Characterization of laser-induced plasmas by atomic emission spectroscopy

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Abstract. In this work, Laser-induced breakdown spectroscopy (LIBS) has been applied to characterization of plasmas generated in air at atmospheric pressure from a calcium hydroxide sample with a known concentration of Mg by using an infrared Nd:YAG laser. The influence of laser irradiance on plasma morphology and emission intensity was studied. Spatially-integrated intensities of Mg I-II lines along the line-of-sight were measured for different laser energies and delay times. The plasma temperature and the electron density were determined in each case by using an algorithm that calculates the optical thickness of the spectral lines and reproduces their experimental profiles in a framework of an homogeneous plasma in LTE that takes into account the effects of self-absorption. The results obtained showed the usefulness of this approach to provide additional information retrieved from the optical thickness of spectral lines for plasma characterization in LIBS experiments.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is based on focusing a laser pulse with enough energy onto a solid, liquid or gaseous sample to produce a plasma useful for spectral analysis. LIBS has unique advantages such as the capability of rapid, in-situ, multi-element measurements with few or no sample preparation. These features allow LIBS to perform measurements under conditions not feasible with conventional analytical techniques (e.g.: ETA-AAS, ICP-AES and ICP-MS) that supported by the actual technology development in the components, make it a very promising technique to be integrated to the established atomic spectroscopic methods [1]. Nevertheless, LIBS quantitative analysis is not a trivial task because the spectroscopic emission of the plasma is determined not only by the concentration of the element in the sample, but also by the properties of the plasma itself, which in turn depend on the experimental conditions [2].
Spectral analysis of the radiation emitted by laser-produced plasmas may be used to obtain its characteristic parameters such as the temperature and the electron density [3]. However, calculating the atom and ion densities from the measured emission spectra is quite troublesome. The most common procedure for quantitative analysis is the construction of calibration curves, by using reference samples, to obtain the chemical composition. In this scenery, plasma characterization is of critical importance to enhance LIBS performance and to provide a deep understanding of the physical processes involved.

Nowadays, LIBS is a very active field of both, basic and applied research [4-7]. The trend is toward the development of compact, relatively low-cost equipments, assembled with sophisticated commercial instruments available on the market [8], that encompass applications ranging from environmental studies to space exploration [9,10]. Nevertheless, some concerns still remain under investigation representing, in our opinion, a real challenge to LIBS. Namely, self-absorption of spectral lines within the plasma plume, spatial inhomogeneity, shielding effect at high laser irradiances and matrix effects [11-20]. Moreover, reference samples are unavailable in many practical situations. For example, when dealing with unique samples (e.g.: museum pieces, archaeological findings), samples with either a complex or unknown matrix (e.g.: rocks from exploratory missions to other planets) or samples requiring a high-cost manufacturing (medical prosthesis), or a combination of these features. Here, an analysis involving rapid, in-situ, non destructive measurements is indispensable.

In order to overcome those difficulties, several works have investigated an alternative LIBS approach to characterize the plasma physical state based in plasma physics under the hypothesis that (i) the composition of the plasma is representative of that of the sample (stoichiometric ablation) and (ii) the plasma is in a state of local thermodynamic equilibrium (LTE) [21-24]. Two recent reviews on plasma radiative models relevant to LIBS and Calibration-Free LIBS summarize the current state-of-the-art in the field and emphasize the necessity of further investigation of the underlying physical processes to consolidate LIBS as a quantitative analytical technique through the optimization of the instrumentation and the method, mainly the calibration-free models which have the potential to carry out standarless analysis, the ultimate goal of analytical spectroscopy.

In a previous work [25], we implemented a model of a collision-dominated plasma in LTE consisting of two zones with different temperatures and optical thicknesses to characterize a laser-induced plasma generated on a metallic alloy by least-squares fitting of experimental and theoretical spectra. The model was subsequently improved by considering a non-uniform plasma with a parabolic temperature distribution [26], based on a simplified approach of Gornushkin et al. [27]. Valuable insight about inhomogeneous plasmas was obtained by confronting it with the experiment. Although the model was still quite complex and time-consuming to be employed in practical situations, it demonstrated that useful information about plasma properties can be obtained from the profiles of spectral lines.

In this work, we propose a simpler approach based on an homogeneous model for the characterization of laser-induced plasmas that provides information about self-absorption by reproducing the profiles of experimental spectral lines.
2. Theoretical

If we consider a cylinder-symmetrical plasma in local thermal equilibrium (LTE), the emission and absorption of radiation are described by an emission coefficient $\varepsilon_\nu (J \text{s}^{-1} \text{m}^{-3} \text{sr}^{-1} \text{Hz}^{-1})$ and an absorption coefficient $\kappa_\nu (m^{-1})$ which generally are distributed within the plasma volume. The intensity $I_\nu (J \text{s}^{-1} \text{m}^{-2} \text{sr}^{-1} \text{Hz}^{-1})$ observed in the surface of an infinitesimal element of plasma emitted along the line of sight (x coordinate) is given by the equation of radiation transfer [28]

$$\frac{dI_\nu (x)}{dx} = \varepsilon_\nu (x) - \kappa (\nu, x)I_\nu (x), \tag{1}$$

which expresses that the increment of $I_\nu$ over the distance $dx$ is composed of the increment by emission $\varepsilon_\nu (x)dx$ and the decrement by absorption $\kappa (\nu, x)I_\nu (x) dx$.

The classical solution to equation (1) for the spectral line intensity, as a function of the wavelength, emitted by an homogeneous plasma is

$$I_\lambda = CU_\lambda (T) \left(1 - e^{-\tau_\lambda (T)}\right), \tag{2}$$

where $C$ is a factor depending on the instrumental setup, $U_\lambda (W \text{m}^{-3})$ is the distribution for blackbody radiation,

$$U_\lambda (T) = \frac{hc}{\pi \lambda^3} \frac{1}{e^{\frac{E_j}{kT}} - 1}, \tag{3}$$

with $h$ (eV s) the Planck’s constant, $c$ (m s$^{-1}$) the speed of light in vacuum, $\lambda$ (m) the transition wavelength, $k$ (eV °K$^{-1}$) the Boltzmann’s constant, $T$ (°K) the temperature, $E_i, E_j$ (eV) the energy levels of the transition; and $\tau_\lambda$ (dimensionless) is the optical thickness of the plasma. For a plasma in LTE the optical depth $\tau_\lambda$ can be separated in different factors [29], as

$$\tau_\lambda (T) = \kappa (\lambda) l = \kappa_e (T) N l P (\lambda), \tag{4}$$

where $\kappa_e (T) (m^2 s^{-1})$ is a coefficient that depends on the atomic parameters of the transition and can be calculated if the plasma temperature is known. Namely,

$$\kappa_e = \frac{\lambda^2}{Q(T)} A_{ji} g_i e^{-E_j/kT} \left(1 - e^{-\frac{E_j}{kT}}\right), \tag{5}$$

$N$ (m$^{-3}$) is the density of the emitting element in the plasma, $l$ (m) is the length of the plasma along the line-of-sight, and $P (\lambda)$ (m$^{-3}$) is the normalized line profile, in general described by a Voigt profile. $Q(T)$ (dimensionless) is the atomic partition function

$$Q(T) = \sum_j g_j e^{\frac{E_j}{kT}}, \tag{6}$$
which can be calculated by using the data from NIST database [30], \( A_j (s^{-1}) \) is the transition probability, \( g_j \) (dimensionless) is the degeneracy of the upper energy level, and \( E_i, E_j \) (eV) are the energy of the levels, respectively.

Equation (4) shows that \( \tau_\lambda \) is directly proportional to \( P(\lambda) \). Consequently, the optical thickness has the same functional form that the line profile and reaches its maximum value \( \tau_0 \) at the line center \( \lambda_0 \). If self-absorption of radiation is negligible, \( \tau_0 \ll 1 \) and the plasma is said optically thin, then

\[
I_\lambda = C U_\lambda (T) \tau_\lambda (T). \tag{7}
\]

For the stronger lines, generally the resonant, the radiation emitted has a large probability of being absorbed, \( \tau_0 \gg 1 \) and the plasma is said optically thick, then

\[
I_\lambda = C U_\lambda (T). \tag{8}
\]

3. Experimental

3.1. Experimental setup

The experimental setup consisted of a good spectral resolution system based on a photomultiplier tube. A schematic diagram is sketched in figure 1 as well as the observation geometry. A Nd:YAG laser (Continuum Surelite II, \( \lambda = 1064 \) nm, 7 ns pulse FWHM, repetition rate of 2 Hz) was employed to generate the plasmas in air at atmospheric pressure using a pellet of calcium hydroxide placed on a rotation stage. This kind of samples has been already employed in a previous work for the determination of traces of heavy metals in liquids [31].

The laser beam was focused at right angles onto the surface of the samples by a quartz lens of 10 cm focal length. The space-integrated emission of the laser-induced plasma along the line-of-sight was collected in a perpendicular direction (x) to the laser beam by a second quartz lens of 20 cm focal length and focused into the entrance slit (50 µm-wide) of a monochromator (Jovin Yvon Czerny-Turner configuration, resolution 0.01 nm, focal length 0.5 m, grating of 2400 lines/mm). The detector was a photomultiplier (PM) whose signal was time resolved and averaged with a Box-Car. The emission line profiles were scanned by moving the diffraction grating of the monochromator, which was controlled by software and synchronized with the data acquisition and the laser firing. Finally, the spectra were recorded and processed by a PC.

As explained in the following section, this experimental setup allowed us to generate plasmas with different irradiances and analyze the radiation emitted with: i) spatial resolution along the direction of plasma expansion (z), ii) spectral resolution in the UV-VIS (200-600 nm), and iii) temporal resolution (1ns-100ms). In each measurement, the emission from 10 laser shots was averaged to obtain a good signal-to-noise ratio. In addition, the plasma morphology can be observed in real-time and the crater produced in the sample surface by the laser shots can be examined by means of an optical microscope.
Figure 1. (a) Experimental setup for LIBS measurement. (b) Observation geometry.
3.2. Spectral lines and measurements
A pellet of calcium hydroxide was manufactured, as described in Ref. [31], with a concentration of 625 ppm of Mg (Figure 2). This concentration was found to be appropriated to measure lines with high upper energy levels. Seven close lines of Mg I and Mg II were registered, listed in table 1. These lines are isolated and practically free from interference of other elements and the substrate, so they are suitable for characterization of the plasma.

### Table 1. Spectroscopic parameters of neutrals (I) and singly ionized (II) atomic lines of Mg used for plasma characterization (data from [30]).

| Element | λ (nm) | $A_{ji}$ ($10^8$ s$^{-1}$) | $E_i$ (eV) | $E_j$ (eV) | $g_i$ | $g_j$ |
|---------|--------|---------------------------|-----------|-----------|-------|-------|
| Mg I    | 278.14 | 5.43                      | 2.711     | 7.168     | 3     | 1     |
| Mg I    | 278.30 | 2.14                      | 2.717     | 7.170     | 5     | 3     |
| Mg I    | 285.21 | 4.91                      | 0.000     | 4.346     | 1     | 3     |
| Mg II   | 279.08 | 4.01                      | 4.422     | 8.864     | 2     | 4     |
| Mg II   | 279.55 | 2.60                      | 0.000     | 4.434     | 2     | 4     |
| Mg II   | 279.80 | 4.79                      | 4.434     | 8.864     | 4     | 6     |
| Mg II   | 280.27 | 2.57                      | 0.000     | 4.422     | 2     | 2     |

The laser irradiance over the sample surface was modified by changing the laser energy and the laser focusing distance. The pulse energy ($E$), which was measured with a calorimeter, was varied in the range 50-200 mJ by using and optical attenuator. The lens-to-sample distance ($f - d$), controlled with a micrometer translation stage, was varied in such a way the beam waist of the focused beam was always placed below the sample surface at a distance $d$ (distance from the sample surface to the focal plane of the lens) from it, varied in the range 0-14 mm, avoiding the air breakdown in front of the target. The laser irradiance was estimated measuring the area of the craters (Figure 3), originated by the laser pulses on the sample surface, for each pair of values of $E$ and $f - d$ by using a microscope equipped with an image acquiring system (Reichert MeF2 Optical Microscope). The resulting irradiance was in the range 0.6-37 GW/cm$^2$.

In order to observe the spatial structure of the plasma plume, we used a lens to create an increased lateral image (1:5) of the plasma on a screen. Then, plasma images were acquired using a camera with an exposure time of 2 min corresponding to the accumulation of the visible light emitted along the line-of-sight by approximately 240 plasmas at the repetition rate used in this work. The shape of the plume can be visualized in real-time during the measurements to study the effect of the irradiance on the induced plasma.
To obtain spatially-resolved measurements along the direction of propagation of the plume \((z)\), the peak intensities of Mg lines were recorded by moving the image of the plasma on the slit of the monochromator using a translation stage to displace the focusing lens \((L_2)\).

The temporal evolution of the line profiles were registered employing suitable delay time with respect to the laser pulse and a gate width, chosen to obtain a good signal-to-noise ratio and avoid strong changes in the plasma parameters during the measurement.

To investigate the feasibility of obtaining information from the line profiles, an algorithm was implemented to calculate the emission spectra from an homogeneous plasma in LTE in which self-absorption is evaluated and compensated. All the intensity measurements carried out in this work correspond to the lateral emission of the plasma spatially integrated along the line-of-sight. The plasma temperature was determined with the Saha-Boltzmann plot using the Mg I-II lines in optically thin conditions, which have a suitable spread of their upper energy levels to perform an accurate calculus. The electron density was obtained from the Stark broadening of the resonant emission lines, with the broadening parameters taken from [32].

4. Results and discussion

4.1. The model

The method developed to perform the characterization of the plasmas is based in the approach of a collision-dominated plasma in LTE in which the standard statistic distributions are employed. Moreover, the plasma is assumed to be homogeneous and the equations of section 2 are used to calculate the emission spectra and to describe its features.

To calculate the line profile \(P(\lambda)\) in equation (4), it is necessary to evaluate the different broadening mechanisms existing in the laser induced plasma. For the present experimental conditions, the Stark effect [33] and the monochromator instrumental function may be assumed to be the dominating
broadening mechanisms that determine both the Lorentzian and Gaussian components of the Voigt profile, respectively. The Stark width of the lines is approximately proportional to the electron density,

\[ w_{\text{Stark}} = 2w \frac{N_e}{10^{16}}, \]  

where \( N_e (\text{cm}^{-3}) \) is the electron density and \( w \) is the electron impact (half) width. The corresponding instrumental function had an estimated width FWHM of 0.0065 nm for the 50-µm width entrance/exit slits.

In optically thin conditions, the intensity profile \( I_\lambda \) has the same functional form that both, \( \tau_\lambda \) and \( P(\lambda) \) (Equations (4) and (7)). In this case, the experimental lines can be fitted to a Voigt profile to obtain information about the plasma parameters. Nevertheless, because of self-absorption the line profiles result distorted. From an experimental point of view, the effect of self-absorption is to decrease the peak intensity and to increase the FWHM of the emission lines.

In practice, estimating the degree of self-absorption is a difficult task that can not be carried out directly. A few works have estimated and compensated its effects in LIBS experiments making some approximations or employing specific approaches. In the works of [34-35], a self-absorption coefficient (SA) was calculated using the experimental line widths measured and comparing them with their corresponding values in optically thin conditions through some empirical relations. In [36], a way to correct self-absorption was proposed through the evaluation of a correction factor by placing a mirror behind the plasma.

The knowledge of the optical thicknesses allows not only to evaluate the degree of self-absorption, but also to correct the experimental line profiles. In fact, from equations (2) and (7), we deduce

\[ \frac{I_\lambda^{\text{thin}}}{I_\lambda} = \frac{\tau_\lambda}{1 - e^{-\tau_\lambda}} \equiv R_\lambda, \]

where a correction factor, \( R_\lambda \) (adim.), has been defined, that can be calculated once the optical thickness has been obtained. Then, the factor \( R_\lambda \) can be applied to the experimental profiles to retrieve the optically thin line profiles for the same number density of emitters,

\[ I_\lambda^{\text{thin}} = R_\lambda I_\lambda. \]

In particular, for the line peak (\( \lambda = \lambda_0 \)) we have

\[ \frac{I^{\text{thin}}(\lambda_0)}{I_0} = \frac{\tau_0}{1 - e^{-\tau_0}} = R_0. \]

Then, the SA factor can be calculated using the ratio of the measured peak intensity over its value in absence of self-absorption

\[ \text{SA} \equiv 1 - \frac{I(\lambda_0)}{I^{\text{thin}}(\lambda_0)} = 1 - \frac{1}{R_0}. \]
This expression allows evaluating self-absorption in a quick, easy way starting from the experimental profile of any line. In figure 4, the factor $SA$ is represented as a function of $\tau_0$. $SA = 0$ if the line is optically thin, while it increases to 1 as the lines becomes self-absorbed. The effect of self-absorption starts to be appreciable when $\tau(\nu) \approx 1$. Therefore, it can be deduced from equation (13) that a line possess a low self-absorption coefficient when $SA \leq 0.35$ approximately.

Calculating $\tau_\lambda$ directly from equation (4) is difficult because all the parameters involved should be estimated previously, which depend on the experimental conditions. To overcome this problem, we obtained $\tau_\lambda$ using a pseudo Voigt profile formed by the convolution of the Gaussian component of the instrument profile and a Lorentzian profile of varying width.

4.2. Calculation procedure

The procedure developed for plasma characterization is based in the model described in the previous section and it is shown in the schematic diagram of figure 5. An algorithm was developed that compute the emission profiles of the lines, by calculating the optical thickness, and match them to the experimental profiles. The fitting is carried out by a least-squares iterative procedure. Self-absorption is evaluated and compensated allowing and accurate determination of the temperature and the electron density of the plasma. The complete procedure is described in the following.

First, measurements of the LIBS spectral lines are recorded and their spectroscopic data, taken from the NIST database [30], are saved. Second, an estimated range of values for the maximum value of the optical thickness and the Stark width are set by the user. It should be noted that the plasma temperature is not a fitting parameter, a value of 1 eV is used by defect and subsequently updated. Third, the fitting routine is run automatically until the profiles that best reproduce the experimental profiles of each line independently are found. At the end of this step, the optical thicknesses of the lines are obtained as a function of the wavelength, as well as their Stark widths. The next step is the correction of self-absorption based on the relations of Section, where the $SA$ factors are evaluated and the optically thin profiles of the lines are retrieved. Finally, the temperature and the electron density of the plasma are determined from the Stark widths and the Saha-Boltzmann plot method. As an example, a typical output of the fitting procedure is shown in figure 6.
4.3. Plasma shape and emission intensity for different focusing distances

4.3.1. Plasma shape. In figure 7 is shown a lateral image, obtained as explained in section 3.2, of the plasma emission in the visible region of the spectrum during the stage of emission of radiation. It can be observed (after software processing) that the plasma plume is formed by several concentric layers given by different colors, which make evident the inhomogeneous character of laser-induced plasmas. Two plasma regions are clearly distinguished: A bright hot core close to the sample surface surrounded by a cold region composed by different layers forming a tail that spreads out normally to the target surface. Thus, in a simplified approach, the plasma can be figured out as composed of a core with higher temperature surrounded by a periphery with lower temperature.

Between the different experimental parameters employed to generate LIBS plasmas, the focusing distance and the laser pulse energy are the most relevant because, for a given wavelength and temporal duration of the laser pulse, they determine the irradiance over the sample surface, which governs the processes of ablation and formation of a plasma from a solid target [37]. The resulting range of irradiances in the experiment was \( \approx 0.6-37 \text{ GW / cm}^2 \).
Figure 6. Visualization of the fitting procedure developed. The deduced parameters of the spectral line analysed are exposed in the table. The obtained optical thickness and the line profile in optically thin conditions are shown at the bottom.

| Parameter        | Value                  |
|------------------|------------------------|
| $\lambda_0$      | 280.27 Mg II           |
| $C$              | 4.97E7                 |
| $w_{\text{tot}}$ | 0.193                  |
| $w_{\text{Stark}}$ | 0.160                 |
| $\tau_0$         | 1.8                    |
| $A$              | 0.345                  |
| $I_{\text{tot}}$ | 0.412                  |
| $I_{\text{tot}}^{\text{thin}}$ | 0.600             |
| $I_0$            | 1.451                  |
| $I_0^{\text{thin}}$ | 3.127                 |
| $S\Delta$ (%)   | 53.6                   |
| $\chi^2$         | 0.414                  |

Fig. 7. Lateral image of the plasma plume emission.
The spatial distribution of the emissivity of plasmas generated with different laser energies, in the range 50-200 mJ, and different focusing distances $d$, in the range 0-14 mm, were analysed in order to study the influence of the irradiance on plasma morphology. The plasma shape showed a remarkable variation with $d$ that we describe next for the plasmas generated with $E = 150$ mJ (Figure 8), as a representative example: For $d = 0-2$ (the focal plane of the lens coincides with or is close to the sample surface) a small core elongated in the direction of laser incidence and having a ring around it near to the sample surface is observed. As the focusing distance decreases, and $d$ increases ($d = 4$), the plasma progressively adopts a spherical shape, where the core comprises practically the whole plume and the external region is very small. Then, for smaller focusing distances ($d = 6$) the core do not suffer a significant change, but the periphery starts to expand forming a tail along the normal direction. The tail reaches its maximum length ($d = 8-10$) and then vanishes, while the core becomes smaller and flatten against the sample surface ($d = 12-14$).

4.3.2. Intensity of emission. In a laser-induced plasma the intensities of emission present a spatial distribution that evolves with time. The analysis of the temporal evolution of the emission lines in different zones of the plasma is very important in order to select the more adequate conditions of measurement and to obtain the best signal-to-noise ratio.

To investigate the spatial distribution of ions and neutral Mg atoms, the peak intensities (spatially integrated along the line-of-sight) of the resonant lines were measured by scanning the plume in the direction of expansion ($z$) with steps of 0.25 mm. The plasmas were generated with $E = 150$ mJ and focusing distances of $d = 14, 4, \text{ and } 2$ mm for which a differential behavior was observed. Results are exposed in figure 9, where each experimental point was obtained by averaging the peak intensities of 50 plasmas in the time window 7-8 $\mu$s, and the error bars correspond to the standard deviations.

It can be seen that for $d = 12$ mm (Figure 9a), the distributions are quite similar but relatively low intensities and there is a very poor emission in the tail of the plume, indicating a very low density of species. For $d = 4$ mm (Figure 9b), the atom and ion distributions are approximately the same and symmetrical, in agreement with the spherical plasma shape observed in this case (Figure 8). For $d = 2$ mm (Figure 9c) the maximum emissivity of Mg I comes mainly from the plasma center ($z = 1.5$ mm), while a considerable high emission of Mg II is detected at the forehead ($z = 2-3$ mm). Thus, we deduce that a larger concentration of Mg II is located close to the plasma front, indicating high ionization and temperature in that region.

Next, the line profiles of the three resonant Mg lines were recorded selecting the emission coming from the plasma core and varying the focusing distance $d$. In figure 10, the total intensities are plotted against $d$. As can be observed, a maximum of the intensity takes place at focus distances $d = 4 – 8$ mm for Mg I and $d = 4$ mm for Mg II.
Figure 8. Plasma morphology for laser-induced plasmas generated in air with different focusing distances (the focal plane of the focusing lens was placed at a distance $d$ below the sample surface).
This remarkable variation of the emissivity with the focusing distance has been already reported in several works, where the existence of the maximum has been explained as a trade off between the shielding effect and the laser irradiance over the sample surface [38-40]. For low values of $d$, the irradiance is high and the plasma absorbs and reflects the incident laser energy, rising the temperature and the electron density. The plasma proceeds like a shield preventing the laser pulses reaching the sample then, the ablated mass decreases as well as the emissivity of atoms and ions. This shielding effect explains the growth of Mg II concentration respect to Mg I observed in the plasma front in figure 9c. As $d$ is increased, the irradiance decreases and the shielding is gradually reduced originating a more efficient ablation of the sample. Finally, as $d$ grows, the low irradiance starts to dominate and a plasma with a lower temperature and emissivity is obtained. This is clearly observed in figure 9a where the peak intensities of Mg I-II have significantly decreased. In addition, the plasma expands along the laser direction and develops a tail with a low temperature that increases its length as $d$ grows. For an intermediate value of approximately $d = 4$ mm, which depends slightly of the laser energies used in this work, a maximum emissivity takes place. For this optimum irradiance, the atom and ion distributions are symmetrical and the plasma has an approximately spherical shape. We may deduce that, in these focusing conditions, the laser-induced plasmas has a maximum emission intensity while inhomogeneity is minimized. Therefore, it is more suitable as a spectroscopic source. Hereafter, all the measurements were carried out generating the plasma with an approximately focusing distance of $d = 4$ and selecting the emission coming from the plasma center.

**Figure 9.** Profiles of spatially – integrated peak intensities along the direction of plasma expansion of neutral atoms and ions of Mg in laser induced plasmas generated for different focusing distances. The insets show the plasma shape in each case.
4.4. Temporal evolution

The intensity profiles of Mg spectral lines listed in table 1 were measured with different time windows and a fixed pulse energy \(E = 100\) mJ. To this aim, the delay gate \((t_d)\) with respect to the laser pulse was varied in the range 1-10 µs with a gate width \((t_w)\) of 1 µs. The line profiles measured were analysed using the proposed model to characterize the plasma at different times through the determination of the temperature and the electron density.

Figure 11 shows a typical Boltzmann plot for Mg neutral atoms and ions obtained for \(t_d = 7\) µs, after self-absorption correction. It can be observed that the slopes of the linear fittings are significantly different, resulting in different temperature values for Mg I \((kT = (0.76 \pm 0.11)\) eV) and Mg II \((kT = (1.01 \pm 0.02)\) eV). Consequently, different values of the electron density were also obtained from these temperatures for Mg I \((N_e = (1.6 \pm 0.9) \times 10^{17}\) cm\(^{-3}\)) and for Mg II \((N_e = (8.4 \pm 1.2) \times 10^{17}\) cm\(^{-3}\)). These results are a consequence of constructing the Boltzmann plot using spatially-integrated line intensities by collecting the plasma emission from one side of an inhomogeneous plasma. The temperature and electron density have apparent values that correspond to population-averaged values [13,41]. The higher apparent temperature obtained for Mg II respect to Mg I agrees with a picture of a high-temperature inner region of the plasma, populated mainly by ions, and a low-temperature external region, populated mainly by neutral atoms.

To improve the accuracy of the calculation of the temperature, a Saha-Boltzmann plot was constructed with the intensities of both, Mg I and Mg II lines. The use of self-absorbed lines to construct the Boltzmann or Saha-Boltzmann plot introduces a systematic error in the evaluation of temperature, which results either underestimated or overestimated. To overcome the problem, the values of the factor \(R_\lambda\) (equation 10) were used for correcting the effects of self-absorption on the corresponding emission lines. As an example, figure 12 shows the Saha-Boltzmann plot constructed before and after correction for \(t_d = 7\) µs. New apparent values of the temperature \((kT = (0.93 \pm 0.01)\) eV) and the electron density \((N_e = (4.6 \pm 0.9) \times 10^{17}\) cm\(^{-3}\)) of the whole plasma were obtained, whose values were between the two apparent values obtained previously from neutral atom and ion Boltzmann plots.
The temporal evolution of plasma temperatures and electron density are observed in figures 13 and 14, respectively, showing exponential decays as the plasma evolves with time due to the processes of expansion, cooling and recombination. The experimental data obtained for the electron density were obtained by averaging the values corresponding to the three resonant lines and the error bars correspond to the standard deviations. Moreover, the values obtained were checked to be larger that the critical value given by the McWhirter’s criterion for existence of LTE ($N_e^* \sim 1 \times 10^{16}$ cm$^{-3}$).

**Figure** 11. Boltzmann plots obtained from spatially integrated measurements of the intensities of neutral atomic and ionic Mg lines at 7 µs delay time. The apparent temperatures deduced from each plot are indicated.

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**Figure** 12. Saha – Boltzmann plot constructed using spatially integrated Mg atomic and ionic lines at 7 µs delay time. Data uncorrected (□) and corrected (•) for self – absorption and the corresponding values of apparent temperatures are shown.
4.5. Effects of the laser energy

The intensity profiles of Mg spectral lines of table 1 were now measured with different laser energies, in the range 50-200 mJ varying in steps of 25 mJ, and a fixed time gate ($t_d = 7 \, \mu s$ and $t_w = 1 \, \mu s$). The plasma exhibited a spherical shape in all the cases, with the only difference of a linear increment of their sizes ($l$) with the pulse energy (Figure 15). The values obtained for the plasma temperature and the electron density are shown in figures 16 and 17, respectively. It can be seen that, for the energies analysed, the temperature grows directly proportional to the pulse energy, while the electron density suffer an exponential increment, being higher that the McWhirter’s threshold for LTE. In summary, when the energy of the laser was increased, the plasmas generated had a larger size and a higher temperature, but a moderate growth of the electron density was achieved.

![Figure 13. Temporal evolution of the plasma temperature.](image13)

![Figure 14. Temporal evolution of the electron density of the plasma.](image14)

![Figure 15. Average plasma length $l$ along the direction of observation as a function of the pulse energy.](image15)
5. Conclusions

Calibration-free LIBS is a very promising alternative method based on the analysis of the profiles of suitable spectral lines which allows to overcome matrix effects and to perform a quantitative analysis without the need of constructing calibration curves. Considering an homogeneous plasma is the simplest approach and then, the spatial inhomogeneity of the plasma should be minimized. Moreover, self-absorption needs to be considered. These two issues are the main concerns affecting the existing standard methods to obtain reliable and accurate quantitative results in LIBS applications. In this work, a characterization method for laser-induced plasmas has been carried out, which provide valuable additional information to the methods used in LIBS technique.

The laser irradiance over the sample surface, determined by the pulse energy and the focusing length, strongly affect the plasma morphology and the intensity of emission. A simple visual examination of an increased image of the lateral plasma shape is very useful to select an optimum focusing distance leading to a plasma with an approximated spherical shape in which both, a more uniform spatial distribution of species in the plume and a higher emission intensity are obtained.

An algorithm was implemented that compute the emission of spectral lines to reproduce the experimental line profiles by calculating their optical thickness. Self-absorption was evaluated and compensated to retrieve the line profiles in optically-thin conditions. Plasma characterization was carried out through the determination of the temperature and the electron density. In this approach, the temporal evolution and the effects of the laser energy were investigated. A qualitative interpretation of the results was achieved by taking into account the plasma shape.

Quantification of Mg in the plasma plume is a difficult task and further investigation is currently in progress. Anyway, we may conclude that the optical thickness save valuable information that can be retrieved from the analysis of profiles of suitable spectral lines, which is of great importance to get a deep insight and to improve the LIBS performance in a wide range of applications.
References

[1] Winefordner J D, Gornushkin I B, Correll T, Gibb E, Smith B W and Omenetto N 2004 Comparing several atomic spectrometric methods to the super stars: special emphasis on laser induced breakdown spectrometry, LIBS, a future super star J. Anal. At. Spectrom. 19 1061-83.

[2] Tognoni E, Palleschi V, Corsi M, Cristoforetti G, Omenetto N, Gorhushkin I, Smith B W and Winefordner J D 2006 Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications ed Miziolek A W, Palleschi V and Schechter I (Cambridge: University Press) chapter 3.

[3] Aragón C and Aguilera J A 2008 Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods Spectrochim. Acta Part B 63 893-916.

[4] Tognoni E, Palleschi V, Corsi M and Cristoforetti G 2002 Quantitative micro-analysis by laser-induced breakdown spectroscopy: a review of the experimental approaches Spectrochim. Acta Part B, 57 1115-30.

[5] Vadillo J M and Laserna J J 2004 Laser-induced plasma spectrometry: truly a surface analytical tool Spectrochim. Acta Part B 59 147–61.

[6] Pasquini C, Cortez J, Silva L M C and Gonzaga F B 2007 Laser Induced Breakdown Spectroscopy J. Braz. Chem. Soc. 18 463-512.

[7] Fantoni R, Canive L, Colao F, Fornarini L, Lazic V and Spizzichino V 2008 Methodologies for laboratory Laser Induced Breakdown Spectroscopy semiquantitative and quantitative analysis – A review Spectrochim. Acta Part B 63 1097-108.

[8] Ocean Optics. http://www.oceanoptics.com/Products/libs.asp.

[9] Sallé B, Mauchien P and Maurice S 2007 Laser-Induced Breakdown Spectroscopy in open-path configuration for the analysis of distant objects Spectrochim. Acta Part B 62 739-68.

[10] Anglos D 2001, Laser-Induced Break-down Spectroscopy in Art and Archaeology Appl. Spectrosc. 55 186-205.

[11] Aragón C and Aguilera J A 2008 Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods Spectrochim. Acta Part B 63 893-916.

[12] Aguilera J A, Bengoechea J and Aragón C 2004 Spatial characterization of laser induced plasmas obtained in air and argon with different laser focusing distances Spectrochim. Acta Part B 59 461-69.

[13] Aguilera J A and Aragón C 2004 Characterization of a laser-induced plasma by spatially resolved spectroscopy of neutral atom and ion emissions. Comparison of local and spatially integrated measurements Spectrochim. Acta Part B 59 1861-76.

[14] Ferretti M and Cristoforetti G, Legnaioli S, Palleschi V, Salvetti A, Tognoni E, Console E and Palaia P 2007 In situ study of the Porticello Bronzes by portable X-ray fluorescence and laser-induced breakdown spectroscopy Spectrochim. Acta Part B 62 1512-18.
[15] De Giacomo A, Dell’Aglio M, De Pascale O, Longo S and Capitelli M 2007 Laser induced breakdown spectroscopy on meteorites Spectrochim. Acta Part B 62 1606-11.

[16] De Giacomo A, Dell’Aglio M, De Pascale O, Gaudioso R, Santagata A and Teghil R 2008 Laser Induced Breakdown Spectroscopy methodology for the analysis of copper-based-alloys used in ancient artworks Spectrochim Acta Part B 63 585-90.

[17] Anzano J M, Villoria M A, Ruiz-Medina A and Lasheras R J 2006 Laser-induced breakdown spectroscopy for quantitative spectrochemical analysis of geological materials: Effects of the matrix and simultaneous determination Anal. Chim. Acta 575 230-35.

[18] Sallé B, Lacour J L, Mauchien P, Fichet P, Maurice S and Manhès G 2006 Comparative study of different methodologies for quantitative rock analysis by Laser-Induced Breakdown Spectroscopy in a simulated Martian atmosphere Spectrochim. Acta Part B 61 301-13.

[19] Laville S, Sabsabi M and Doucet F R 2007 Multi-elemental analysis of solidified mineral melt samples by Laser-Induced Breakdown Spectroscopy coupled with a linear multivariate calibration Spectrochim. Acta Part B 62 1557-66.

[20] Aragón C and Aguilera J A 2008 Spatial and temporal scaling and common apparent excitation temperature of laser-induced plasmas generated at constant irradiance with different pulse energies J. Appl. Phys. 103.

[21] Hermann J, Boulmer-Leborgne C and Hong D 1998 Diagnostic of the Early Phase of an Ultraviolet Laser Induced Plasma by Spectral Line Analysis Considering Self-absorption J. Appl. Phys. 83 691-96.

[22] Bulajic D, Corsi M, Cristoforetti G, Legnaïoli S, Palleschi V, Salvetti A and Tognoni E 2002 A procedure for correcting self-absorption in calibration free-laser induced breakdown spectroscopy Spectrochim. Acta Part B 57 339-53.

[23] Aguilera J A, Bengochea J and Aragón C 2003 Curves of growth of spectral lines emitted by a laser-induced plasma: influence of the temporal evolution and spatial inhomogeneity of the plasma Spectrochim. Acta Part B 58 221-37.

[24] Yaroshchyk P, Body D, Morrison R and Chadwick B 2006 A semi-quantitative standard-less analysis method for laser-induced breakdown spectroscopy Spectrochim. Acta Part B 61 200-09.

[25] D’Angelo C A, Díaz Pace D M, Bertuccelli G and Bertuccelli D 2008 Laser induced breakdown spectroscopy on metallic alloys: Solving inhomogeneous optically thick plasmas, Spectrochim. Acta Part B 63 367-74.

[26] Díaz Pace D M, D’Angelo C A and Bertuccelli G 2009 Semiempirical model for analysis of inhomogeneous optically thick laser-induced plasmas Spectrochim. Acta Part B 64 999-1008.

[27] Gornushkin I B, Stevenson C L, Smith B W, Omenetto N and Winefordner J D 2001 Modeling an inhomogeneous optically thick laser induced plasma: a simplified theoretical approach Spectrochim. Acta Part B 56 1769-85.
[28] Zwicker H 1968 Plasma diagnostics ed Loghte-Holtgreven W (John Wiley and Sons: Amsterdam) chapter 3.

[29] Aragón C, Bengoechea J and Aguilera J A 2001 Influence of the optical depth on spectral line emission from laser-induced plasmas Spectrochim. Acta Part B 56 619-28.

[30] NIST electronic database, in http://physics.nist.gov/PhysRefData.

[31] Díaz Pace D M, D’Angelo C A, Bertuccelli D and Bertuccelli G 2006 Analysis of heavy metals in liquids using Laser Induced Breakdown Spectroscopy by liquid-to-solid matrix conversion Spectrochim. Acta Part B 61 929-33.

[32] Griem H R 1964 Plasma Spectroscopy (McGraw-Hill: New York).

[33] Griem H R 1974 Spectral Line Broadening by Plasmas (Academic Press: New York).

[34] El Sherbini A M, El Sherbini Th M, Hegazy H, Cristoforetti G, Legnaioli S, Palleschi, V Pardini L, Salvetti A and Tognoni E 2005 Evaluation of self-absorption coefficients of aluminum emission lines in laser-induced breakdown spectroscopy measurements, Spectrochim. Acta B 60 1573-79.

[35] Bredice F, Borges F O, Sobral H, Villagran-Muniz M, Di Rocco H O, Cristoforetti G, Legnaioli S, Palleschi V, Pardini L, Salvetti A and Tognoni E 2006 Evaluation of self-absorption of manganese emission lines in Laser Induced Breakdown Spectroscopy measurements, Spectrochim. Acta Part B 61 1294-1303.

[36] Moon H-Y, Herrera K K, Omenetto N, Smith B W and Winefordner J D 2009 On the usefulness of a duplicating mirror to evaluate self-absorption effects in laser induced breakdown spectroscopy Spectrochim. Acta B 64 702-13.

[37] Cremers D A and Radziemsky L J 1987 Laser Spectroscopy and its Applications ed Radziemsky L J, Solarz R W and Paisner J A (Marcel Dekker: New York).

[38] Aguilera J A and Aragón C 2008, Characterization of laser-induced plasmas by emission spectroscopy with curve-of-growth measurements. Part I: Temporal evolution of plasma parameters and self-absorption Spectrochim. Acta Part B 63 784-92.

[39] Aguilera J A and Aragón C 2008, Characterization of laser-induced plasmas by emission spectroscopy with curve-of-growth measurements. Part II: Effect of the focusing distance and the pulse energy Spectrochim. Acta Part B 63 793-99.

[40] Aragón C and Aguilera J A 2008 Spatial and temporal scaling and common apparent excitation temperature of laser-induced plasmas generated at constant irradiance with different pulse energies J. Appl. Phys. 103.

[41] De Giacomo A, Dell'Aglio M, Gaudìuso R, Cristoforetti G, Legnaioli S, Palleschi V and Tognoni E 2008, Spatial distribution of hydrogen and other emitters in aluminum laser-induced plasma in air and consequences on spatially integrated Laser-Induced Breakdown Spectroscopy measurements Spectrochim. Acta B 63 980-87.