Determination of excitation temperature in laser-induced plasmas using columnar density Saha-Boltzmann plot

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Original Article

Abstract

In exploiting the analytical capabilities of plasma-based spectroscopy method, the evaluation of plasma parameters, particularly the plasma temperature, is a crucial step. In this work, a modified Saha-Boltzmann plot, which uses the columnar densities of atomic and ionic ground levels, is utilized to calculate the plasma temperature in a laser-induced plasma from an aluminum alloy target. The columnar densities are here calculated by quantifying the self-absorption of resonance lines. It is demonstrated that this is a promising method for accurate determination of plasma temperature. To validate the capability of this technique, plasma emission is measured at different gate delay times. For each delay, excitation temperature is calculated both by the conventional Saha-Boltzmann plot (by using the excited states) and by exploiting the new Columnar Density Saha–Boltzmann (CD-SB) plot. The results suggest that at later times of the plasma evolution, the CD-SB plot can be more suitable for the determination of plasma temperature than conventional Saha-Boltzmann plot. These findings provide a new approach for physical characterization of plasmas and give access to a wealth of information about the state of plasma.

Introduction

Over the past decades, laser-induced breakdown spectroscopy (LIBS) technique has matured into an interesting, simple, sensitive, and rapid tool for the quantitative and qualitative analyses of a large group of samples [1–5]. It has been used for a wide range of applications including industrial [6,7], medical [8,9], forensic...
[10,11], and cultural heritage fields [12,13]. In this technique, a high-power laser pulse is used to create a plasma on the sample surface. Spectroscopic analysis of the plasma emission can provide valuable information about sample composition. A more detailed description of the LIBS technique has been reported in the literature [1,14–16].

To exploit the analytical capabilities of the LIBS technique, the characterization of the LIBS plasma, i.e. the evaluation of plasma parameters, is a crucial step. The physical characterization of plasma and diagnostic approaches for the evaluation of plasma parameters have been the focus of several publications. It is well known that among the plasma parameters, plasma temperature plays an important role [17–24]. The knowledge of plasma temperature has a great significance in describing other plasma characteristics such as the relative populations of energy levels and the velocity distribution of particles [16]. In particular, in applying the CF-LIBS procedure introduced by Ciucci et al. in Ref. [25] for the quantitative analysis of plasma composition, the accurate determination of the plasma electron temperature is crucial. Although several spectroscopic methods exist for determining the excitation temperature in LIBS, Boltzmann plot and Saha-Boltzmann plot methods [26] are by far the most used. However, it must be emphasized that both of these methods have important limitations, particularly at long delay times when the plasma becomes cooler and the population of atoms in the lower state increases. In these conditions, the emission originates mainly from resonance transitions or from low-lying energy levels which are more prone to self-absorption, resulting in an inaccurate estimation of the plasma temperature. Furthermore, at long delay times, ionic lines tend to disappear because of ion recombination, making the Saha-Boltzmann method hardly exploitable. It should also be kept in mind that both Boltzmann and Saha-Boltzmann plot methods have an additional intrinsic limitation. Both methods, in fact, make use of the population of excited states and usually rely on the hypothesis that plasma is in Local Thermodynamic Equilibrium (LTE), which extends the validity of temperature calculation to all the energy levels. Actually, this approach may be inaccurate since ground levels are largely the most populated levels, slight deviations from LTE or small uncertainties in determining the population of excited levels can lead to significant errors in the description of excitation and ionization equilibrium.

In the following section, it is shown that the above-mentioned limitation is overcome by using a columnar density Saha-Boltzmann plot approach since columnar densities of ground levels can be directly calculated. Moreover, the presence of strong self-absorption in resonance lines guarantees the LTE of the atomic system. Therefore, this approach, originally introduced by Cristofoletti and Tognoni [27], opens up a new way to calculate plasma temperature accurately.

### Methodology

In this section, the basic theoretical framework for calculating the ground-level temperature of an element through a modified Saha-Boltzmann plot called ‘Columnar Density Saha–Boltzmann (CD-SB)’ plot is outlined. A more detailed description of this method is available in Ref. [27].

Similar to other LIBS methodologies, in the CD-SB plot method it is assumed that plasma is spatially homogenous in the measurement time interval. In order to obtain ground level temperature, the ratios of number densities between successive ionization stages can be expressed by the Saha–Eggert equation [28]:

\[
n_e^i / n_e^j = (2\pi m_i k_B T)^{3/2} \frac{2U_i^j(T)}{\hbar^3} e^{-\frac{E_{i}}{k_B T}}
\]

where superscripts I and II respectively refer to the neutral and singly ionized species of the element, \( U_i \) is the partition function of the species (dimensionless), \( n_e \) (cm\(^{-3}\)) is the free electron density, \( E_{i} \) (eV) is the first ionization energy of the element, \( T \) (K) represents the electron temperature, \( h \) (eV s) is the Planck constant, \( k_B \) (eV K\(^{-1}\)) is the Boltzmann constant, and \( m_e \) (g) is the electron mass.

Eq. (1) can be written in terms of the number density of the lower level of an ionic transition:

\[
n_e^i = \frac{(2\pi m_i k_B T)^{3/2}}{n_e^j \hbar^3} \frac{2U_j^i(T)}{\sqrt{ \frac{e^{\frac{E_{i}}{k_B T}} - 1}{e^{\frac{E_{i}}{k_B T}} + 1} }}
\]

where \( E_j^i \) (eV) is the lower level energy of the ionic transition and \( g_e^i \) is the degeneracy of the i level. Multiplying both sides of Eq. (2) by the optical path length \( l \) and taking the natural logarithm, the coordinates of the spectral lines in the columnar density Saha–Boltzmann plane are given:

\[
y = ml + b
\]

\[
where \ b = \ln \left( \frac{n_e^i \xi}{U_j^i(T)} \right) \text{ and } m = -\frac{1}{k_B T}
\]

\[
x = \begin{cases} E_j^i & \text{for neutral lines} \\ E_j^i + E_{ion} & \text{for ionic lines} \end{cases}
\]

\[
y = \begin{cases} \ln \left( \frac{\xi}{\tau_j} \right) & \text{for neutral lines} \\ \ln \left( \frac{\tau_j}{\xi} \right) - \ln \left( \frac{2\pi m_i k_B T^2 \hbar^2}{n_e^j \hbar c \tau_j} \right) & \text{for ionic lines} \end{cases}
\]

This modified Saha–Boltzmann expression is similar to the classical Saha–Boltzmann plot, the slope of the linear plot being related to the plasma temperature. Comparing it with the conventional Saha–Boltzmann plot, however, it is evident that some differences exist between them in the calculation of plasma temperature. In particular, variable \( y \) is determined by using the columnar density \( n(n_i) \) rather than line intensity for both atomic and ionic lines of the desired elements. In addition, coordinate \( x \) represents the lower (rather than the upper) level energy values. For the construction of the CD-SB plot, electron density and also spectroscopic data for both atomic and ionic lines should be available. In principle, the plasma electron temperature should be determined iteratively, because of the explicit dependence of \( y \) on \( T \) in Eq. (6). However, the iteration of the calculation procedure is not needed in practice since the dependence of \( y \) on \( T \) is weak and involves only a logarithmic term.

As seen in Eq. (6), the columnar density \( n(n_i) \) must be known for both atomic and ionic lines of the elements of interest. A simple method is presented below to calculate columnar density which is based on measuring the self-absorption coefficient of optically thick lines. The equation of radiative transfer is considered as follows [29]:

\[
I(\lambda) = \frac{8\pi c}{\lambda_0^2} \frac{n_e}{n_i \xi} (1 - e^{-k(\lambda)l})
\]

where \( i \) and \( j \) respectively refer to the lower and upper levels of the transition, \( I(\lambda) \) is the spectral line intensity (erg s\(^{-1}\) cm\(^{-3}\)), \( \lambda_0 \) is the central wavelength (cm) of the transition, \( c \) is the speed of light (cm s\(^{-1}\)), \( n_e, n_i, \xi, \xi_i \) and \( \xi_i \xi \) are the number densities (cm\(^{-3}\)) and degeneracies (dimensionless) of the levels, \( k(\lambda) \) is the absorption coefficient (cm\(^{-1}\)), and \( l \) is the absorption path length (cm).

In Eq. (7), the value of \( k(\lambda)l \) (the optical depth) is crucial in determining the self-absorption degree of the emission line and can be expressed as
where \( f \) is the line oscillator strength (dimensionless) and \( L(\lambda) \) is the normalized spectral emission profile.

In order to quantify the strength of self-absorption on an emission spectral line, the SA parameter can be used, defined as the ratio of the spectral peak height to the expected peak magnitude in the optical thin regime [30], i.e.

\[
SA = \frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l}
\]  

SA value is close to 1 if the line is thin and tends to zero in significant self-absorption conditions. The optical depth value \( k(\lambda_0)l \) can thus be estimated by measuring the SA parameter. Among the various methods proposed to measure SA, the line width ratio method of El-Sherbini et al. [31] is utilized here:

\[
\frac{\Delta \lambda}{\Delta \lambda_0} = (SA)^{\alpha}
\]  

where \( \Delta \lambda \) is the FWHM of the measured emission line, \( \Delta \lambda_0 \) is the expected FWHM of line profile in optically thin conditions, and \( \alpha = -0.54 \) for Lorentzian line profiles. In typical LIBS plasma conditions, the Stark effect is the dominating line broadening mechanism and the value of \( \Delta \lambda_0 \) can thus be calculated using the relation

\[
\Delta \lambda_0 = 2w_s \left( \frac{\lambda}{10^4} \right)
\]

where \( w_s \) is the half-width Stark parameter of the line [32], and the electron number density can be obtained using, for example, the Stark broadening of the hydrogen Balmer alpha line at 656.3 nm, as suggested in Ref. [16]. The use of the H\(_a\) line for the calculation of the electron density has the advantage of providing a result which is not affected by the self-absorption effect.

Finally, the value of the optical depth \( k(\lambda_0)l \) can be numerically evaluated from the SA parameter by utilizing Eq. (9). It is evident from the relation that the estimation of optical depth is more accurate when the emission line is more broadened, i.e. when the self-absorption is high. In the last step, by rewriting Eq. (8) in practical units, columnar density \((cm^{-2})\) can be estimated by the following equation

\[
nl = 1.77 \frac{\Delta \lambda_0}{\Delta \lambda} k(\lambda_0)l \times 10^{20}
\]

where \( \lambda_0 \) and \( \Delta \lambda_0 \) are in Angstrom units.

**Experimental setup**

A schematic picture of the experimental setup used in the current work is shown in Fig. 1. A Q-switched Nd-YAG laser (Continuum, Surelite III: 60 mJ at 1064 nm, pulse duration of 10 ns, and repetition rate of 5 Hz) was employed. All the measurements were performed in air at room temperature. A lens with a focal length of 50 mm was used to focus the laser pulse on the sample surface. The laser and ICCD camera were triggered and controlled by an independent pulse-delay generator (DG 535, Stanford Research System). The spatially integrated LIBS signal was collected using an optical fiber placed at an angle of 45° with respect to the normal of the sample surface. Emission spectra were acquired using an Echelle spectrograph (Catalina, model SE 200) with a spectral range from 220 nm to 850 nm, coupled to an intensified CCD camera (Andor, model iStar DH734-18F). The resolving power of the spectrograph was \( \lambda/\Delta \lambda = 2100 \). The detector gate delay was varied from 0.5 to 5 \( \mu \)s while the gate width was fixed at 0.5 \( \mu \)s. The instrumental profile broadening was measured using spectral lines emitted from a low-pressure argon–mercury lamp. To enhance the signal-to-noise ratio, data acquisition was performed by averaging over 80 laser pulses, delivering 40 pulses at two different points of the sample’s surface.

The sample used in the present study was a standard aluminum alloy (Al 7079) with a composition of Al (89.9%), Mg (4.4%), Zn (4.1%), Fe (0.3%), Cu (0.67%) and minor constituents (Si, Mn, Cr, Ti, Pb) with a weight percentage of less than 0.3%.

![Fig. 1. Scheme of the experimental set-up.](image-url)
Results

The CD-SB method was used for obtaining the ground state temperature which was compared at different delay times with the excitation temperature of plasma calculated by means of the conventional Saha–Boltzmann plot. Three strongly self-absorbed Mg emission lines were used to estimate the ground state temperature. These lines are resonance lines and have high transition probabilities, as shown in Table 1, and therefore are suitable candidates for the calculation of line optical depths and columnar densities of ground states. Indeed, a good knowledge of the Stark width and oscillator strength values for these lines is also an indispensable ingredient for building a reliable CD-SB plot.

A typical spectrum of the Al 7079 sample including both Mg I and Mg II emission lines is presented in Fig. 2, in the wavelength region from 279 to 286 nm. The absence of any dip at the center of the line profiles confirms that self-reversal is negligible and therefore suggests that plasma inhomogeneity is not pronounced in the optimized conditions of the present experiment.

In the CD-SB plot method, the spectral line fitting procedure is the most critical step in calculating the line width. For this purpose, the spectral line profile is fitted by pseudo-Voigt function and Gaussian instrumental broadening is then deconvolved from the measured line width in order to obtain the FWHM of the self-absorbed line, from which the SA value and optical depth can be obtained. The values of SA parameter and columnar density for Mg I (285.2 nm) and Mg II (280.3 nm) have been reported as a function of gate delay in Fig. 3. It is evident that for both lines and for all gate delays, SA values are much smaller than 1, confirming that the Mg lines are suffering from strong self-absorption in the conditions of measurement. Furthermore, it is seen that the self-absorption coefficient of the neutral Mg line rapidly decays with time and reaches a minimum value for the longest gate delay time here investigated. However, a different trend is observed for the ionic line shown in Fig. 3b, in which self-absorption coefficient values remain almost the same, independent of the variation of the gate delay. Accordingly, different behaviors of the values of the columnar density have been obtained. As can be seen, columnar density values of the neutral Mg line show an increasing trend during plasma evolution. On the contrary, as expected, in the case of singly-ionized line, columnar density decreases with time, due to the decrease of the ion/atoms ratio at long delay times associated with the cooling of the plasma.

The calculated optical depth and columnar density of Mg lines allow us to build the CD-SB plot shown in Fig. 4. As in the classical Saha–Boltzmann plot, the plasma temperature can be obtained from the slope of the line best fitting the experimental points.

Excitation temperature was also determined by using the conventional SB plot from a set of neutral and ionized lines of Mg which do not suffer from strong self-absorption. In Table 2, the Mg spectral lines used for the calculation are listed along with their spectroscopic parameters taken from the NIST atomic database. The estimated uncertainty for the transition probabilities of the lines reported in Table 2 is lower than 3%. The temporal behavior of the plasma temperature is illustrated in Fig. 5. Data points are the average of 80 laser pulses acquired at two different locations on the sample surface. The last version of the LIBS++ software, realized by ALS Lab in Pisa, was used for the analysis of LIBS spectra.

In Fig. 5, it can be seen that the two temperature values, calculated by resonance transitions or high-lying energy transitions, behave in a similar way. Moreover, for each gate delay time, both plasma temperature values are comparable validating the CD-SB approach. However, for the longest gate delay, only the modified SB plot could be utilized. Due to lack of ionization lines from high-lying levels, the conventional SB method could not be used to calculate the temperature. It is therefore clear that at later times, the CD-SB plot can be introduced as an efficient method for determining plasma temperature.

Discussion

Considerations on local thermal equilibrium

It is worth mentioning that both methods are based on the hypothesis that in the observed time window the plasma is in local thermal equilibrium (LTE). When the conventional SB plot is utilized, one has to check the validity of LTE conditions to ensure that the calculated temperature in the distribution of all the energy levels is the same one value which determines the ionization equilibrium. For this purpose, the measured electron density is usually compared with the electron number density required to fulfill the McWhirter criterion which is a necessary condition for LTE, as expressed by the relation below:

\[
    n_e > \frac{2.55 \times 10^{11}}{g_i T^2 (\Delta E_{ij})^3}
\]

where \( g_i \) is the Gaunt factor averaged over the electron energy distribution function and \( \Delta E_{ij} \) is the largest energy gap between the

![Fig. 2. Typical spectrum of the aluminum alloy 7079 in the region of interest, showing resonance Mg I and Mg II lines.](Image)
upper and lower energy states (usually corresponding to the allowed transition between the ground state and the first excited state). $\Delta E_g$ and $T$ are expressed in eV and K, respectively.

In the present case, for gate delays from 0.5 to 5 $\mu$s, the $n_e$ values were 4.16, 2.4, 1.6, 0.83, and $0.55 \times 10^{17}$ cm$^{-3}$. Considering $\Delta E \approx 4.34$ eV for the resonant neutral line Mg I 285.2 nm, the lower limit value of the electron density given by Eq. (12) is less than $4 \times 10^{16}$ cm$^{-3}$, suggesting that LTE could be verified.

However, the McWhirter criterion is a necessary but not sufficient condition for ensuring the LTE condition. Therefore, a further checking of additional conditions related to the temporal evolution of the plasma and its inhomogeneity effects is needed to verify that LTE holds [35]. This procedure needs a suitable experimental apparatus which makes the approach usually difficult to implement in most LIBS measurements.

Here, the attention is devoted to the CD-SB method. It has already been remarked that this approach is more accurate when the resonance emission lines are strongly self-absorbed. This usually occurs for matrix or major elements and/or for long delay times of acquisition. Furthermore, when the CD-SB is used, even the experimental conditions can be chosen with the precise aim of maximizing self-absorption in order to apply this approach. In optically-thick plasma conditions, the LTE approximation is usually fulfilled, and this guarantees a-priori the validity of the CD-SB approach. The reason is that in thick line conditions, self-absorption tends to repopulate the upper level of the transition, re-equilibrating the level population toward LTE. In fact, in the case of complete self-absorption (full thermal equilibrium blackbody conditions), the intensity of the lines saturates at the level of blackbody emission. Consequently, the value of electron density needed to guarantee LTE equilibrium through collisional excitation is relaxed by 1–2 orders of magnitude with respect to the McWhirter criterion [36,37]. The same mechanism tends to reduce the time needed to reach LTE equilibrium, relaxing also the LTE conditions related to time evolution and inhomogeneity by the same magnitude [36,37]. It is well known that the ground states are the levels which are more prone to deviate from LTE, because of the larger energy gap which separates them from the excited levels. In CD-SB approach, resonance lines are usually utilized, and self-absorption assures the LTE equilibrium between ground and resonance states. This usually implies (unless metastable states play a determinant role) that LTE is valid for the whole system including the ionization equilibrium. This makes the CD-SB approach intrinsically correct since in the conditions that it can be applied, LTE is certainly verified.

### Considerations on the accuracy of the CD-SB method

A discussion on the accuracy of the plasma temperature determination is needed here. In the application of conventional Saha-Boltzmann plot for determining excited state temperature, numerous studies have discussed the accuracy of the determined plasma temperature [16,38]. The accuracy of the measurement depends on the uncertainties of transition probabilities, relative calibration of the detection system, and the statistical errors of line intensity calculations. In addition, special attention should be paid to the selection of the spectral lines and avoidance of self-absorption effects. Finally, as discussed above, temperature determination is strongly affected by deviations from LTE conditions which are hard to evaluate.

On the other hand, the accuracy of the plasma temperature measured using the columnar density approach is influenced by the uncertainties of the Stark broadening coefficient, the SA parameter, the oscillator strength, and the free electron density [27]. It is worth mentioning that the last two sources of indetermination are common to both methods. The uncertainty on the value of Stark coefficients can sometimes be as large as 50%. However, accuracy is usually much higher for resonant and/or strong lines, with errors below 10–20%, which is therefore acceptable for the analysis. The
experimental error on the SA value is also a significant source of uncertainty, often affected by inhomogeneity in the plasma. However, the SA value can be directly measured, using e.g. the duplicating mirror approach [39] which is less affected by the uncertainties deriving from the fitting of the line profile. Another potential source of error may be the spatial inhomogeneity of the plasma which can affect the applicability of LIBS methods in general. In fact, typical LIBS plasmas have some degree of inhomogeneity, in which case the plasma is described by apparent parameter values corresponding to average local values. Practically, the quantification of inhomogeneity effects in LIP is not a simple task since it needs a suitable experimental apparatus. However, the spatially resolved spectroscopic measurements using different configurations of collection optics and detection systems is the most common way of evaluating plasma homogeneity. This issue has been the subject of several experimental studies [40–43]. The presence of self-reversal behavior in LIBS spectra, on the other hand, can be considered as the preliminary evidence of having a large spatial gradient of species inside the plasma. The above considerations highlight the need to use the optimal experimental conditions to minimize errors due to the plasma inhomogeneity effect. Luckily, deviations from homogeneity approximations can be negligible at later times of plasma evolution. In fact, at these times, ambient air strongly affects the dynamics of plasma expansion and emission, resulting in plasma volume saturation because of ambient air confinement and stabilization of atom/ion density due to the stopping of plasma expansion. Interestingly, these conditions are attributed to the smaller spatial gradients of the LIP and better fulfillment of plasma homogeneity approximation as shown by Aguilera et al. [44].

It is also worth mentioning that the CD-SB plot method does not make use of the spectral efficiency of the detection system, which is often a significant source of error, in particular when spectral lines are measured in different regions of the spectrum. Finally, the accuracy is not limited by the possible violation of the LTE approximation, which in this case is intrinsically verified, and the method makes use of the population of the atomic and ionic ground states without extrapolations from the population of high-lying excited states. In these conditions, therefore, whenever Stark parameters are accurately known and SA value can be carefully determined, the CD-SB plot can provide a more accurate and reliable value for plasma excitation temperature.

### Conclusions

In this work, laser-induced plasmas were characterized by means of the Columnar Density Saha-Boltzmann (CD-SB) plot method, a modified Saha–Boltzmann plot approach that uses the columnar densities of the species instead of their line intensities. It has been shown that the spatially-averaged electron temperature of the plasma can be calculated straightforwardly by employing the columnar density of resonance lines. In fact, whenever self-absorption of emission lines is precisely evaluated via the SA parameter, the optical depth and columnar density of the emitting species can be obtained and used to calculate the plasma temperature. The temperatures of the ground and excited states were studied at different delay times after plasma formation and it was observed that they almost have the same value which experimentally validates the proposed approach. At long delay times, when thin ionization lines from highly excited levels are barely observable, the CD-SB method is still able to measure the plasma temperature. The CD-SB plot approach proposed here is thus a viable alternative to conventional Saha–Boltzmann plot for the determination of plasma temperature. Furthermore, it was shown that in many cases of interest, the CD-SB approach can be more accurate than conventional Saha–Boltzmann plot since its application is not affected by possible breaches of the LTE approximation and by the uncertainty related to the spectral efficiency of the detection system.

### Conflict of interest

The authors have declared no conflict of interest.

### Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.
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