

# Evaluation of self-absorption coefficients of aluminum emission lines in laser-induced breakdown spectroscopy measurements

A.M. El Sherbini<sup>a</sup>, Th.M. El Sherbini<sup>a</sup>, H. Hegazy<sup>b</sup>, G. Cristoforetti<sup>c,\*</sup>, S. Legnaioli<sup>c</sup>,  
V. Palleschi<sup>c</sup>, L. Pardini<sup>c</sup>, A. Salvetti<sup>c</sup>, E. Tognoni<sup>c</sup>

<sup>a</sup> *Laboratory of Lasers and New Materials, Physics Department, Faculty of Science, Cairo University, Egypt*

<sup>b</sup> *Atomic Energy Authority, Nuclear Research Center, Plasma Physics Department, Enchass 13759, Egypt*

<sup>c</sup> *Applied Laser Spectroscopy Laboratory, Institute for Chemical-Physical Processes Research Area of National Research Council, Via G. Moruzzi, 1 56124 Pisa, Italy*

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## Abstract

In quantitative Laser Induced Breakdown Spectroscopy (LIBS) measurements it is essential to account for the effect of self-absorption on the emission lines intensity. In order to quantify this effect, in this paper we propose a simple method for evaluating the ratio between the actual measured line intensity and the intensity expected in absence of self-absorption and, if necessary, correcting the effect of self-absorption on line intensity. The method, based on a homogeneous plasma model, is applicable when the plasma electron density is known and in particular to lines whose Stark broadening parameter is available.

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## 1. Introduction

The problem of self-absorption in optical emission spectroscopy has been the subject of a number of papers, in recent years; several methods for evaluating the reduction in line intensity due to this effect have been proposed. Omenetto et al. experimentally studied the self-absorption phenomenon in Inductively Coupled Plasma (ICP) [1] and discussed the main equations describing the self-absorption process in a flame [2]. The results were interpreted by means of the Curve of Growth (COG) method [3, 4], which later Gornushkin et al. [5] also applied to Laser-Induced Breakdown Spectroscopy (LIBS). The same COG method was used by Bulajic et al. [6] and Corsi et al. [7] for correcting self-absorption effect in calibration-free LIBS (CF-LIBS) [8]. Lazic et al. [9] presented a simple model for constructing calibration curves of intensity from a thick homogenous plasma. Aragón et al. [10] studied the influence

of the optical depth on spectral line emission from laser-induced plasmas. More recently, several authors also faced the problems of modeling laser-induced plasma inhomogeneities to account for self-reversal phenomena [11–13] produced by the presence of cold absorbing atoms in the periphery of the plasma.

All the mentioned approaches rely on some modeling of the laser-induced plasma parameters (size, temperature, electron density) for obtaining information about the effect of self-absorption on the emission lines. However, the complexity of the laser–target interaction mechanism and the fastness of the plasma evolution reduce the applicability of most of these models, in real situations, to quantitative analytical LIBS measurements.

Therefore, a method allowing the evaluation of self absorption effect directly from the analysis of the LIBS spectrum could be extremely useful in the experimental practice. This is the purpose of the method presented in this paper: in fact, provided the electron density can be derived from the spectrum, the measurement of the Lorentzian width of the emission line allows one to evaluate the self-absorption effect.

\* Corresponding author. Tel.: +39 050 3152222; fax: +39 050 3152230.

E-mail address: gabriele@ipcf.cnr.it (G. Cristoforetti).

## 2. Line emission in the presence of self-absorption

The model proposed here assumes a plasma homogenous where temperature and electron density gradients, and in particular their effect on line profiles, are neglected.

The emission intensity ( $\text{erg s}^{-1} \text{cm}^{-3}$ ) along the line profile corresponding to the transition between two atomic or ionic levels  $j$  and  $i$  (upper and lower, respectively) is [14]

$$I(\lambda) = \frac{8\pi hc^2}{\lambda_0^5} \frac{n_j}{n_i} \frac{g_i}{g_j} \left(1 - e^{-k(\lambda)l}\right) \quad (1)$$

where  $h$  is the Planck's constant ( $\text{erg s}$ ),  $c$  is the speed of light ( $\text{cm s}^{-1}$ ),  $\lambda_0$  is the central wavelength ( $\text{cm}$ ) of the transition,  $n_j$ ,  $n_i$ ,  $g_j$  and  $g_i$  are the number densities ( $\text{cm}^{-3}$ ) and the degeneracies of the upper and lower levels, respectively,  $k(\lambda)$  is the absorption coefficient ( $\text{cm}^{-1}$ ) and  $l$  is the absorption path length ( $\text{cm}$ ).

In general, the absorption coefficient  $k(\lambda)$  is well represented by a Voigt function (convolution of a Gaussian and a Lorentzian curve), whose Lorentzian width is dominated by the Stark broadening and the Gaussian width is associated to the Doppler broadening.

In typical LIBS conditions, the Gaussian component of the line width is negligible with respect to the Lorentzian one ( $\Delta\lambda_G \ll \Delta\lambda_L$ ), therefore the optical depth  $k(\lambda)l$  can be expressed as:

$$k(\lambda)l \approx K \frac{\Delta\lambda_0}{4(\lambda - \lambda_0)^2 + \Delta\lambda_0^2} \quad (2)$$

where  $K = 2 \frac{e^2}{mc^2} n_j f \lambda_0^2 l$ ,  $e$  and  $m$  are the charge (statcoulomb) and the mass (g) of the electron,  $f$  is the oscillator strength (dimensionless) of the transition and  $\Delta\lambda_0$  ( $=\Delta\lambda_L$ ) is the line FWHM. For low values of the optical depth, i.e. for  $k(\lambda)l \ll 1$ , Eq. (1) can be approximated as:

$$I_0(\lambda) \approx \frac{8\pi hc^2}{\lambda_0^5} \frac{n_j}{n_i} \frac{g_i}{g_j} k(\lambda)l \quad (3)$$

$I_0(\lambda)$  therefore represents the line profile in conditions of negligible self-absorption. From Eqs. (1) and (3), it is clear that, in the presence of self-absorption, the intensity of the line at its maximum (i.e. for  $\lambda = \lambda_0$ ) is lower than in the optically thin condition, according to the relation:

$$\frac{I(\lambda_0)}{I_0(\lambda_0)} = \frac{(1 - e^{-k(\lambda_0)l})}{k(\lambda_0)l} = \Delta\lambda_0 \frac{(1 - e^{-\frac{K}{\Delta\lambda_0}})}{K} \equiv SA \quad (4)$$

The self absorption coefficient SA is thus defined as the ratio of the measured peak height to the value of the line peak in absence of self-absorption. SA is equal to one if the line is optically thin, while it decreases to zero as the line becomes optically thick.

The value of the line width is also affected by the self-absorption. In order to find out the expression of the FWHM

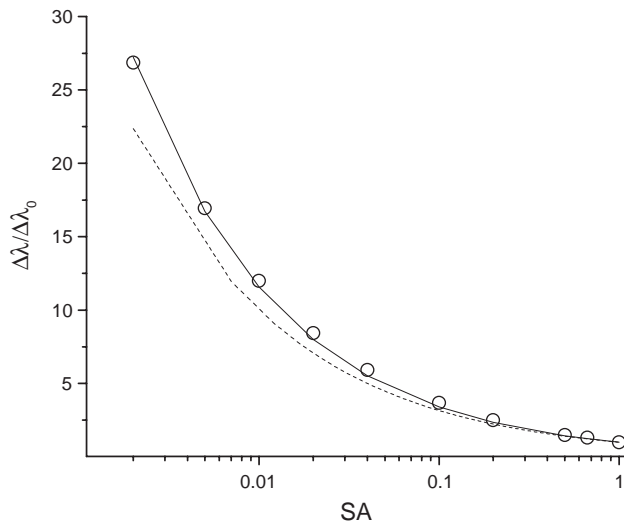


Fig. 1.  $\Delta\lambda/\Delta\lambda_0$  as a function of the SA coefficient (note the logarithmic scale on the x axis). Circles: numerical solution of Eq. (5); full line: predictions of Eq. (6); dashed line: predictions of Eq. (7).

$\Delta\lambda$  of an optically thick line in terms of SA and  $\Delta\lambda_0$ , we can use the relation:

$$\frac{I(\lambda)}{I(\lambda_0)} = \left( \frac{1 - e^{-\frac{-K \frac{\Delta\lambda_0}{4(\lambda - \lambda_0)^2 + \Delta\lambda_0^2}}{1 - e^{-\frac{K}{\Delta\lambda_0}}}}}{1 - e^{-\frac{K}{\Delta\lambda_0}}} \right) \quad (5)$$

Eq. (5) can be solved numerically for  $\Delta\lambda$  considering that (by definition of FWHM) for  $\lambda = \lambda_0 \pm \Delta\lambda/2$  the intensity  $I(\lambda)$  must be equal to  $I(\lambda_0)/2$ . The exact relation between the observed ( $\Delta\lambda$ ) and the corresponding non self-absorbed ( $\Delta\lambda_0$ ) widths can be parameterized, using Eq. (4), as

$$\frac{\Delta\lambda}{\Delta\lambda_0} = (SA)^\alpha \quad (6)$$

with  $\alpha = -0.54$ . In a previous work [6], the observed width  $\Delta\lambda$  of the emission line in presence of moderate self-absorption was related to the true width  $\Delta\lambda_0$ , through the empirical relation:

$$\frac{\Delta\lambda}{\Delta\lambda_0} = (SA)^{-0.5} \quad (7)$$

The validity of expression (7) was demonstrated for  $SA > 0.2$ . A comparison of the numerical solution of Eq. (5) with the predictions of Eqs. (6) and (7) is shown in Fig. 1.

The effect of self-absorption on the measured integral intensity ( $\bar{I}$ ) of the line can also be numerically evaluated in terms of SA and of the non-self absorbed integral intensity ( $\bar{I}_0$ ) and then parameterized as:

$$\frac{\bar{I}}{\bar{I}_0} = \frac{\int_{-\infty}^{+\infty} (1 - e^{-k(\lambda)l}) d\lambda}{\int_{-\infty}^{+\infty} k(\lambda)l d\lambda} = (SA)^\beta \quad (8)$$

with  $\beta = 0.46$ . According to the empirical model of Ref. [6], in the limit  $0.2 < SA \leq 1$ , the integrated intensity should scale as:

$$\frac{\bar{I}}{\bar{I}_0} \approx \frac{I(\lambda_0)\Delta\lambda}{I_0(\lambda_0)\Delta\lambda_0} = (SA)^{0.5} \quad (9)$$

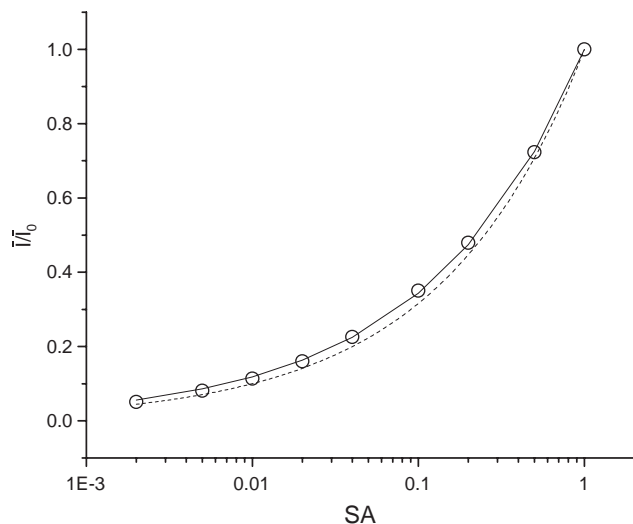


Fig. 2.  $I/I_0$  as a function of the SA coefficient (note the logarithmic scale on the  $x$  axis). Circles: numerical solution of the integrals in Eq. (8); full line: predictions of the parameterization in Eq. (8); dashed line: predictions of Eq. (9).

Fig. 2 shows the predictions of Eq. (9) together with the numerical solution of Eq. (8).

It should be now considered that the standard theory of Stark broadening allows to correlate the true line width  $\Delta\lambda_0$  to the plasma electron density  $n_e$  ( $\text{cm}^{-3}$ ). When the atom and ion impact contribution to the broadening can be considered negligible, the following linear approximation can be adopted:

$$\Delta\lambda_0 = 2w_s n_e \quad (10)$$

where  $w_s$  is the half-width Stark parameter. By substitution of  $\Delta\lambda_0$  in the expression (6) we obtain:

$$\Delta\lambda = \Delta\lambda_0 (SA)^\alpha = 2w_s n_e (SA)^\alpha \quad (11)$$

On the basis of Eq. (11), the quantity  $\frac{\Delta\lambda}{2w_s} = n_e (SA)^\alpha$  can be interpreted as a sort of ‘equivalent electron density’ ( $n_e^*$ ) which coincides with the real plasma electron density  $n_e$  when the emission line is optically thin but becomes higher than  $n_e$  (by the factor  $SA^\alpha$ ) when the optical depth increases. Thus, provided  $\Delta\lambda$  and  $n_e$  can be measured from the spectrum and

the  $w_s$  parameter of the investigated line is known from the literature, the use of Eq. (11) allows attaining the evaluation of the SA coefficient as

$$(SA) = \left( \frac{\Delta\lambda}{2w_s} \frac{1}{n_e} \right)^{1/\alpha} \quad (12)$$

In turn, the knowledge of the coefficient SA allows to correct for the peak line intensity and integrated line intensity reduction, according to the relations (4) or (8), respectively.

The evaluation of  $n_e$  through the measure of the Stark broadening of atomic or ionic lines requires the use of non self-absorbed emission lines. To this purpose El Sherbini et al. recently proposed [15], for the analysis of spectra from metallic alloys, the use of the  $H_\alpha$  line at 656.27 nm, according to the relation [16,17]

$$n_e (\text{cm}^{-3}) = C(\lambda, T) (\Delta\lambda_{1/2})^{3/2} \quad (13)$$

where  $\Delta\lambda_{1/2}$  is the measured FWHM of the  $H_\alpha$  line in Angstrom and  $C(\lambda, T)$  is a coefficient, weakly depending on electron density and temperature, tabulated by Griem [17].

Hydrogen emission is always present in the LIBS spectra taken in ambient air, because of the water vapor due to the natural humidity of the air. The use of the  $H_\alpha$  line for the measurement of the electron density has the definite advantage of providing a result which is not affected by self-absorption, unless the sample itself would contain high levels of hydrogen. Moreover, the linear Stark effect acting on hydrogen lines results in a large broadening which reduces the relative uncertainty of the measurement compared to the case of lines emitted by other elements.

### 3. Experimental setup

For testing the method above described, we studied several Al lines in LIBS spectra emitted from pure aluminum (99.9%) samples. Two experiments were carried out with different equipment, at the Physics Department of Cairo University (Egypt) and at the Applied Laser Spectroscopy Laboratory in Pisa (Italy), respectively. The measurements at Cairo University

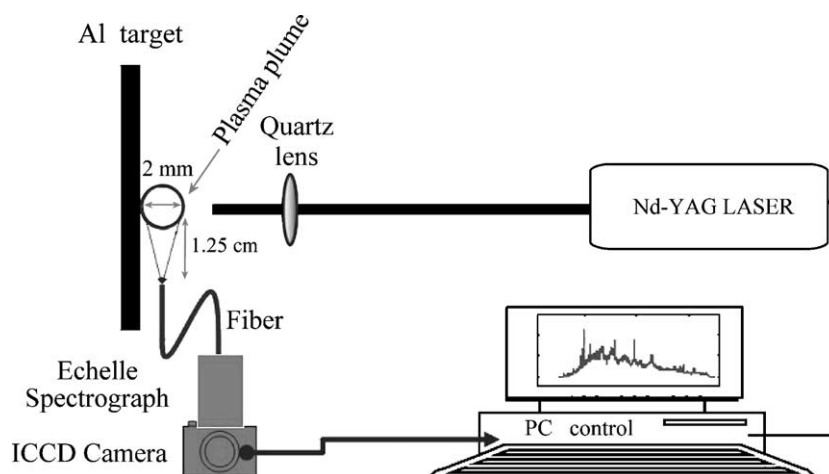


Fig. 3. Experimental setup for LIBS measurements used at Cairo University.

were performed using the experimental setup sketched in Fig. 3. A high power Nd-YAG laser (Brilliant B, Quantel), delivering up to 800 mJ in 6 ns FWHM at 1064 nm was focused through a 10 cm focal length lens on a plane solid alloy target in air. The spectra were collected through an optical fiber coupled to a SE200 Echelle spectrograph (with spectral resolving power  $\lambda/\Delta\lambda=4500$ ) equipped with a time gated ICCD (iStar DH734-18 F, Andor). The spectra were acquired using a gate time of 1  $\mu$ s, which provided a good signal to noise ratio, necessary for a precise measurement of the spectral line widths. The time delay after the laser pulse ranged between 0.1 and 5  $\mu$ s.

The measurements done at Pisa laboratory were performed using Modi (Mobile Dual-Pulse Instrument), a mobile LIBS instrument using a double-pulse laser realized by the Applied Laser Spectroscopy group in collaboration with Marwan Technology s.r.l. The Modi double-pulse laser delivers up to 150 mJ per pulse in about 8 ns FWHM. The two laser pulses can be delayed each other from 0 (single pulse) to 60  $\mu$ s. The laser pulse is focused on the target surface using a 10 cm focal length lens; the LIBS signal is then collected using an optical fiber and analyzed with an Echelle spectrometer (Multichannel Instruments, spectral resolving power of  $\Delta\lambda/\lambda=7500$ ) coupled to a PCO DiCam Pro ICCD. The LIBS spectra were acquired from a pure aluminum target (99.9%) using the same timing parameters as in Cairo experiment.

While the experiments performed in Cairo were carried out in single pulse configuration (at a laser energy of 760 mJ), in Pisa the measurements were performed both in single pulse (at a laser energy of 160 mJ) and in double pulse (80+80 mJ with a 2  $\mu$ s delay between the pulses) collinear configuration.

#### 4. Results and discussion

Three Al lines (Al I at 394.4 nm, Al II at 281.6 nm and Al II at 466.3 nm) were considered for studying the self-absorption coefficients, as a function of the time delay after the laser pulse (after the second pulse in double pulse case).

In all the spectra, the electron density was calculated from the optically thin  $H_\alpha$  line, according to expression (13). The equivalent electron density  $n_e^*$  was evaluated as defined in expression (11) from the above mentioned Al lines, where the Stark parameters of the lines were taken from Refs. [17,18]. Fig. 4a shows the comparison between the electron density and the parameter  $n_e^*$  obtained from the Cairo measurements, while Fig. 4b,c refer to the same quantities obtained from the Pisa measurements in single and double pulse configuration, respectively. It is clear that the values of both  $n_e$  and  $n_e^*$  are probably slightly underestimated at the lower delay times of acquisition because of the signal integration all over the observation gate; in addition, a distortion of the lines due to temporal inhomogeneities is possible at the same times.

As expected, the electron density calculated from the  $H_\alpha$  line in the Cairo experiment is higher than in the other two cases, due to the higher laser energy used. On the other hand, the electron density measured in single pulse configuration (Fig 4b) is higher than that found in the double pulse case (Fig 4c), in agreement with previous works [19–21].

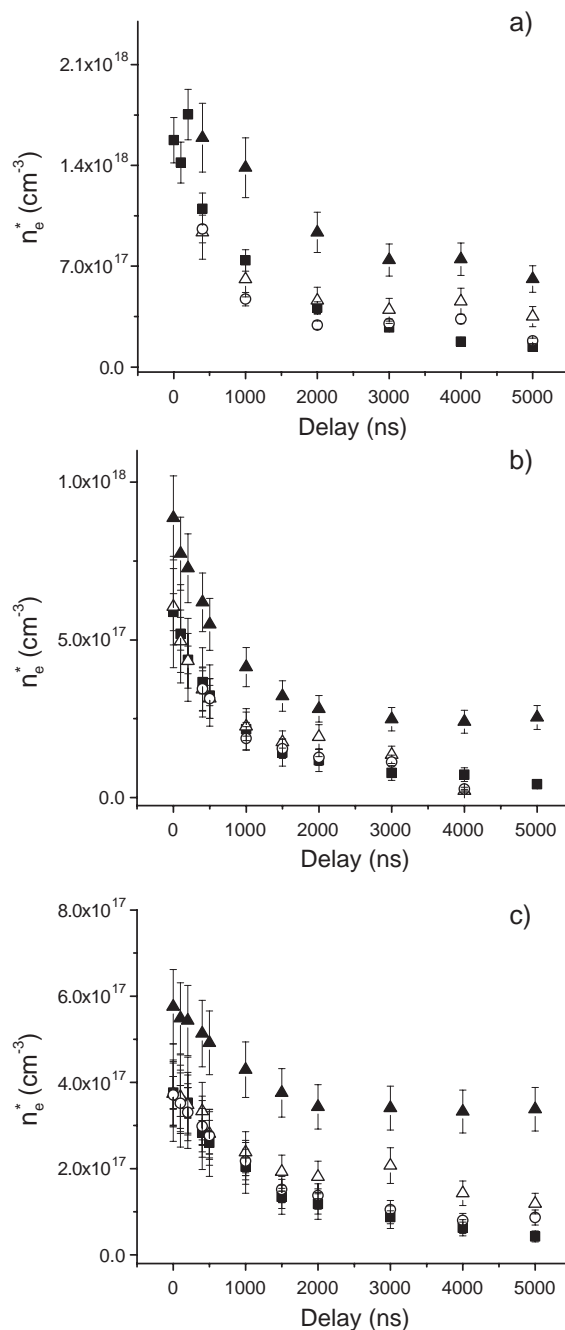


Fig. 4. Equivalent electron density derived from Al I line at 394.4 nm (solid triangles), Al II line at 281.6 nm (open triangles) and Al II line at 466.3 nm (open circles), compared with the electron density derived from the  $H_\alpha$  line at 656.3 nm (solid squares). The error of the electron density is 10%, for the equivalent electron density of Al I line is 15% and for the equivalent electron densities of Al II lines is 20%. (a) Measurements performed at Cairo University, single pulse, pulse energy 760 mJ; (b) measurements performed at Pisa laboratory, single pulse, pulse energy 160 mJ; (c) measurements performed at Pisa laboratory, double pulse, pulse energy 80 mJ per pulse, delay between pulses 2  $\mu$ s.

From the inspection of all the graphs, it is clear that the equivalent electron density calculated from the two Al II lines at 281.6 and 466.3 nm is comparable, particularly for lower acquisition delays, to the electron density measured from the  $H_\alpha$  line. This implies that the self-absorption is low. On the

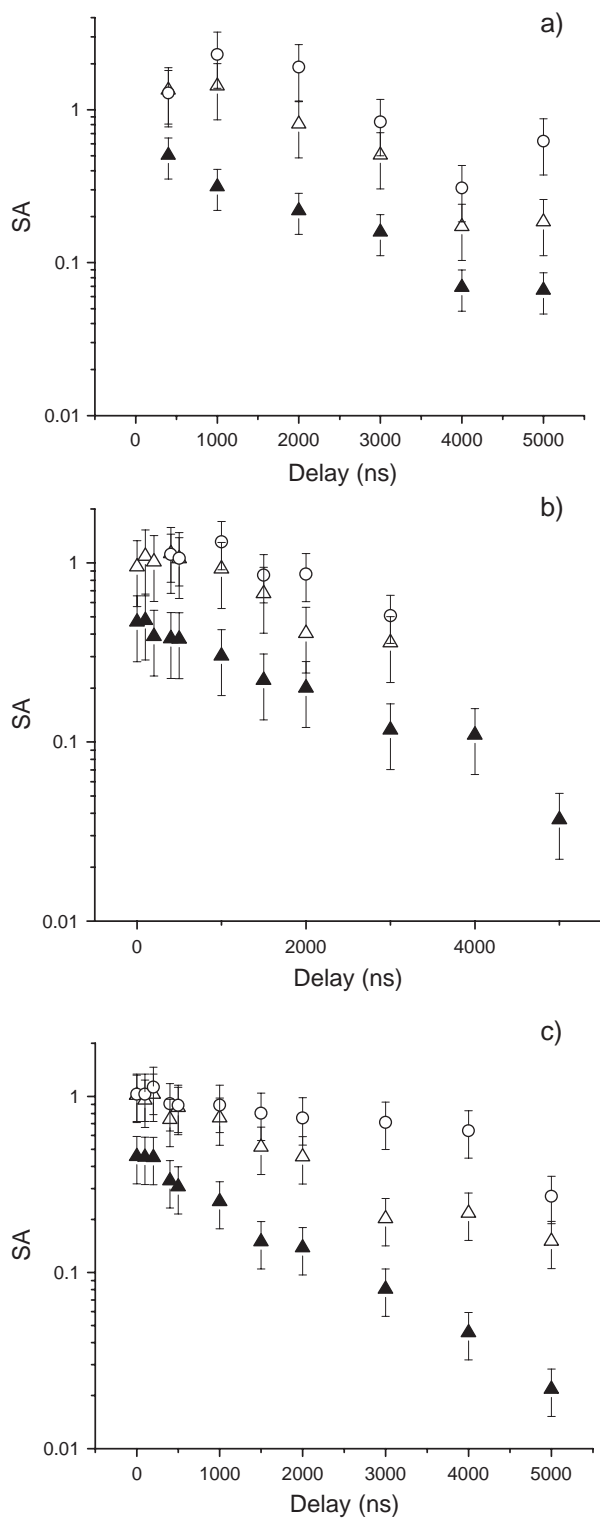


Fig. 5. Self absorption coefficient SA for Al I line at 394.4 nm (solid triangles) Al II line at 281.6 nm (open triangles) and Al II line at 466.3 nm (open circles). The errors of the coefficient SA for the Al I line is 30% while for the Al II lines is about 40%. (a) Measurements performed at Cairo University, single pulse, pulse energy 760 mJ; (b) measurements performed at Pisa laboratory, single pulse, pulse energy 160 mJ; (c) measurements performed at Pisa laboratory, double pulse, pulse energy 80 mJ per pulse, delay between pulses 2  $\mu$ s.

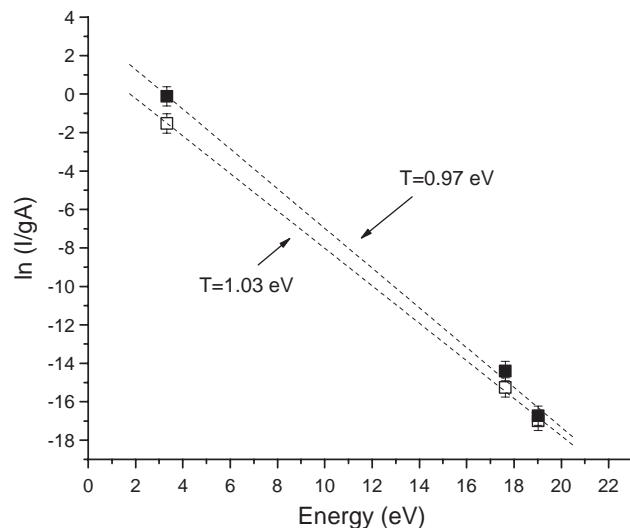


Fig. 6. Comparison between the Saha–Boltzmann plot obtained from the intensities of the three Al lines considered in this paper, with (solid squares) and without (open squares) the correction for self-absorption. The dashed lines correspond to the best linear fitting of the data; plasma temperature is inversely proportional to the slope of the best fitting curve. The plot shown in the figure refers to double pulse configuration, at an acquisition delay of 4  $\mu$ s after the second laser pulse.

contrary, the equivalent electron density obtained from the neutral Al I line at 394.4 nm is much higher than the true value for all the delay times considered. This is a clear indication of a strong self-absorption effect on this Al I resonant line.

More direct information about the self absorption degree can be extracted from the values of the SA coefficients derived for the three Al lines from the same spectra of Fig. 4a–c, as shown in Fig. 5a, b and c.

It is worth noticing that the Al I line at 394.4 nm shows a stronger self-absorption in the spectra taken at Cairo (Fig. 5a) than in the other two cases; this is probably due the higher electron density (caused by the higher laser energy) that, according to the Saha equation, implies a larger presence of neutral atoms in the plasma.

Looking at Fig. 5, it is evident that also the ionized aluminum lines show a low to moderate self absorption for longer acquisition delay times, while they are optically thin for delay times lower than about 3  $\mu$ s. The growth of the optical thickness of the plasma at longer delay times is testified also by the Al I at 394.4 nm line's behavior and is probably due to the cooling of the plume, which brings to a growth of the population of the atomic and ionic lower energy levels.

The error bars in Fig. 5 represent the uncertainty evaluated by error propagation on the basis of expression (12): considering that the line width  $\Delta\lambda$  and the electron density  $n_e$  have relative uncertainties of 5–10%, and that the Stark broadening coefficient  $w_s$  have relative uncertainties of 10–20%, the resulting uncertainty on the SA coefficient is about 30–40%. It is important to remark that the uncertainties of the correction factor  $(SA)^B$  for the integrated intensities reduce to

10–20%. These values can be slightly higher at the lower delay times because of the temporal evolution of the plasma during the acquisition time. The appeal of this figures must be evaluated by comparison to the possible alternatives. In the absence of any correction, the intensity of self-absorbed lines may be easily underestimated even by more than one order of magnitude. On the other hand, the model described in Ref. [6], based on the evaluation of the line optical depth according to the relations (2) and (4), also suffers from large uncertainty values, mainly due to the estimation of the atom number density  $n_i$  and of the optical path  $l$ . However, it must be borne in mind that the method here presented can be applied only to the lines whose Stark broadening coefficient is available.

The values of the SA coefficient can be used for correcting the effect of self-absorption on the corresponding emission lines. As an example, Fig. 6 shows the Saha–Boltzmann plot obtained from the intensities of the three Al lines here considered, before and after the correction for self-absorption,

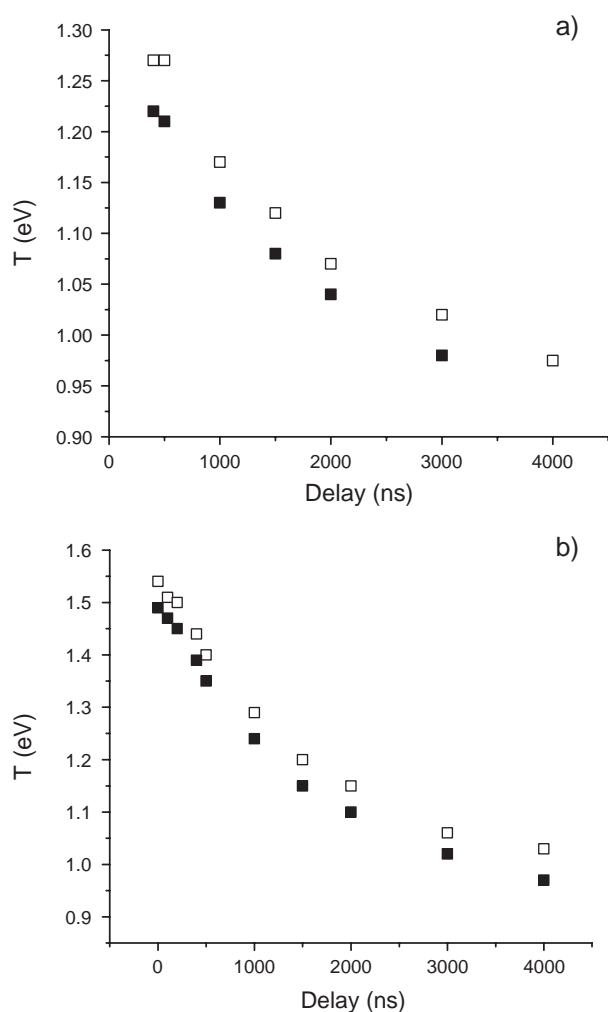


Fig. 7. Plasma temperature vs. acquisition delay before (open squares) and after (solid squares) self-absorption correction in single pulse (a) and double pulse (b) configurations. The plasma temperature is measured using the Saha–Boltzmann method.

in case of double pulse measurements at an acquisition delay of 4  $\mu$ s. The Saha–Boltzmann plot is a generalization of the Boltzmann plot method which allows using lines coming from different ionization stages of the same element for the determination of plasma temperature, given the knowledge of the plasma electron density (see Ref. [22] for more details). The comparison of the self absorption corrected Saha–Boltzmann plot with the uncorrected one clearly shows how the correction here proposed significantly affects only the point corresponding to the highly self absorbed Al I line at 394.4 nm, while the points corresponding to the other two slightly self absorbed Al II emission lines are proportionally less affected.

The temperatures calculated before and after the self absorption correction for all the spectra acquired in single and in double pulse configurations are shown, as an example, in Fig. 7a (single pulse) and b (double pulse). As expected [20,23] the temperature calculated in the double pulse case is slightly higher than in the single pulse case. In both cases, it is clear from the figures that the use of the self-absorption corrections allows to avoid the systematic error in the electron temperature produced by the use of the uncorrected values of the line intensities.

## 5. Conclusion

We have proposed a simple method for quantifying the effect of self-absorption on atomic and ionic emission lines in LIBS measurements. The method relies on the quantification of the line width and on the evaluation of the electron density, which are easily measurable from an experimental emission spectrum; for this reason the method seems preferable to others which require the estimation of non directly measurable parameters as the optical path or the atomic number density in the plasma. On the other hand, the validity of the method is restricted to the cases where the spatial (and temporal along the acquisition window) plasma inhomogeneities can be neglected (i.e. self reversal effect is not present).

The error associated to the self absorption evaluation is mainly caused by the line width and the electron density measurement and is affected by the accuracy of the Stark parameter  $w_s$ ; this implies that a very accurate evaluation of the SA parameter can be obtained from the optimization of the experimental apparatus and by using lines whose Stark parameters are known with good precision.

In particular, in our test measurements, performed in air on pure aluminum samples in single and in double pulse configurations, the electron density was measured from the Stark broadening of the optically thin  $H_\alpha$  line at 656.3 nm. In these conditions, the self-absorption coefficient SA can be evaluated with a 30% uncertainty, which turns out to be a definite improvement compared to our previous approach.

We have also shown that the calculated self-absorption coefficients can be used for improving the precision in plasma temperature determination, which is highly desirable in quantitative analysis using standard-less techniques.

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