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Spectrometric Measurement of Plasma Parameters Utilizing the Target Ambient Gas O I & N I Atomic Lines in LIBS Experiment

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ABSTRACT

In this article, we shall report the results of the spectroscopic measurements of the plasma parameters utilizing the spectral lines emitted from the air atoms surrounding plasma (O I line at 777.19 nm and N I at 746.83 nm). The plasma was created via irradiation of plane solid aluminum target in open air by a high peak power Nd: YAG laser pulses at fundamental wavelength of 1064 nm. The emission spectra were recorded using Echelle type spectrograph in conjunction with a time gated ICCD camera at different delay time from 1 to 5 μs and at a fixed gate time of 1 μs. The plasma electron density was measured utilizing the Stark broadening of the N I and O I lines and then compared to the reference density as deduced from the optically thin H_α-line at 656.27 nm appeared in the same emission spectra. The results show that under our experimental conditions the air lines are subjected to moderate absorption. The plasma electron temperature was measured utilizing the relative spectral intensity of the air (O I to N I) lines after correcting their spectral radiance against absorption. The standard temperature was measured utilizing the Al II ionic lines. A comparison to the reference temperatures shows a very close agreement after correcting the emission spectral radiance of the air lines against self absorption, which emphasizes the importance of correction process.

Keywords: LIBS; Self Absorption; O I-N I Lines; Plasma Parameters

1. Introduction

The laser induced breakdown spectroscopy (LIBS) is the spectral analysis to the emitted light from the plasma generated via the interaction of pulsed laser with matter. Over the past decades the LIBS-technique becomes a distinguished applied analytical technique used in different application fields, because of its reliability, non-contact optical nature and its freedom from sample preparation [1]. Different fields of applications were already established e.g. elemental analysis [2-4], the quality of steel manufacturing [5], characterization of jewellery products [6,7], in soil studies [8,9], pulsed laser thin film deposition [10,11], the quality of pharmaceutical products [12], cleaning [13], culture heritage (cleaning of old papers, wood preservers, old paintings) [14-16] and *in situ* planetary exploration [17].

However, there are more investigations to improve the technique from the physical point of view; e.g. correction of the emitted spectral lines against optical thickness [18-22], improvement of the limit of detection [23], effect of ambient gas pressure on laser ablation process [24,25] and finally an enhancement of the LIBS signals through different suggested schemes e.g. Double pulse LIBS [26].

Two major parameters in LIBS namely electron density and temperature has to be given by experiment in what is called the plasma diagnostics. Different diagnostic techniques were established and utilized [27,28]. The most direct method is the optical emission spectroscopy (OES) in which the light emerging from the plasma is studied using a standard experimental setup.

Spectroscopically, the plasma electron temperature can be measured from the relative intensity of two or more optically thin lines having small separation in the emission wavelength and large separation in their upper excited states (Boltzmann plot method) [27]. Moreover, the ionization temperature can be calculated from the relative intensity of two or more lines originating from two consecutive ionization stages. This method enhances the precession in measuring temperature due to enhancement of the separation of the upper excited states by the ionization energy (Saha-Boltzmann plot) [28]. As an exten-

sion to the method, the relative intensity of two spectral lines emerging from different elements but belongs to the same ionization stage can be utilized in measurement of the plasma electron temperature provided that the relative abundance is known [29].

On the other hand, the electron density can be measured utilizing the Stark broadening of optically thin emitted spectral lines from neutral atoms or ions with the help of the precise Stark broadening parameters that can be found in different standard tables [30-33]. In a previous publication, it was suggested that the use the H line at a wavelength of 656.27 nm can garantee a standard measure to the electron density in the laser-plasma experiments in open air because of its inherent properties, *i.e*. the line was found optically thin under similar experimental conditions [34-36].

It is worth noting that, the lines emitted from the air atoms surrounding the plasma e.g. O I, N I, were previously utilized in the measurement of electron density but not the temperature [37-40].

In this research paper we will demonstrate the ability to assess the plasma diagnostics (measurement of electron density and temperature) via utilizing the lines emitted from the plasma surrounding air atoms, N I at 746.8 nm and O I at 777.2 nm after getting rid of the effect of self absorption.

2. Measurements of Plasma Parameters and the Effect of Absorption

2.1. Plasma Parameters

The plasma state (LTE-local thermodynamical equilibrium) can be determined knowing two plasma parameters namely the electron temperature and density. Both parameters should experimentally be measured utilizing the principle of the optical emission spectroscopy technique, assuming that the emitted light from the plasma is sufficiently influenced by the plasma parameters.

At an intermediate electron density range at concentration of (~10^{17} cm^{-3}) in the laser-plasma experiments, the electron density can be measured utilizing the Stark broadening of the spectral lines. This effect manifests itself on the form of Lorentzian broadening to the emitted radiation line of full width at the half of maximum (FWHM) $\Delta\lambda_o$ For neutral atoms, the following expression can be used, after neglecting the ion contribution to the broadening, to calculate the electron density, [31,32].

$$\Delta\lambda_o = \left(\frac{2\omega_s(\lambda, T_e)}{N_r} \right) n_e \qquad (1)$$

$\omega_s(\lambda, T_e)$ is the temperature dependant Stark broadening parameter of the line under investigation which can be found in tables [30,33]. N_r is the reference electron density; in the case of neutral atoms is 10^{16} cm^{-3}.

On the other hand, one can easily shows that at the LTE plasma state the electron temperature can be spectroscopically measured from the relative intensity of two lines belonging to two different elements in the same ionization stage, provided that the relative abundance (relative concentration) is known. In our case, the electron temperature will be evaluated utilizing the relative spectral radiance of O I line at 777.19 nm to the N I line at 746.83 nm, utilizing the good knowledge of the relative abundance of nitrogen to the oxygen in open air. The following expression can be used [29];

$$kT_e = \left(\frac{E_N - E_O}{\log\left(\left[3.72\, I_O Z_O C_O \lambda_O / A_O g_O \right] / \left[I_N Z_N C_N \lambda_N / A_N g_N \right] \right)} \right) \qquad (2)$$

Whereas, 3.72 is the relative abundance of the nitrogen to oxygen in the open air [29], I_O, I_N are the spectral line intensities measured at the central emission wavelengths, λ_O, λ_N are the transition wavelengths, C_O, C_N are the correction coefficients against relative response of the detection system (camera and spectrograph), while Z_O, Z_N are the partition functions. A_O, A_N & g_O, g_N and E_O, E_N are the transition probabilities, statistical weights and level energies of the upper states of both O I and N I lines used in the calculation, respectively. A generalization to Equation (2) to include several lines is known as multi-elemental Boltzmann plot [29].

2.2. Effect of Self Absorption on the Spectral Line Shape

Two major effects of self absorption on the emission spectral line shape can be recognized [30-33]. First, it acts to decrease the spectral line intensity because of the re-absorption to the number of the emerging photons from the inner core of the plasma medium. The second effect is that it acts to distort (enlarge) the Lorentzian FWHM component of the line [32]. In that case we say that the plasma become optically thick to the line [33].

Quantification to the amount of the plasma absorption (optical depth) to different emission spectral lines was already defined in terms of the coefficient (SA) [35]. It was expressed in terms of the ratio of the Lorentzian components of the line, $\Delta\lambda$ in the case if the line is optically thick (actually measured) to that if the line is optically thin *i.e*. in the limit of the extremely small concentration $\Delta\lambda_o$ [35]. Or better in terms of electron density derived from the optically thin hydrogen H -line to that measured from the optically thick suspected line $n_e(\text{line})$ [35];

$$SA = \left(\frac{\Delta\lambda}{\Delta\lambda_o} \right)^{\frac{1}{\alpha}} = \left(\frac{n_e(line)}{n_e(H_\alpha)} \right)^{\frac{1}{\alpha}} \text{ with } \alpha = 0.54 \qquad (3)$$

In this expression, $\Delta\lambda = 2\omega_s n_e(\text{line})$ is the Lorentzian FWHM of the spectral line subjected to absorption and $\Delta\lambda_o = 2\omega_s n_e^*(\text{line}) = 2\omega_s n_e(H_\alpha)$ is the Lorentzian FWHM of the same line, in the limit of optically thin condition. These FWHM's were replaced by the electron densities as measured from the line subjected to absorption (which will yield an extra large density value) to that from the optically thin H_α-line. It is vital to note that if a certain line is optically thin, it will yield the same electron density value as deduced from the H_α-line. It is worth noting that in Equation (3) we have been utilized the properties of the H_α-line present in the emission spectra to calculate the amount of absorption to any suspected spectral line. Moreover, this expression shows that this coefficient $1 \geq SA \geq 0$. SA reaches unity in the case of optically thin line and decreases to the limit of zero in the case of complete self absorbed line [35].

On other hand, the self absorption acts to decrease the number of the emerged photons contained in the line *i.e.* the spectral intensity of the emission line will be decreased. Therefore, the coefficient self absorption (SA) was expressed in terms of the relative spectral intensities of the same spectral line in the limits of optically thin $I_o(\lambda_o)$ to that of completely optically thick value $I(\lambda_o)$;

$$SA = \left(\frac{I(\lambda_o)}{I_o(\lambda_o)}\right) = \left(\frac{1-\exp(-\tau)}{\tau}\right) \qquad (4)$$

where $\tau = \int_{-\ell}^{0} \kappa(\lambda_o, T_e) \cdot d\ell$; is the optical depth of the plasma of length ℓ at the line center (λ_o), $\kappa(\lambda_o, T_e)$ is the linear absorption coefficient of the plasma at the line centre (λ_o) [41]. Equation 4 indicates that the SA varies from unity in case of pure optically thin line to the limit of zero in case of completely self absorbed line [35] and can be used to correct the spectral line intensity against the effect of self absorption.

3. Experimental Details

3.1. Experimental Setup

A Nd-YAG laser working at the wavelength of 1.06 μm was used to irradiate a polished solid aluminum target contains some traces of magnesium in a humid air and is shown in **Figure 1**. The data was acquired using an echelle type spectrograph (type Catalina, model SE200) with a resolving power of 2400 in conjunction with time integrated ICCD-camera (type Andor iStar) at the binning mode of 1 × 1. The laser energy was kept fixed at the level of 670 mJ at the target surface and was brought into focus with a 10 cm quartz convex lens. The emitted light from the plasma was collected using a 25 μm diameter quartz optical fiber cable positioned at distance of 12.5 mm normal to the laser axis and arranged to observe a circle of cross section of only 2 mm in front of the target. The identification of the different lines was carried out by spectrum analyzer software version 1.6. Other calculations were done using home-made routines under the MATLAB® package (Ver. 7). The relative response of the detection system was measured using a standard Deuterium Tungsten-Halogen calibration light source (type DH-2000-CAL). Over the entire experiment the gate time was kept at 1 μs and the delay time was changes in equal steps from 1 - 5 μs. The instrumental bandwidth was measured from the FWHM of the Hg lines and was found to be, at the wavelengths of interest, 0.12 ± 0.02 nm.

3.2. Calculation Procedures

An example of the plasma emission is given at **Figure 2**, at different delay times. One can notice the existence of the continuum emission appeared under the lines that is decreases in advance of the delay time. Therefore, at the start of the calculations, one should remove such component. This was achieved via utilizing a home-made

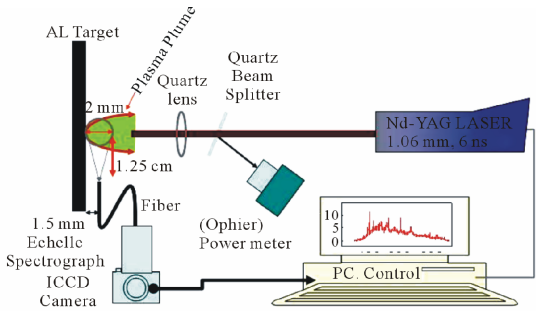

Figure 1. The experimental setup.

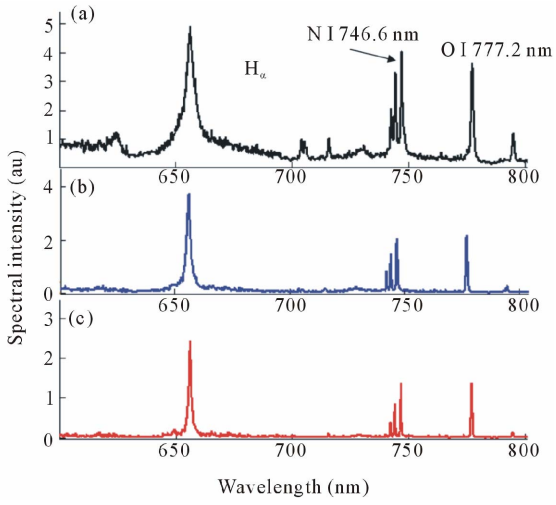

Figure 2. The emitted spectra from the air plasma at the long wavelength side recorded at a delay time of 1 μs (a), delay of 3 μs (b) and delay of 5 μs (c).

software that can fit the continuum to a polynomial function of the 8th order over the entire wavelength scale (200 - 1000 nm) and then we have carefully subtracted the resulted polynomial function (new base line) from the emitted spectrum.

On the other hand, in order to evaluate the electron density from a spectral line, a Voigt fitting procedures to the line was adopted. This Voigt profile contain the contribution from three effects, one is the Stark broadening which manifested itself on the form of a Lorentzian distribution of emitted light across the line profile. While the two other mechanisms are of Gaussian nature, one is resulted from the thermal motion of the emitting species at a kinetic temperature (Doppler effect) and the other, which can't be neglected, is the instrumental band-width which was measured using a low pressure Hg-calibration lamp and was found as ~0.12 nm. A convolution between these three functions was carried out using the MATLAB processing and the resulted Voigt line shape was compared to the experimentally measured line profile. The fitting is automated via a home-made computer program (Using MATLAB 7) and we have followed the principle of least square fitting between the theoretical profile and the measured line profile. The fitting is repeated at different electron density values used as an input independent free running parameter until the best fitting was achieved. At this step the program is automatically terminated and the values of the electron density from the three lines are recorded.

4. Results and Discussion

The emitted spectrum at the longer wavelength region from the O I lines at 777.2 nm and the N I lines at 746.8 nm as well as the H_α line at 656.27 nm are shown in **Figures 2(a)-(c)** at different delay times namely 1, 3 and 5 μs as indicated at the vertical scale.

Also, one can notice the existence of the continuum component under the lines of interest. This component is resulted from free-free transition in the plasma (bremsstrahlung) and free-bound transitions and displaying a decreasing trend as shown in **Figures 2(a)-(c)** as the delay time is changed from 1 to 5 μs. This continuum was carefully removed from each spectrum before utilizing the spectral lines shapes in the measurements of the plasma parameters.

The measurement of the electron density utilizing the Stark component of emission spectral line requires extraction of the Lorentzian component (FWHM) from the lines together with knowledge of the Stark broadening parameters for the different lines as given in **Table 1**. This was done with the help of fitting of the emitted line shape to the Voigt function. An example of the Voigt profile fitting to the emitted lines of the O I at 777.19 and the N I at 746.8 nm together with the H_α line at 6565.27 nm is shown in **Figures 3(a)-(c)** at different delay times namely 1, 3 and 5 μs. The fitting is automated via a home-made computer program (Using MATLAB 7). It is worth noting that, because of the finite symmetry of the H_α-line, especially at the early delay times, the fitting to the symmetric Voigt function is almost limited as shown at a delay of 1 μsec.

Table 1. Atomic parameters of the used spectral lines.

(nm)	$\omega_s \times 10^{-3}$ (nm)	E_u (eV)	g	$A \times 10^7$ (sec^{-1})
O I 777.19	**3.15**	**10.74**	**15**	**3.69**
N I 746.83	**4.75**	**11.99**	**4**	**1.93**

ω_s is the Stark broadening parameter, g is the statistical weight of the upper state and A is the transition probability

With the help of Equation (1), the electron densities from the different lines were calculated. The temporal variation of the measured electron densities with delay time is plotted and shown at **Figure 4**. We noticed that the measured electron density utilizing the H line gives the lowest values, which means that the lines originated from the ambient air atoms O I, N I are subjected to some absorption. Because of the nature of the spatially integrated method of detection of the light one can attribute this absorption to passage of at least half of the photons from the air lines across the plasma body in its way to the spectrograph. Moreover, the deduced values of the electron densities from the O I and N I atoms is shown to display a decreasing trend with delay time at different rates and finally approaching the standard density values as measured utilizing the H_α line, which means that the lines are drifting toward the optically thin values with delay time or better with the cooling of the plasma. This fact can better understand in terms of the weak absorption of the cold plasma to the lines at the infrared region as given in Ref. [41].

Figure 5 demonstrates the variation of the calculated coefficients of the self absorption of the plasma to the air O I, N I lines with delay time. It is noticed that the lines are showing a less absorption in advance with delay time. Moreover, the amount of absorption to the O I line is a bit larger than that of the N I by a factor of 2, regardless that the relative abundance of the nitrogen to oxygen gas is nearly 4. This can be explained in terms of the absorption oscillator strength of both lines (0.468 for the O I at 777.2 nm and 0.109 at the N I 746.8 nm).

Figure 6 shows the Boltzmann plot utilizing the Al II ionic lines appeared in the same spectra at an arbitrary delay time of 1 μs, indicating a reference electron temperature of 1.14 eV. The overall variation of reference electron temperature utilizing the Al II lines is shown in

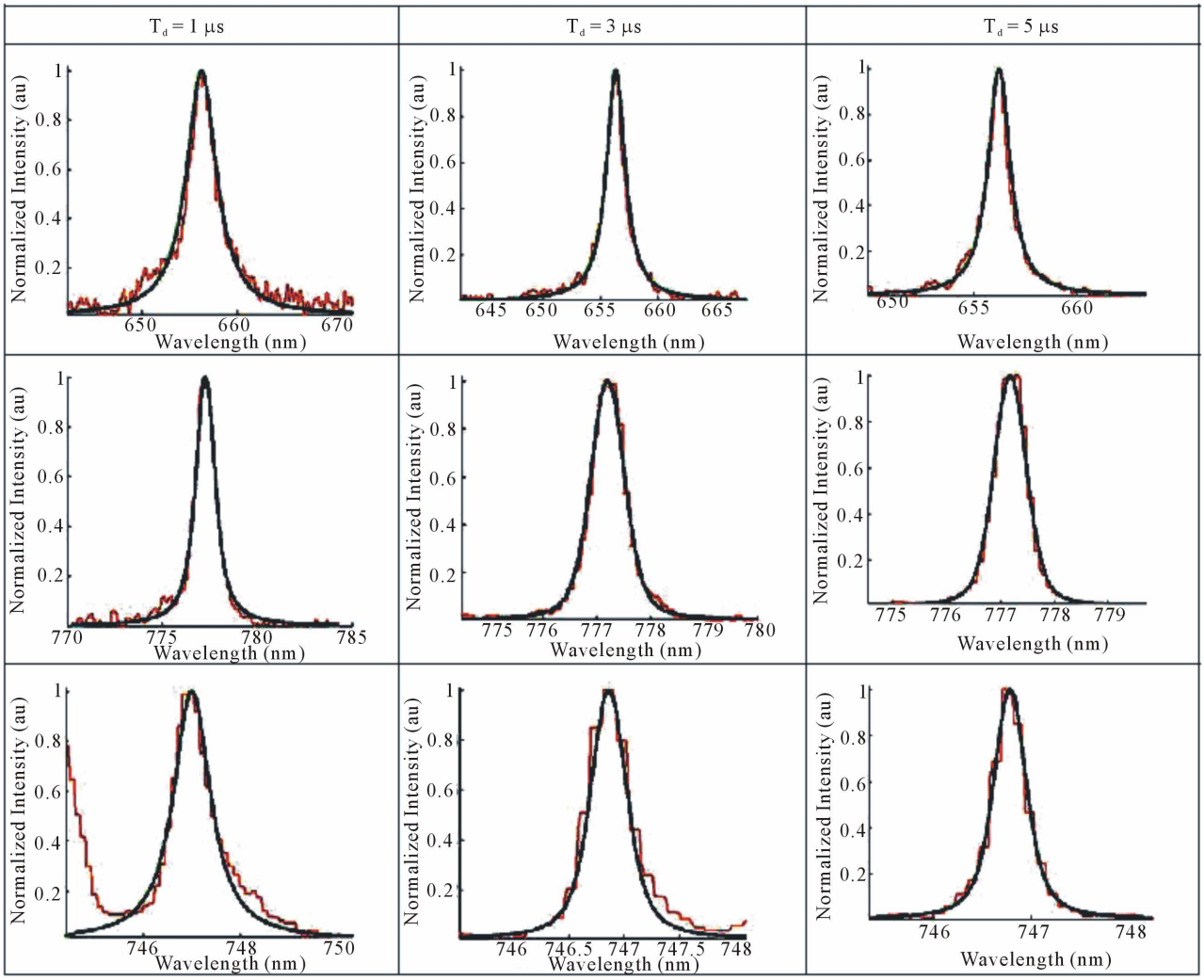

Figure 3. Voigt fitting to different spectral lines O I, N I and Hα at a delay time of 1 μs (a), delay of 3 μs (b) and delay of 5 μs (c).

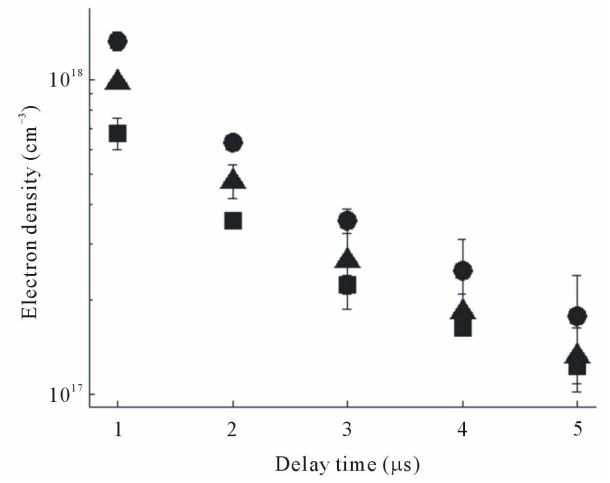

Figure 4. The temporal variation of the measured electron density from the H_α-line (squares), from the N I line (Triangles) and from the O I (solid circles).

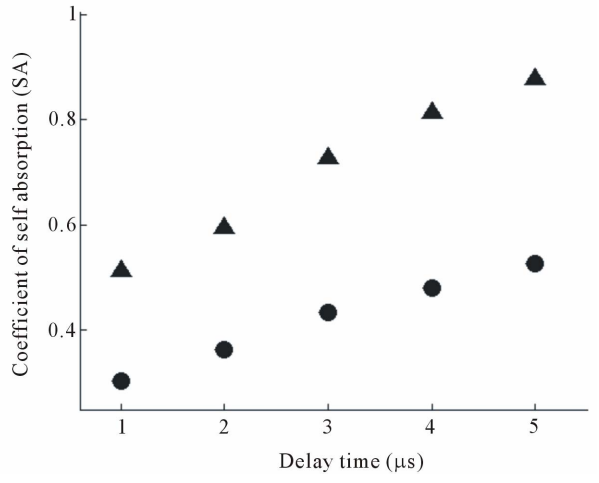

Figure 5. Shown is the temporal variation of the coefficients of self absorption to the N I line (triangles) and O I line (solid circles).

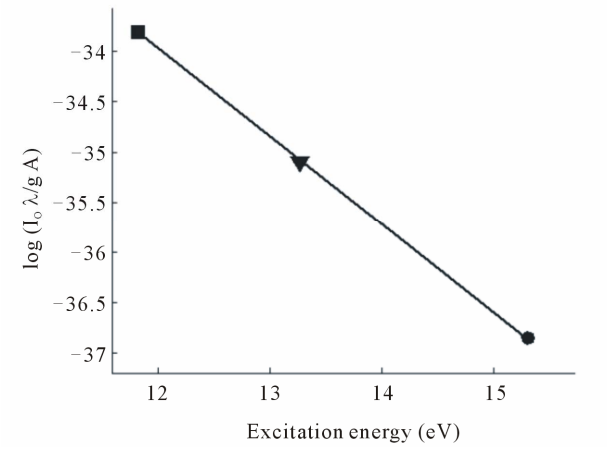

Figure 6. This figure demonstrates the Boltzmann plot utilizing the Al II ionic lines (281.6 nm (square), 466.2 nm (inverted triangle) and 358.6 nm (solid circle) taken at an arbitrary delay and gate times of 1 μs. The slope of the best fit straight line indicated temperature of 1.14 eV.

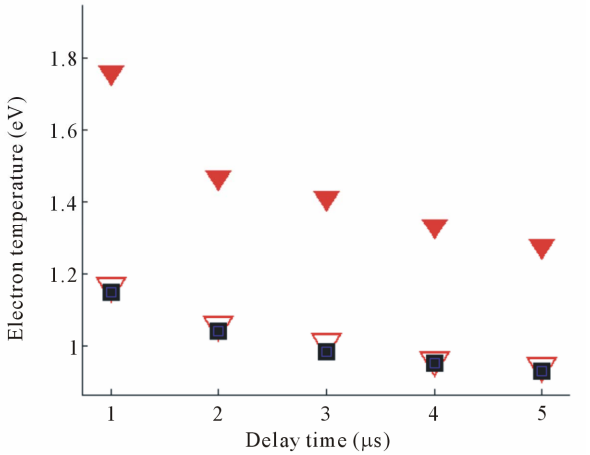

Figure 7. The temporal variation of the plasma electron temperature utilizing the relative spectral intensity of the O I line at 777.2 nm to the N I line at 746.6 nm in comparison to the standard reference temperature utilizing the Al II ionic lines (solid black squares) both before correction (solid inverted red triangles) and after correction against the effect of self absorption (open inverted triangles).

Figure 7 at the different delay times (solid squares).

In our analysis we have assumed the existence of the plasma species in a local thermodynamical equilibrium (LTE) with the ambient air spices. Therefore, we have compared the measured electron temperature evaluated from the air atoms (O I & N I-atomic lines) utilizing Equation (2) to the reference temperature values as measured from the Al II ionic lines. **Figure 7** shows the result of this comparison at different delay times without correction of the spectral lines intensities from the air atoms (O I, N I) against effect of absorption of the plasma (solid red inverted triangles) and after correction as made utilizing Equation (4) (red open inverted triangles). One can notice the relatively insignificant large values of the electron temperature as measured from the air atoms without correction against absorption. But after applying the correction procedures to the spectral line intensities, there is a very close agreement between the temperatures from the air atoms and the standard reference temperatures as deduced utilizing the spectral intensities emitted by the Al II lines.

It is worth noting that, a limitation on the use of this method can be provided as following;

1) If the H_α-line becomes optically thick. This condition might exist if the concentration of the water vapor around the target becomes relatively large [34].

2) At the early delay time of 0 μs, the H_α-line was inspected I a separate publication and was found to contain some optical thickness, and in that case the line cannot be used any more [36].

5. Conclusion

These results confirms the reliability of using of the either of O I, N I lines at wavelengths of 777.2, 746.8 nm respectively, to measure to the electron density and temperature to a plasma generated via the interaction of laser with solid target in air. This will gives rise to the question upon the coupling of the plasma generated from aluminum target and the surrounding air atoms. This mixing was confirmed for the hydrogen in a previous study at Ref. [40]. This mechanism concerning the origin of the emission from the oxygen and nitrogen atoms will be subjected to further experimental investigation in the future.

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