Contents lists available at ScienceDirect



Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Laser-induced plasma characterization through self-absorption quantification



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ARTICLE INFO

Article history: Received 26 January 2018 Revised 6 April 2018 Accepted 6 April 2018 Available online 11 April 2018

Keywords: Laser-induced breakdown spectroscopy (LIBS) Self-absorption quantification Electron temperature Absolute species number density

ABSTRACT

A self-absorption quantification method is proposed to quantify the self-absorption degree of spectral lines, in which plasma characteristics including electron temperature, elemental concentration ratio, and absolute species number density can be deduced directly. Since there is no spectral intensity involved in the calculation, the analysis results are independent of the self-absorption effects and the additional spectral efficiency calibration is not required. In order to evaluate the practicality, the limitation for application and the precision of this method are also discussed. Experimental results of aluminum-lithium alloy prove that the proposed method is qualified to realize semi-quantitative measurements and fast plasma characteristics diagnostics.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a well-known analytical technique based on the atomic emission spectroscopy. The elemental composition and relative abundance information can be obtained by analyzing the plasma radiation generated by focusing high-energy pulsed laser on the sample. It has a wide range of applications in industrial analysis, environmental monitoring and biomedical field due to its advantages of rapid, simultaneous multi-element analysis and no or minimal need for sample preparation [1–8]. In LIBS, self-absorption is a phenomenon of re-absorption (by unexcited atoms in the periphery of the plasma plume) of the emitted radiation as it passes outwards from the central region of the plasma. It not only reduces the spectral line intensity and increases its full width at half maximum (FWHM) [9-12], but also produces saturation effects. As a consequence, self-absorption is usually an undesirable effect in LIBS measurements. There have been numerous studies investigating its mechanism and developing efficient methods to achieve proper correction. Omenetto et al. interpreted the selfabsorption mechanism in inductively coupled plasmas by using equations and the curve of growth method [13,14]. Bulajic et al.

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https://doi.org/10.1016/j.jqsrt.2018.04.009 0022-4073/© 2018 Elsevier Ltd. All rights reserved. proposed a self-absorption effect model to extend the calibrationfree LIBS (CF-LIBS) to optically thick plasmas, and enhanced the measurement precision by almost one order [15]. St-Onge et al. investigated two typical response curves for resonance and non-resonance lines of sodium, and discussed the relationships between self-absorption degree, selection of spectral lines, detection sensitivity, and dynamic content range [16]. Sherbini et al. developed a method to calculate the self-absorption (SA) coefficients of emission lines such that the precision in quantitative LIBS analysis could be improved [17]. Bengoechea et al. studied the effects of self-absorption, collection time window, ablation pit size, and spatial inhomogeneity on laser-induced plasma emission lines [18]. Sun et al. chose a weakly self-absorbed internal reference line to correct the self-absorbed aluminum lines and obtained more regular Boltzmann plots [19]. Li et al. developed a LIBS assisted laser-stimulated absorption technique to make the ground-state atoms transit up to an excited state and avoid the serious selfabsorption effect [20]. As can be seen, these existing methods either rely on some ideal assumptions or approximate modeling to correct the self-absorbed spectral lines, or employ additional devices to minimize the self-absorption effect on a particular line. However, the complex laser-target interaction process and the fast plasma evolution can reduce the applicability of these assumptions or models for real quantitative LIBS analysis [17].

In this paper, a self-absorption quantification LIBS analysis method, which utilizes the intensity independent information in the self-absorbed spectral lines, is proposed to characterize the induced plasma and perform semi-quantitative measurements. The electron temperature, elemental concentration ratio, and absolute species number density can be deduced by directly quantifying the self-absorption degree. LIBS analysis of aluminum-lithium alloy was performed to verify the practicability, advantages, limitations, and precision of this method.

2. Methodology

Assuming the plasma is in local thermodynamic equilibrium (LTE) condition during the spectra acquisition period, the spectral line intensity that corresponds to the transition between two levels (upper level j to lower level i) is [17,21]:

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

where *h* (erg.s) is the Planck's constant, *c* (cm.s⁻¹) is the speed of light, λ_0 (cm) is the central wavelength of the emission line, *n* (cm⁻³) is the number density, *g* is the degeneracy, $k(\lambda)$ (cm⁻¹) is the absorption coefficient, and *l* (cm) is the length of the absorption path. The $k(\lambda)l$, also called as optical depth, determines the self-absorption degree of the line.

The SA coefficient is defined as the ratio of the measured intensity of the emission line at its maximum over the value of the intensity expected in absence of self-absorption [12,15]:

$$SA = \frac{l(\lambda_0)}{l_0(\lambda_0)} = \frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l}.$$
(2)

The relationship between *SA* and the FWHM of a self-absorbed line can be expressed as [17]:

$$SA = \left(\frac{\Delta\lambda}{\Delta\lambda_0}\right)^{1/\alpha} = \left(\frac{\Delta\lambda}{2w_s}\frac{1}{n_e}\right)^{1/\alpha},\tag{3}$$

where $\alpha = -0.54$, $\Delta\lambda_0$ (Å) is the expected FWHM of the spectral line in optically thin conditions, $\Delta\lambda$ (Å) is the actual FWHM of the spectral line, w_s is the half-width Stark parameter, n_e (cm⁻³) is the electron density by measuring the Stark broadening of H_{α} line [22]. Once *SA* is obtained according to Eq. (3), $k(\lambda_0)l$ can be calculated by Eq. (2). The optical depth can also be expressed as:

$$k(\lambda)l = \pi \frac{e^2}{mc^2} n_i f \lambda_0^2 l L(\lambda), \qquad (4)$$

where *e* (statcoulomb) and *m* (g) are the charge and the mass of the electron, respectively, *f* is the oscillator strength of the transition, the parameter $n_i l$, that is area density (cm⁻²), is the product of the species number density and the absorption path length of the species along the line of sight, representing the number of atomic or ionic species per unit area integrated along the path length, and $L(\lambda)$ is a normalized line profile function:

$$L(\lambda) = \frac{2}{\pi} \frac{\Delta \lambda_0}{4(\lambda - \lambda_0)^2 + \Delta \lambda_0^2}.$$
(5)

So the area density of the emitting species at the lower level i can be obtained by simply rewriting Eq. (4) as:

$$n_i l = \frac{mc^2}{2e^2} \frac{\Delta\lambda_0}{f\lambda_0^2} k(\lambda_0) l = 1.775 \times 10^4 \frac{\Delta\lambda_0}{f\lambda_0^2} k(\lambda_0) l.$$
(6)

On this basis, if the electron temperature is known, the total area density of the species can be obtained according to the Boltz-mann distribution:

$$\frac{n_i}{N} = \frac{g_i \cdot \exp(-E_i/k_B T)}{Z},\tag{7}$$

where N (cm⁻³) is the total number density of species in an atomic or ionic state, E (eV) is the level energy, k_B (eV-K⁻¹) is the Boltzmann constant, T (K) is the electron temperature, and Z is the partition function. Furthermore, if the absorption path length is known, the absolute number density of atoms/ions in the plasma can also be calculated.

For electron temperature determination, the Saha-Eggert equation, which describes the degree of ionization for a plasma in thermal equilibrium [23], can be merged with the Boltzmann distribution function as:

$$\frac{n_i^l}{g_i^l} = \frac{N^l}{Z^I} \exp\left(-\frac{E_i^l}{k_B T}\right),\tag{8a}$$

$$\frac{n_i^{II}}{g_i^{II}} = \frac{2(2\pi mk_B T)^{3/2}}{n_e h^3} \frac{N^I}{Z^I} \exp[-\frac{(E_i^{II} + E_{ion} - \Delta E_{ion})}{k_B T}],$$
(8b)

where the superscripts *I* and *II* indicate the neutral and singly ionized species, respectively, E_{ion} (eV) is the first ionization energy, k_B here is in erg·K⁻¹ unit, and ΔE_{ion} (eV) is the reduction of ionization energy caused by the experimental conditions. Since ΔE_{ion} is usually one to two orders lower than the sum of $E_i^{II} + E_{ion}$ in LIBS, it can be ignored in the following equation.

Multiplying *l* on both sides of Eq. (8) and then taking a logarithmic operation yields a modified Saha–Boltzmann plot as:

$$\ln\frac{n_i^l l}{g_i^l} = -\frac{E_i^l}{k_B T} + \ln\left(\frac{N^l l}{Z^l(T)}\right),\tag{9a}$$

$$\begin{bmatrix} \ln\left(\frac{n_i^{ll}l}{g_i^{ll}}\right) - \frac{1}{k_B T} \ln\left(\frac{2(2\pi m k_B T)^{3/2}}{n_e h^3}\right) \end{bmatrix} = -\frac{\left(E_i^{ll} + E_{ion}\right)}{k_B T} + \ln\left(\frac{N^l l}{Z^l(T)}\right),$$
(9b)

where Eq. (9a) is for neutral lines and Eq. (9b) for ionic lines. Similar to the traditional Boltzmann or Saha–Boltzmann plot, the relation in Eq. (9) can deduce a linear plot versus E_i , and the electron temperature can be deduced from the slope of such a plot.

In brief, the total area density of the emitting species can be obtained by exploiting Eq. (7) and the total area density of an element can be calculated by summing over the corresponding area densities of atomic and singly ionized species. For two elements *a* and *b*, by considering their different atomic masses, the elemental concentration (in weight) ratio w_a/w_b in the plasma can be thereby obtained. The absolute number density of the species in the plasma can be calculated by dividing the area density by the path length *l*, estimated by dual-wavelength differential imaging [24,25] or space-resolved spectroscopy.

For a more intuitive description, the flowchart of this selfabsorption quantification method is shown in Fig. 1. The electron temperature, the elemental concentration ratio, and the absolute species number density can be deduced from step 4, 6, and 7, respectively.

3. Experimental

The LIBS spectrum of an aluminum-lithium alloy (nominal weight composition: Al 95.0%, Mg 1.6%, Li 0.8%, Cu 2.39%, Mn 0.21%) was used to calculate the spatially-averaged electron temperature, the concentration ratio between Mg and Al, and the species number densities using the proposed self-absorption quantification method.

The experimental LIBS system, as we previously described in detail [26,27], consisted of a focused Nd: YAG laser (Innolas, SL-100, wavelength: 1064 nm, repetition rate: 10 Hz, pulse energy: 100 mJ) that generated the plasma, an echelle spectrograph (Lasertechnik Berlin GmbH LTB, ARYELLE Butterfly) that equipped with a time-gated ICCD (Andor, iStar DH334T), and an additional



Fig. 1. Flowchart of the self-absorption quantification method for laser-induced plasma characterization.

ICCD Camera (Andor, iStar DH334T) that recorded the plasma images. The laser was focused by a plano-convex lens of 200 mm focal length to produce a focal spot diameter of 0.7 mm. The emission from the plasma plume was collected along the line of sight perpendicular to the laser beam direction, above the target surface 1.3 mm and then was guided to the echelle spectrograph by using an all-silica optical fiber. Each spectrum was obtained by averaging 120 spectra with background subtracted. The acquisition delay and integration times of the ICCDs were both set to 1 μ s.

4. Results and discussions

4.1. Experimental results

In LIBS, it is usually believed that the LTE condition exists in most plasmas obtained with metallic samples [23,28]. This assumption seems to be valid in our experiment.

For step 1, the *SA* coefficients of four strongly self-absorbed lines, Al I 308.21 nm, Al II 281.62 nm, Mg I 285.21 nm, and Mg II 280.27 nm were calculated. Since the instrumental line broadening exhibits a Gaussian profile, the Stark line width $\Delta\lambda$ can be extracted from the measured line width $\Delta\lambda_{observed}$ by subtracting the instrumental line broadening $\Delta\lambda_{instrument}$, by approximating $\Delta\lambda \approx \Delta\lambda_{observed} - \frac{\Delta\lambda_{instrument}^2}{\Delta\lambda_{observed}}$ [29]. In our case, $\Delta\lambda_{instrument}$ were

0.01 nm at 254 nm (corresponding to the four self-absorbed lines) and 0.03 nm at 546 nm (corresponding to the H_{α} line), which were determined by measuring the FWHMs of the Hg lines emitted by a standard low-pressure Hg-Ar lamp. Combined with step 2 and 3, the detailed spectroscopic parameters of the four lines, together with their *SA* coefficients, optical depths, and area densities of the emitting Al and Mg species at lower levels are listed in Table 1. The relative small *SA* coefficients indicate the existence of strong self-absorption behavior.

Then for step 4, the spatially averaged electron temperature calculated by exploiting the modified Saha–Boltzmann plot is shown as the red part in Fig. 2. As can be seen, the electron temperatures determined by Mg and Al are 0.96 eV and 0.97 eV, respectively. In order to validate the modified Saha–Boltzmann plot, the traditional Boltzmann plot was also performed to make a comparison by using six Al I lines with and without self-absorption correction [17] (the blue part of Fig. 2). The electron temperature after self-absorption correction is shown as 0.99 eV, which is in good accordance with that generated by the modified Saha–Boltzmann plots.

For step 5, the area densities of emitting Mg and Al species were obtained by the Boltzmann distribution. After that, by ignoring the second order and above ionization of plasma in this study, the total area densities of Mg and Al elements were calculated by summing over the corresponding area densities of neutral and singly ionized species according to step 6 and the calculated area

Spectroscopic parameters of the spectral lines and characteristics of the species.							
Species	Wavelength λ (nm)	Half-width Stark parameter ω (Å)	SA	kl	$n_i l (\mathrm{cm}^{-2})$	Nl (cm ⁻²)	N (cm ⁻³)
Al I	308.21	2.81×10^{-2}	0.2930	3.28	2.74×10^{14}	$1.10 imes 10^{15}$	5.52×10^{19}
Al II	281.62	4.29×10^{-3}	0.3540	2.62	4.71×10^{13}	3.64×10^{16}	1.65×10^{17}
Mg I	285.21	4.13×10^{-3}	0.1560	6.41	8.54×10^{12}	1.79×10^{13}	8.93×10^{12}
Mg II	280.27	$7.92 imes 10^{-4}$	0.0023	434.8	$6.83 imes 10^{14}$	$7.03 imes 10^{14}$	3.20×10^{15}



Fig. 2. A comparison between the proposed modified Saha-Boltzmann plots for Al and Mg species and the traditional Boltzmann plots for Al species with and without self-absorption correction.



Fig. 3. The dual-wavelength differential images for species Al I and Al II at 1 μs delay.

densities *Nl* are listed in Table 1. Considering the atomic masses, the weight ratio w_{Mg}/w_{Al} in the plasma was calculated as 0.0171, which is in coincidence with the nominal value of 0.0150.

For step 7, considering that in laser-induced plasma, different species may have different spatial distributions, the dualwavelength differential imaging technique [24,25] was employed to measure the exact absorption path lengths of the species. A typical 2-D distribution of the species in a plasma is shown in Fig. 3, with Al I in red and Al II in green, from which the path lengths of species Al I and Al II were estimated as 2.0 mm and 2.2 mm, respectively. Regrettably, it was difficult to obtain the differential image of Mg species due to the intense interference from adjacent spectral lines. Since magnesium and aluminum have the similar physical and chemical properties (such as melting point, atomic mass, chemical activity, etc.), we approximated that, in this work, the absorption path lengths of the Mg species were same as those of the Al species. Then the absolute number densities of the species were obtained by dividing the area densities by these path lengths and listed in Table 1. In our experiment, the electron density calculated from the H_{α} line broadening was 1.72×10^{17} cm⁻³, which is comparable with the absolute Al singly ionized number densities $(1.65 \times 10^{17} \text{ cm}^{-3})$. Evidently, the free electrons present in the plasma are mainly contributed by the single ionized matrix element Al (with a nominal weight composition of 95%), accounting for more than 95.9% of contribution. In other words, the electron contribution of the other elements presented in the alloy as well as the air can be ignored.

4.2. Advantages and limitations

Self-absorbed emission lines can be fruitfully used to characterize the plasma. This method mainly employs the self-absorption degree (except for the spectral intensity) of the self-absorbed lines to directly deduce plasma characteristics including optical depth, electron temperature, elemental concentration ratio, and absolute species number density. Therefore, not only the analysis results are not affected by the self-absorption effects, but also the spectral efficiency calibration of the optical detection unit is not required. This is especially important for prolonging the calibration period of online LIBS application.

Table 1



Fig. 4. The RSD of $k(\lambda_0)l$ and RE of "1/SA approximation" versus SA.

From Eq. (2), the relationship between $k(\lambda_0)l$ and SA indicates that the method is accurate when $SA \ll 1$. In this case, the spectral line is strongly affected by the self-absorption, and the $k(\lambda_0)l$ tends to the limit value of 1/SA. In our experiments, the SA values of the spectral lines were no more than 0.354, the errors between the inverse $k(\lambda_0)l$ values and the true ones were less than 7.8%. Therefore, the $k(\lambda_0)l$ can be calculated by the 1/SA approximation. However, when SA is close to 1, the method will be no longer suited for calculation due to the significant increase in optical depth uncertainty. In this experiment, the relative standard deviation (RSD) of SA was about 5%, in which the corresponding RSD of $k(\lambda_0)l$ and the relative error (RE) of "1/SA approximation" versus the SA are shown in Fig. 4. As can be seen, both the RSD of $k(\lambda_0)l$ and RE of "1/SA approximation" increase monotonously with SA. For $k(\lambda_0)l$ calculation by using Eq. (2), if the permitted RSD of $k(\lambda_0)l$ is 10%, the SA coefficients of the selected lines should be limited to SA < 0.56. Furthermore, for $k(\lambda_0)l$ calculation by using "1/SA approximation", if the permitted RE of $k(\lambda_0)l$ is 10%, the SA coefficients should be limited to SA < 0.38.

4.3. Error analysis

In summary, this self-absorption quantification method consists of two assumptions: the plasma is homogeneous, where the temperature and electron density gradients have no effects on the spectral line profiles; the plasma is in the LTE condition, where the energy level distribution of species follows the Boltzmann distribution law [17,21]. Under these assumptions, one can assume a point emission source located in the center of the plasma, which is surrounded by uniform plasma of thickness *l* and absorption coefficient $k(\lambda)$. In addition, there are three approximations: the emission line has a normalized Lorentzian profile that depends on the Stark effect, other broadening mechanisms are neglected; for optical depth calculation, the effect of stimulated emission with respect to plasma absorption is neglected [9,12]; the second- and higher- order ionization states of species are ignored. Since this method uses a number of developed theories to calculate the plasma characteristic parameters, and each theory has its applicable model and corresponding approximation, it is only a semiquantitative analysis method.

The analysis precision of this method was also evaluated by using the classical error propagation theory. Firstly, the SA error can be estimated from Eq. (3) as:

$$\frac{\Delta SA}{SA} = \left|\frac{1}{\alpha}\right| \sqrt{\left(\frac{\Delta w_S}{w_S}\right)^2 + \left(\frac{\Delta n_e}{n_e}\right)^2} = \left|\frac{1}{\alpha}\right| \sqrt{\left(\frac{\Delta w_S}{w_S}\right)^2 + \frac{9}{4} \left(\frac{\Delta w_H}{w_H}\right)^2}.$$
(10)

Here, the w_s errors for the four lines Al I 308.21 nm, Al II 281.62 nm, Mg I 285.21 nm, and Mg II 280.27 nm were 15%, 8%, 20%, and 20%, respectively [30–32], while the w_H (of H_α) error was 10% [22]. Consequently, the *SA* errors for the four lines were calculated to be 39%, 31%, 46%, and 46%, respectively.

Secondly, because the expression of Eq. (2) is an implicit function type, the $k(\lambda_0)l$ error caused by *SA* can only be solved numerically. In our experiment, the *SA* coefficients of the four lines were 0.293, 0.354, 0.156, and 0.0023, respectively, which correspond to $k(\lambda_0)l$ errors of 52%, 42%, 59%, and 58%.

Then, the $n_i l$ error can be estimated from Eq. (6) as:

$$\frac{\Delta n_i l}{n_i l} = \frac{\Delta k(\lambda_0) l}{k(\lambda_0) l}.$$
(11)

Thus, the $n_i l$ errors equal to the $k(\lambda_0) l$ errors.

Next, the *T* error was estimated by calculating the relative error of the slope of the modified Saha–Boltzmann plot, which is about 2%.

The *Nl* error can be estimated from Eq. (7) as:

$$\frac{\Delta Nl}{Nl} = \sqrt{\left(\frac{\Delta n_i l}{n_i l}\right)^2 + \left(\frac{\Delta Z}{Z}\right)^2 + \left(\frac{E_i}{k_B T}\right)^2 \left(\frac{\Delta T}{T}\right)^2},$$
(12)

where the partition function error was neglected when it was compared to the other two higher sources of error [33]. Thus, the Nl errors were found to be 52%, 44%, 59%, and 58%, respectively, for the four species of Al I, Al II, Mg I, and Mg II. Obviously, the N errors equal to the Nl errors.

The total area density $N_{total}l$ error of an element can be estimated as:

$$\frac{\Delta N_{total}l}{N_{total}l} = \frac{\Delta N^l l + \Delta N^{ll} l}{N_{total}l},$$
(13)

where $N_{total}l = N^l l + N^{ll} l$. The $N_{total}l$ errors were calculated to be 44% for Al and 58% for Mg.

Finally, the w_{Mg}/w_{Al} error can be estimated as:

$$\frac{\Delta\left(w_{Mg}/w_{Al}\right)}{w_{Mg}/w_{Al}} = \sqrt{\left(\frac{\Delta N_{total,Mg}l}{N_{total,Mg}l}\right)^2 + \left(\frac{\Delta N_{total,Al}l}{N_{total,Al}l}\right)^2},$$
(14)

where $N_{total,Mg}l$ and $N_{total,Al}l$ represent the total area density of Mg and Al, respectively. The w_{Mg}/w_{Al} error was calculated to be 73%.

5. Conclusions

In this work, we proposed a self-absorption quantification method to directly obtain the plasma characteristics from the selfabsorbed spectral lines, such as optical depth, electron temperature, elemental concentration ratio, and absolute species number density. Experimental results performed on aluminum-lithium alloy showed that the mean electron temperatures obtained by the modified Saha-Boltzmann plots was 0.965 eV, which is close to that by the traditional Boltzmann plot with self-absorption correction. The weight ratio w_{Mg}/w_{Al} in the plasma was calculated as 0.0171, which is approximately coincident with the nominal value of 0.0150. The absolute singly ionized number density of matrix element Al was 1.65×10^{17} cm $^{-3}$, which was comparable with the electron density (1.72×10^{17} cm $^{-3}$). In addition, the limitations and the precision of the method were also discussed. For $k(\lambda_0)l$, the SA coefficients in the numerical calculation and the "1/SA approximation" were limited to less than 0.56 and 0.38, respectively. The errors estimated for temperature and elemental concentration ratio were 2% and 73%, respectively, while the errors of absolute number density of species Al I, Al II, Mg I, and MgII were 52%, 44%, 59%, and 58%, respectively. The advantage of this method is that the analysis results are not affected by the self-absorption effects, and no spectral efficiency calibration is required. This self-absorption quantification method is of great significance for semi-quantitative LIBS analysis, especially for the CF-LIBS.

Acknowledgments

This work was supported by National Key R&D Program of China (2017YFA0304203), Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (IRT13076), National Natural Science Foundation of China (NSFC) (61475093, 61775125), and Major Special Science and Technology Projects in Shanxi Province (MD2016-01).

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