3p⁶ 4s² → 3p⁶ 4s 4p | 0.0000000 | 2.9325119 |
| 428.30          | 2.17 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8858075 | 4.7797840 |
| 428.93          | 1.80 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8793402 | 4.7690283 |
| 429.89          | 1.40 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8858075 | 4.7690283 |
| 430.25          | 6.80 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8989349 | 4.7797840 |
| 430.77          | 1.99 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8858075 | 4.7631682 |
| 431.86          | 2.20 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4p³ | 1.8989349 | 4.7690283 |
| 442.54          | 1.49 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4s 4d | 1.8793402 | 4.6801799 |
| 443.57          | 1.03 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4s 4d | 1.8858075 | 4.6801799 |
| 445.48          | 6.10 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4s 4d | 1.8989349 | 4.6813270 |
| 518.88          | 2.00 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4s 5d | 2.9325119 | 5.3212843 |
| 526.22          | 6.00 x 10⁷     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5212633 | 4.8767178 |
| 526.56          | 1.30 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5229867 | 4.8769583 |
| 527.03          | 2.50 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5256821 | 4.8775482 |
| 558.87          | 3.40 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5256821 | 4.7435268 |
| 559.45          | 1.90 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5229867 | 4.7385667 |
| 559.85          | 1.30 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5212633 | 4.7352531 |
| 610.27          | 2.90 x 10⁷     | 3p⁶ 4s 4p → 3p⁶ 4s 5s | 1.8793402 | 3.9103990 |
| 612.22          | 8.61 x 10⁷     | 3p⁶ 4s 4p → 3p⁶ 4s 5s | 1.8858075 | 3.9103990 |
| 616.22          | 1.43 x 10⁸     | 3p⁶ 4s 4p → 3p⁶ 4s 5s | 1.8989349 | 3.9103990 |
| 643.91          | 4.80 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5256821 | 4.4506470 |
| 646.26          | 3.30 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5229867 | 4.4409544 |
| 649.38          | 2.20 x 10⁸     | 3p⁶ 3d 4s → 3p⁶ 3d 4p | 2.5212633 | 4.430117 |

**Notes:**
- The data are from the 8th International Conference on Theoretical and Applied Physics.
- The wavelength region is 200 nm – 900 nm.
- The plasma temperature estimation is obtained using the Boltzmann plot method.
Table 2 Spectroscopic parameters of selected Ca II emission spectral lines used to estimate plasma temperature using Boltzmann plot method.

| Wavelength (nm) | \( g_s A_0 \) (s\(^{-1}\)) | Transition | \( E_i \) (eV) | \( E_k \) (eV) |
|----------------|-----------------|------------|--------------|--------------|
| 315.89         | 1.20 \( \times 10^9 \) | \( 3p^6 4p \rightarrow 3p^6 4d \) | 3.123349     | 7.047169     |
| 317.93         | 2.20 \( \times 10^9 \) | \( 3p^6 4p \rightarrow 3p^6 4d \) | 3.150984     | 7.049551     |
| 370.60         | 1.80 \( \times 10^8 \) | \( 3p^6 4p \rightarrow 3p^6 5s \) | 3.123349     | 6.467875     |
| 373.70         | 3.40 \( \times 10^8 \) | \( 3p^6 4p \rightarrow 3p^6 5s \) | 3.150984     | 6.467875     |
| 393.36         | 5.88 \( \times 10^8 \) | \( 3p^6 4s \rightarrow 3p^6 4p \) | 0.000000     | 3.150984     |
| 396.85         | 2.80 \( \times 10^8 \) | \( 3p^6 4s \rightarrow 3p^6 4p \) | 0.000000     | 3.123349     |

Table 3 Spectroscopic parameters of resonant spectral lines from Ca I and Ca II

| Element | Wavelength (nm) | \( g_s A_0 \) (s\(^{-1}\)) | Transition | \( E_i \) (eV) | \( E_k \) (eV) |
|---------|----------------|-----------------|------------|--------------|--------------|
| Ca I    | 422.67         | 6.54 \( \times 10^8 \) | \( 3p^6 4s^2 \rightarrow 3p^6 4s 4p \) | 0.0000000    | 2.9325119    |
| Ca II   | 393.36         | 5.88 \( \times 10^8 \) | \( 3p^6 4s \rightarrow 3p^6 4p \) | 0.0000000    | 3.150984     |
| Ca II   | 396.85         | 2.80 \( \times 10^8 \) | \( 3p^6 4s \rightarrow 3p^6 4p \) | 0.0000000    | 3.123349     |

Figure 1 Boltzmann distribution function plot of calcium atomic emission spectral lines (Ca I) detected under air surrounding at pressure of (a) 760 Torr and (b) 5 Torr, respectively using all identified calcium atomic emission lines.
Figure 2 Boltzmann distribution function plot of calcium ionic emission spectral lines (Ca II) taken under air surrounding at pressure of (a) 760 Torr and (b) 5 Torr, using all identified calcium emission spectral lines.

Figure 1 shows Boltzmann distribution function plot of calcium atomic emission lines. Figure 2 shows Boltzmann distribution function plot of calcium ionic emission lines. The Boltzmann distribution function plot was obtained using Equation 1 where the red lines are the slope of graphs. The Boltzmann distribution function plot was made for two different pressures of the surrounding gas, namely high pressure of 760 Torr (a) and low pressure of 5 Torr. The plasma temperature was determined from the slope of the Boltzmann distribution plot.

Figure 3 Boltzmann distribution function plot of calcium atomic emission spectral lines with air surrounding at pressure of (a) 760 Torr and (b) 5 Torr, using all identified calcium atomic spectral lines without the resonant spectral line (Ca I 422.67 nm).
There are different slopes in Boltzmann distribution function plot in Figure 1 and Figure 2 showing plot using all identified calcium emission spectral lines. The similar plots were made without inclusion the resonant spectral lines shown in Figure 3 and Figure 4 for atomic spectral lines (Ca I) and ionic spectral lines (Ca II), respectively. There is only one atomic resonant spectral line at wavelength of 422.67 nm (Ca I 422.67 nm) while there are two ionic resonant spectral lines, namely Ca II 393.37 nm and Ca II 396.85 nm. The influence of the resonant lines to the estimated temperature is shown in Figure 5.

Figure 4 Boltzmann distribution function plot of calcium ionic emission spectral lines with air surrounding at pressure of (a) 760 Torr and (b) 5 Torr, using all identified calcium ionic spectral lines without using the resonant spectral lines.

Figure 5 Comparison between the plasma temperature estimated using all identified calcium emission spectral lines either by inclusion the resonant spectral lines and that without inclusion the resonant spectral lines at pressure of (a) 760 Torr and (b) 5 Torr, respectively.
The plasma temperature was calculated in two variations of pressures of the surrounding gas of the plasma generation namely 760 Torr and 5 Torr. Figure 4 (a) shows the estimated plasma temperature at a pressure of 760 Torr of air surrounding. The estimation of plasma temperature was classified for excitation temperature using atomic spectral lines (Ca I) and ionization temperature using ionic emission spectral lines (Ca II). The plasma temperature obtained using all identified calcium emission lines (including the resonant spectral lines) and without inclusion the resonant spectral lines was compared. The annotation was added on the upper right corner of the graphs for distinguishing between the estimated temperature that includes the resonant spectral lines from that not includes the resonant spectral lines. In case of a pressure of the air surrounding at 760 Torr, using all calcium atomic emission spectral lines (Ca I) including the resonant spectral lines (Ca I 422.67 nm), the plasma temperature was obtained about 11891 K while without inclusion the resonant spectral lines it was only about 7111 K, about 4000 K lower. Similarly, when using all calcium ionic emission lines (Ca II) including the resonant spectral lines (Ca II 393.36 nm and Ca II 396.85 nm) the temperature was about 11114 K while it was far lower, only about 3614 K when the resonant spectral lines were excluded. This result shows that there is a large discrepancy in the obtained plasma temperature when the estimation was made with inclusion and without inclusion the resonant spectral lines. The obtained plasma temperature is significantly higher when estimation was made using all emission spectral lines including the resonant spectral lines. It is very important to note that even though there is only one atomic resonant spectral line (Ca I 422.67 nm) and two ionic resonant lines (Ca II 393.36 nm and Ca II 396.85 nm), the obtained plasma temperature shows a very significant change when it was included in the plot of Boltzmann distribution function. Similar results were also observed in case of a low pressure of air surrounding gas. Figure 4 (b) shows the temperature estimation using calcium atomic spectral lines (Ca I) under low pressure of the ambient gas. It can be seen that the plasma temperature obtained using calcium atomic emission spectral lines (Ca I) sharply changes from 8057 K in case of inclusion the resonant spectral lines to 5924 K in case of exclusion the resonant spectral lines. The temperature estimated using calcium ionic emission spectral lines (Ca II) steeply changes from 13418 K in case of inclusion the resonant spectral lines to 4446 K in case of exclusion the resonant spectral lines. Figure 4 explicitly demonstrates influence of the resonant spectral line to the determination of temperature of the laser induced plasma using Boltzmann plot method. Very significant changes in the obtained plasma temperature when inclusion the resonant spectral lines in the plot indicates that the resonant spectral lines greatly influence the accuracy of temperature estimation.

4. Conclusion
The estimation of temperature of the laser induced plasma produced on the clamshell sample using a Nd:YAG laser under air surrounding at low and high pressures of 760 Torr and 5 Torr, respectively was made by employing Boltzmann plot method. The acquired emission spectra were heavily dominated by calcium emission lines. There are 26 emission spectral lines classified into groups of atomic and ionic spectral lines has been successfully identified. The calcium atomic and ionic resonant spectral lines was identified including the resonant spectral lines. Boltzmann distribution function was plotted using all identified emission spectral lines including the resonant spectral lines, both atomic or ionic spectral lines, obtained under high and low pressures of the air surrounding. Boltzmann distribution function was also plotted using all identified emission spectral lines excluding the resonant emission lines. There is only one atomic resonant spectral line (Ca I 422.67 nm) and two ionic resonant spectral lines (Ca II 393.37 nm and Ca II 396.85 nm). It was found that when Boltzmann plot was made for all identified emission spectral lines including the resonant spectral lines, the plasma temperature greatly changes as compared to the case when the resonant spectral lines were excluded. When determination was made using all identified calcium atomic (Ca I) and calcium ionic (Ca II) emission spectral lines, the temperatures of the laser induced plasma produced in air at atmospheric pressure (760 Torr) was approximately 11891 K and 11114, respectively. While when estimation was made without inclusion the resonant spectral lines, the plasma temperature was far lower, about 7111 K and 3614 K, respectively. Similar tendency was also found in low pressure of 5 Torr, the plasma
temperature estimated using all atomic spectral lines (Ca I) and all ionic spectral lines (Ca II) was about 8057 K and 13418 K, respectively. While estimation without inclusion the resonant spectral lines, the plasma temperature at low pressure surrounding gas determined using atomic spectral (Ca I) and ionic emission spectral (Ca II) was about 5924 K and 4446 K, respectively. These results clearly demonstrate the crucial effect of the resonant spectral lines in accuracy of temperature estimation of the laser induced plasma using Boltzmann distribution function plot.

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