The effect of self-absorption correction using internal reference on determining heavy metals concentration by laser induced breakdown spectroscopy

Fatemeh Salehi-Marzijarani[a], Seyede Zahra Shoursheini[a,*], Hamidreza Shirvani-Mahdavi[b], and Somayye Pashaei-Adl[a]

[a]Department of Physics, University of Alzahra, Tehran, Iran
[b]Department of Physics, Islamic Azad University (Central Tehran Branch), Tehran, Iran

*Corresponding Author: zshinie@alzahra.ac.ir

ABSTRACT— The identification and concentration of heavy metals, which may be so harmful for the body, is determined by the method of calibration-free laser-induced breakdown spectroscopy using a special strategy. First, the plasma temperature is obtained using the Boltzmann plot. Then, a line with an inappreciable self-absorption is considered for each element as the reference. The modified intensities of other lines of the element are calculated through their self-absorbed intensities in terms of the reference intensity. The plasma temperature is again computed by line pair ratio method. This procedure is carried out by an iterative algorithm until the self-absorption coefficient of selected lines converges on one. In the last step, the corrected temperature is evaluated by the Boltzmann plot drawn using true (non self-absorbed) line intensities of each element. The concentration of the elements is finally determined by the corrected temperature and intensities. The results indicate that the accuracy of this method in determining the concentrations is significantly better than the normal way.

KEYWORDS: LIBS, plasma temperatures, quantitative analysis, self-absorption, heavy metals.

I. INTRODUCTION

Over the past three decades heavy metals pollution, which is considered as a serious threat to life on the earth ecosystem, has substantially increased. Heavy metal pollution can arise from many sources but is most commonly caused by the purification of metals. The term "heavy metals" refers to metallic elements that have relatively high atomic densities (greater than 4 g/cm^3) and are generally toxic or poisonous even at low concentration. Although some of these elements, in very small amounts, are necessary to support life; however in larger amounts, they become toxic and create reactive radicals which damage cell structures including DNA and cell membranes [1]. The most notable heavy metals are mercury, lead and cadmium. Since lead, as a common environmental pollutant, interferes with metabolism of bones and teeth and alters the permeability of blood vessels and collagen synthesis, it can be seriously harmful to the developing immune system. For instance, lead exposure is a risk factor for asthma in children [2]. Dissolution of lead in drinking water pipes is one of the most significant ways to enter it to the body. Lead exposure is also one of the major concerns of occupational and community environments in the world.

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique of atomic emission spectroscopy (AES) that laser generated plasma is used as the emitting source. In this method, a pulsed laser beam is focused by a lens on the target material, of which a small volume is intensely heated and thus converted to a transient plasma state. In

the condition of high temperature and electron density, a part of sample is broken down, vaporized, atomized, and partially ionized, and the plasma releases energy by emission of radiation across a broad spectral range between 200 and 980 nm. However, a precise compositional analysis of alloys by LIBS requires a clear understanding of the main effects influencing the LIBS spectrum, and in particular self-absorption effect. The self-absorption effect causes the intensity of selected lines at low excitation energies of upper levels becomes lower than its theoretical value, and thus the calculated plasma temperature is obtained higher than expected. Therefore, the accuracy of the quantitative results of the LIBS method may be extremely destroyed by the self-absorption effect which must be regarded [3].

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. With the purpose for correcting the self-absorption effect, the CF-LIBS procedure has been updated by Bulajic et al., in which a self-absorption correction step is implemented by using a recursive algorithm based on the curve of growth (COG) [3]. In order to correct the self-absorption effect, the COGs of all the analytical lines in the Boltzmann plot should be constructed. The construction of the COGs requires calculating the plasma temperature, electron density, Gaussian broadening, Lorentzian broadening and optical path length. However, this procedure is complex and time-consuming, because it requires calculating theoretical values of many variables and measuring the observed half-widths of all analytical lines [4]. Lazic et al. [5] presented a simple model for constructing calibration curves of intensity from a thick homogenous plasma. Arago´n et al. [6] studied the influence of the optical depth on spectral line emission from laser induced plasmas. Heh-Young Moon et al. [7] illustrates the application of the well-known approach of duplicating the emission from a plasma by placing a spherical mirror behind it in order to characterize the degree of self-absorption of atomic transitions. Another simplified model which takes into account the nonlinear relationship between concentration and intensity in optically thick plasmas has been recently developed by Lanxiang Sun et al. [8] named internal reference for self-absorption correction. They first chose a line as an internal reference for each species, then compared the intensities of other spectral lines of the species with the reference line to estimate the self-absorption degrees of other spectral lines, and finally achieved an optimal correction by a regressive algorithm. In this method, the points on the Boltzmann plot become more regular, and the evaluation of the plasma temperature is more accurate than the conventional CF-LIBS.

In this paper, identification and quantification of heavy metals is carried out by laser-induced breakdown spectroscopy through a method called internal reference for self-absorption correction in brass alloys used in fittings and valves. Initially, the self-absorption coefficient, SA, for each emission line of a species (which is originally defined as the ratio of the measured peak height to the value of the line peak in absence of self-absorption) can be approximately obtained by the intensity ratio of the emission line to an internal reference line (with negligible self-absorption) of the species. Calculation of the self-absorption coefficients requires the plasma temperature, which can be preliminarily evaluated from the Boltzmann plot without any self-absorption correction. The line intensities obtained by the previous temperature are used to calculate a new temperature. Since the evaluation of the plasma temperature depends on the self-absorption coefficients, the optimal temperature can be determined by an iterative procedure until the convergence of the correlation coefficients and thus the convergence of SA, on one.

II. THEORETICAL ANALYSIS

The procedure of CF-LIBS has been described in detail by Ciucci et al. [9]; therefore, we only introduce the basic characteristics of this

method. Assuming the plasma is in local thermodynamic equilibrium (LTE) in the temporal window of signal acquisition, the measured integral line intensity can be expressed as:

$$I_\lambda^{ij} = SA \cdot F \cdot C_\alpha \frac{A_{ij}}{U_\alpha(T_e)} g_i \exp\left(\frac{-E_i}{kT_e}\right) \qquad (1)$$

where λ is the wavelength corresponding to the transition between two energy levels, E_i and E_j, of an atomic or ionic species α; C_α is the concentration of the emitting species α; A_{ij} is the transition probability for the given line; g_i is the degeneracy of the level i; F is a constant that takes into account the optical efficiency of the collection system as well as the total plasma number density and volume; k is the Boltzmann constant; T_e is the plasma temperature; $U_\alpha(T_e)$ is the partition function for the emitting species and the self-absorption coefficient SA is defined as the ratio of the measured peak height to the value of the line peak in absence of self-absorption.

If we select the internal reference line with a low transition probability A_{mn} or/and a high excitation energy level E_m, the self-absorption effect of the internal reference line can be negligible, and thus the relevant $SA_R \approx 1$. Therefore, using Eq. (1) the self-absorption coefficient of other emission lines associated with the species can be evaluated based on the following equation:

$$SA = \frac{I_\lambda^{ij} A_{mn} g_m}{I_{\lambda_R}^{mn} A_{ij} g_i} \exp\left(\frac{E_i - E_m}{kT_e}\right)$$

At first the plasma temperature can be preliminarily evaluated from the Boltzmann plot without any correction. According to Eq. (2), the line intensities obtained by the previous temperature are used to calculate a new temperature through the intensity ratio of a pair of spectral lines (e.g. the internal reference line and a selected line of the same species). At this stage, if the resultant SA coefficient for selected lines is closely equal to one, the new intensities are virtually identical to non-self-absorbed ones, and can be used to determine true concentration of the elements. Otherwise, the previous stage must be successively carried out by an iterative procedure until the convergence of SA on one

III. APPARATUS

A schematic of the apparatus for plasma emission measurements is shown in Fig. 1. An Nd:YAG laser (Brilliant, 360 mJ maximum pulse energy at 1064 nm and maximum repetition rate of 10 Hz) was focused on the sample surface with a quartz lens (20 cm focal length). In this work, the laser was operated at 1 Hz and was characterized by a pulse energy 126±5 mJ and the duration 5 ns. All measurements were performed at ambient pressure. In order to avoid the formation of deep craters, the position of laser light must be successively changed. For this purpose, the samples were connected to an adjustable XYZ manual micro-positioner. The light emission of the plasma was collected by an optical fiber (UV 600/660 type with SMA-905 connector and 1m length) using a quartz lens. The fiber output was coupled to the entrance slit of a compact wide range spectrometer (200-1100 nm) model S150 Solar Laser Systems TM (50 mm focal length, transmission diffraction grating with 200 grooves/mm with 0.02 mm×3.0 mm of entrance slit and 0.5 nm spectral resolutions). A charge-coupled device (CCD) detector array (Toshiba TCD 1304AP with 3648 pixels) was used to detect the dispersed light. The CCD camera was triggered ~2 μs after the onset of laser shot using a suitable delay generator in order to reduce the continuum due to bremsstrahlung radiation. A humidifier was also used to increase steam, and thus hydrogen molecules.
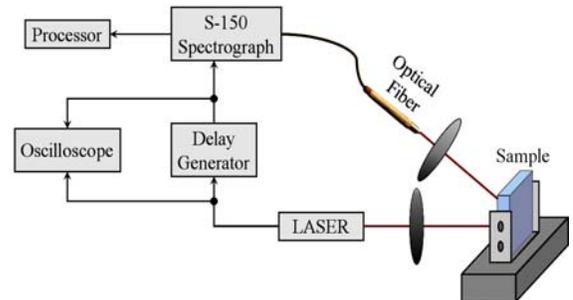

Fig. 1: Schematic of the experimental setup of the apparatus for LIBS.

IV. RESULTS AND DISCUSSION

Three different types of brass alloys (pipe fittings) were used in this experiment to investigate. The samples were provided from a manufacturer of pipe fittings and valves. The concentration of the elements in each of the samples was certified by a special piece of equipment known as Quantameter. The samples were irradiated by a pulsed Nd:YAG beam, the laser beam is focused on the sample surface by a convergent lens as shown in Fig 1. The spectral emissions of micro plasma were conducted to the spectrometer via fiber using a collection optics aligned at an angle of ~20° respect to the direction of the Nd:YAG beam. Each emission spectrum was collected 2μs after the onset of laser shot. The mean and standard deviation of 10 successive spectra were statistically taken into account for the concentration evaluation. In typical LIBS measurement conditions, only neutral atomic species and singly ionized species are present to a significant degree, and accordingly we only considered the two kinds of species. The Fig 2 shows the emission spectra of analytical lines for the first sample.

Fig. 2: Ten shots averaged LIBS spectrum of the first brass alloy sample.

Using the theoretical treatment described in previous section, we have evaluated the self-absorption coefficients of 9 intense Cu I lines (Cu I at 324.754; 327.396; 427.511; 458.698; 465.112; 510.554; 515.324; 521.820; 578.213 nm) and 7 intense Zn I lines (Zn I at 330.258; 334.50; 328.233; 468.014; 472.216; 481.053; 636.235 nm). These lines have been chosen

since they are free from interferences of other lines; therefore they are good candidates for analytical LIBS measurements. The internal reference line for each species was selected according to a low transition probability A_{mn} and a high excitation energy level E_m.

Fig. 3: (a) Boltzmann plots of the copper and zinc line intensity emitted by brass alloy (sample one) (b) correcting the self–absorbed.

In this work intense Cu I line at 458.698 nm and intense Zn I line at 468.015 nm were selected as references. Nevertheless, for the species Pb I, since almost all lines at low energy levels encounter seriously self-absorption, the correction process of self-absorption should fall back on the temperature information from other species. For example, the calculation of the self-absorption coefficient relevant to emission line 324.754 nm of copper, are summarized in table 1.

The Boltzmann plots, determined by the basic CF-LIBS method, are shown in Figs. 3-5. From Figs. 3(a)-5(a) before correction, the self-absorbed lines make the points on

Boltzmann plots very scattered. The self-absorption effect causes the plasma temperature calculated higher than real values, the intercepts lower than expected, and finally large errors in the quantitative results. After correction based on our method (see Figs. 3(b)-5(b)), points on the Boltzmann plots linearly stretch, and all the fitting lines are almost parallel.

Table 1: self-absorption coefficient for temperature correction in emission line 324.754 nm of copper related to the first sample.

SA	I	-1/KT	T (K)
……	2603	1.08589	12596
0.2195	11855	0.9130	10591
0.4989	23762	0.8412	9758
.	.	.	.
.	.	.	.
.	.	.	.
0.9995	53142	0.7709	8994
0.9997	53153	0.7709	8942

T_{cu} = 15395 K
T_{zn} = 6807 K

T_{cu} = 9914 K
T_{zn} = 8951 K
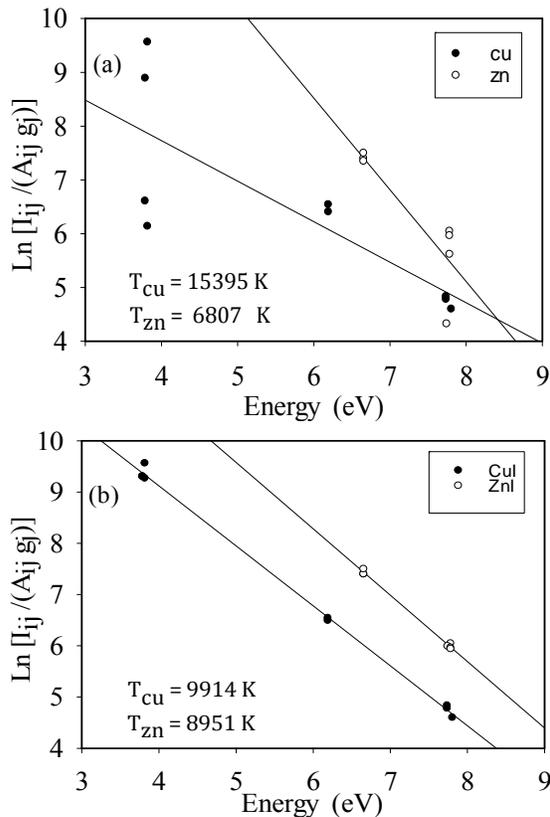
Fig. 4: (a) Boltzmann plots of the copper and zinc line intensity emitted by the second sample (b) correcting the self –absorbed

T_{cu} = 14408 K
T_{zn} = 6768 K

T_{cu} = 9547 K
T_{zn} = 8903 K
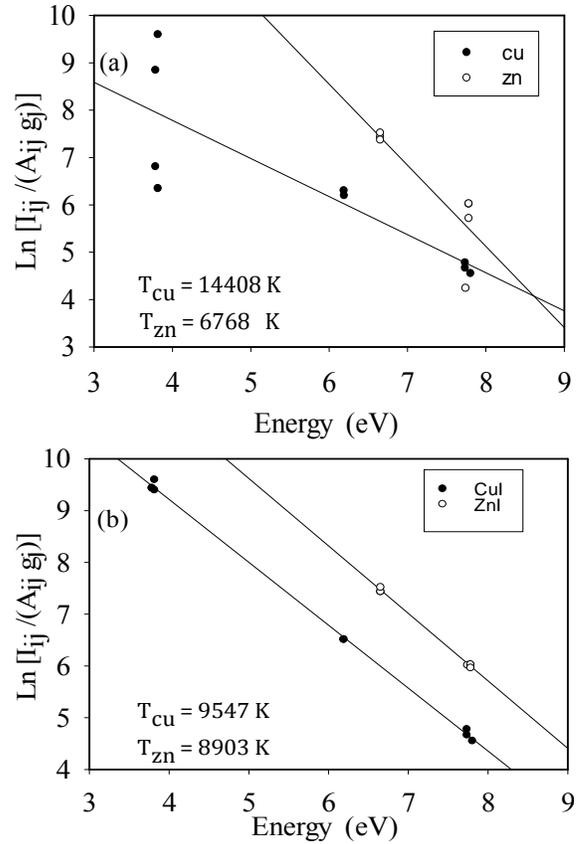
Fig. 5: (a) Boltzmann plots of the copper and zinc line intensity emitted by the third sample (b) correcting the self -absorbed

Under present conditions, when the plasma temperature lies within 7000 - 10000 K, the contribution of the first ionization state should be used for the quantitative analysis of the desired elements, whereas higher ionization stages could safely be neglected at the given plasma temperature [10,11]. Here, no significant spectral lines were found due to the first ionization state. In order to estimate the element concentration, the plasma electron density ne during the time gate of detection is determined based on the stark effect. The use of Hα line for the electron density measurement has got a major advantage to provide data in order to avoid self-absorption [12]. The linear Stark effect acting on hydrogen lines results in a large broadening which reduces the relative uncertainty of the measurement respect to characteristic emissions from the other elements. The electron density is given by Eq. 3 based on Stark broadening, which takes into account

quasistatic ion and impact-electron-broadening effects [13]:

$$n_e = 8.02 \times 10^{12} \left(\Delta\lambda_s / \alpha_{1/2} \right)^{3/2} \qquad (3)$$

where $\alpha_{1/2}$ is a coefficient, weakly depending on electron density and temperature, tabulated by Griem [14] and line width $\Delta\lambda_s$ is corresponding to the typical characteristic H_α line at 656.27 nm. The Gaussian instrumental line shape ($\Delta\lambda_{ins}$) is corresponding to the spectrometer resolution, which was determined to be ~ 0.33 nm by measuring the FWHM of the Hg lines emitted by a mercury lamp at low pressure [12]. Therefore, Lorantzian Stark line width is then determined by $\Delta\lambda_s = \left(\Delta\lambda_{fit}^2 - \Delta\lambda_{int}^2 \right)^{\frac{1}{2}}$. The corresponding electron densities are summarized in table 2.

Table 2: Calculated electron density for three samples of brass alloy

Electron density	First sample	Second sample	Third sample
$n_e \times 10^{16}$ cm^{-3}	8.22	5.61	5.95

Afterwards, it is possible to deduce the concentration ratio of the other ionization stages by making use of Saha-Boltzmann equation [12]. Therefore, during plasma formation, the ablated material includes atomic and ionic species. For an element α, the concentration C^α can be approximated as:

$$C^\alpha = C^{\alpha_0} \left(1 + R_\alpha \right) \qquad (4)$$

where R_α is the ratio of the ionic to atomic concentration $\left(C^{\alpha_1} / C^{\alpha_0} \right)$ in the plasma, those were calculated for each element using Saha-Boltzmann equation. Then, the elemental concentration according to simplified form is expressed as Eq. 5 [12]:

$$C^\alpha = \left[1 + \sum_{\alpha' \neq \alpha} \frac{C^{\alpha'_0} \left(1 + R_{\alpha'} \right)}{C^{\alpha_0} \left(1 + R_\alpha \right)} \right]^{-1} \qquad (5)$$

Hence, the concentration of alloys' compositions is straightforwardly estimated. The calibration-free analyses as well as competitive quanta meter method of ternary

alloys are summarized in table 3. It was shown that the relative errors were reduced. The table 3 shows that correcting the self-absorption, results in an accurate determination of the amount of lead which is of great importance.

Table 3: Comparison of quantitative analysis for the alloys. The third and fourth columns indicate the values obtained with CF-LIBS procedure with and without self-absorption correction (SAC). The concentration values are in weight percentage.

Pb	Certified values	C (without SAC)	C (with SAC)	error without SAC (%)	Error with SAC (%)
First sample	2.4	4.3	2.48	7.91	3.3
Second sample	4.81	6.62	4.71	37.6	2.07
Third sample	2.62	2.77	2.70	5.72	3.05

V. Conclusion

CF-LIBS is effectively used for lead concentration measurements mainly because of matrix effect elimination. The concentration can be directly determined through ionic characteristic lines of desired element using Eq. 5. Alternatively, in this work the concentration can be measured using Stark broadened bandwidth due to H_α corresponding to humidity in air such that the electron density of plasma is determined to obtain ionic to atomic concentration R_α using Saha equation.

In laser-induced breakdown spectroscopy, the plasma produced is often optically thick, especially for the strong lines of major elements. The measured spectral intensities of self-absorbed lines are lower than expected, which induces low concentration predictions for the elements analyzed. In order to correct the self-absorption effect, we proposed a recursive algorithm, which selects an internal reference line for each species as a standard line, estimates self-absorption levels of other lines based on the reference line, and finally obtains an optimal correction by a regressive procedure. The results indicate that after implementing the internal reference for self-absorption correction, the plasma temperature and quantitative analysis are more accurate

than the ones obtained by the basic CF-LIBS. In this work we have shown the correction of self-absorption effect results in the accurate concentration of the sample's elements; which may be utilized for evaluation of the allowable amounts of toxic materials in the equipment used by people.

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Fatemeh Salehi-Marzijarani received B.Sc. degree in physics from Arak University, Iran, in 2010. She also received M.Sc. degree in atomic and molecular physics from Alzahra University, Tehran, Iran, in 2013. She has worked on laser induced breakdown spectroscopy.

Hamidreza Shirvani-Mahdavi received the Ph.D. degree in photonics from Laser and Plasma Research institute, Shahid Beheshti University, Tehran, Iran, in 2010. He is currently the director of Photonics Research Laboratory (PRL) of department of physics, Islamic Azad University (Central Tehran Branch). His research fields are photonics of organic and polymeric materials, liquid crystals and its applications, laser spectroscopy, optical trapping, electro-optic modulation of laser beams, and optimization of lasers' properties.

Seyede Zahra Shoursheini received the Ph.D. degree in atomic and molecular physics from Alzahra University, Tehran, Iran, in 2009. She is currently one of directors of Laser and Photonics Laboratory of physics department, Alzahra University. Her research fields are laser spectroscopy, and applied optics.

Somayye Pashaei-Adl received M.Sc. degree in atomic and molecular physics from Alzahra University, Tehran, Iran, in 2013. She has worked on laser induced breakdown spectroscopy.