Improving the Limit of Detection in Laser-Induced Breakdown Spectroscopy and Measuring the Associated Plasma Parameters

H. Hegazy

Department of Physical Sciences, College of Science, Jazan University, P. O. Box 114, Jazan 45142, Kingdom of Saudi Arabia
hhegazy[at]jazanu.edu.sa

Abstract: ***The current study aimed to measure the plasma parameters corresponding to the improved limit of detection and precision for the technique of laser-induced breakdown spectroscopy (LIBS). In this study, the plasma was generated by focusing a 6 ns pulsed Nd:YAG laser at the fundamental wavelength of 1064nm and at the second harmonic wavelength of 532nm on an aluminium (Al) target in air at atmospheric pressure. The emission spectrum was recorded using an Echelle spectrometer equipped with an ICCD camera. The thermometric lines used for the determination of plasma temperature based on the Boltzmann plot were O I and Mn I spectral lines. Additionally, the Stark broadening method was employed for electron density measurements. Several spectral lines, such as the Hα line for hydrogenic species and O I, Al II, and Si I lines for non-hydrogenic species, were used to determine the electron density from the Stark full-width at half-maximum (FWHM).***

Keywords: Laser-Induced Breakdown Spectroscopy, LIBS, Laser-produced Plasma Temperature and density, and Optical Emission Spectroscopy

1. Introduction

In recent years, there has been a significant amount of interest in studying Laser Induced Plasma (LIP) when solid targets are exposed to high energy or high-power laser radiation [1-3]. Laser Induced Breakdown Spectroscopy (LIBS) is a technique that can analyse and identify solids, liquids [4,5], aerosols, and gas samples [6] with minimal or no sample preparation. To understand and explain the phenomena associated with the plasma produced in experiments, it is necessary to measure the population of ionization stages of the atomic or ionic species in the plasma plume, plasma temperature, and electron densities. The emission of radiation is one of the key aspects of plasma behaviour. During the recombination process, excited particles formed during recombination decay to the ground state and often emit radiation.

In our previous work [7,8], we investigated different parameters that directly affect the improvement of the detection limit and precision of spectral lines emitted from LIBS plasma generated by first and second harmonic lasers. However, the focus of our previous work was on improving the limit of detection (LOD) and precision of spectral lines emitted from the plasma by optimizing the parameters that affect the LIBS technique at both laser wavelengths (1064 and 532nm). The LOD in LIBS is influenced by various experimental parameters such as interferences, self-absorption, spectral overlap, signal-to-noise ratio (SNR), and matrix effect. To determine the optimum operating parameters for LIBS, we performed the following steps: studying self-absorption and SNR for different spectral lines of different elements present in the sample. This was carried out at different delay times and for different laser energies.

In the present study, we aim to establish a relationship between the improvements in detection limit and precision of LIBS with the plasma parameters of temperature and density under the current LIBS operating conditions, which are directly linked to the plasma state at the improved operating conditions. Temperature is determined from the Boltzmann plot of various thermometric elements present in the LIBS spectrum, such as Mn I and O I [9-10], while density is determined from the Stark FWHM of selected broadened hydrogenic and non-hydrogenic spectral lines [11].

2. Experimental Setup

The experimental setup utilized in the present study is depicted in Figure 1. A Q-switched Nd:YAG laser was employed, operating at both the fundamental wavelength of 1064 nm and the second harmonic wavelength of 532 nm. The plasma was generated by focusing a laser pulse with a duration of 6 ns onto the target in air, at various laser energies ranging from 20 to 400 mJ. A time-resolved diagnostic technique was employed to investigate the emission spectra emitted by the generated plasma. The emission spectra were imaged onto the entrance port of an Echelle spectrograph, equipped with an intensified charge-coupled device (ICCD) detector, using a 1:1 quartz lens. This spectrometer enabled the acquisition of time-resolved spectral data over the entire UV-NIR range (200-1000nm). A low-pressure Hg lamp was employed for wavelength calibration purposes. The entire system operation and data acquisition were under the complete control of a PC program.

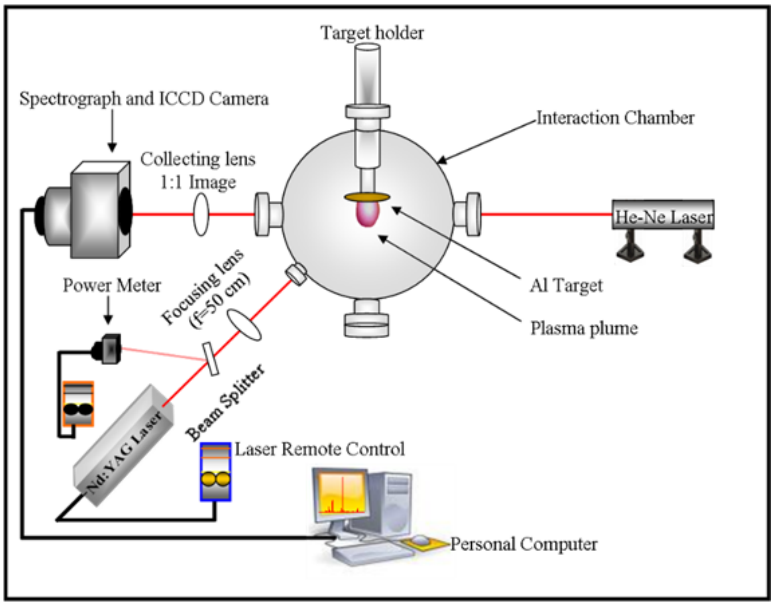

Figure 1: Schematic diagram of the experimental set-up [7,8].

3. Results and Discussions

In the present study, plasma spectra were collected parallel to the target surface at an angle of 450 with respect to the incident laser beam.

To enhance the signal of laser-induced breakdown spectroscopy (LIBS) and improve its signal-to-noise ratio (SNR), the accumulation of consecutive measured spectra (10, 20, 50, and 100) was previously investigated and discussed in Ref [7,8]. Figure 2 shows a typical emission spectrum emitted from an aluminium target in air at different numbers of accumulations. The optimal number of accumulations is found to be 50, which results in a high SNR at a delay time of 4ms for the fundamental wavelength of 1064 nm and 3ms for the second harmonic laser of 532 nm. This enhanced SNR at the optimum condition also reduces the self-absorption effect of various spectral lines tested in the previous sections for determining the elemental composition of the test sample. Table 1 presents the improvements in the limit of detection (LOD) resulting from the enhanced SNR under the optimized LIBS conditions with laser energies of approximately 200mJ for both the 1064nm and 532nm lasers.

As mentioned above, this study aims to investigate the relationship between the improved LOD and precision and the plasma parameters (temperature and density) under the optimized LIBS conditions.

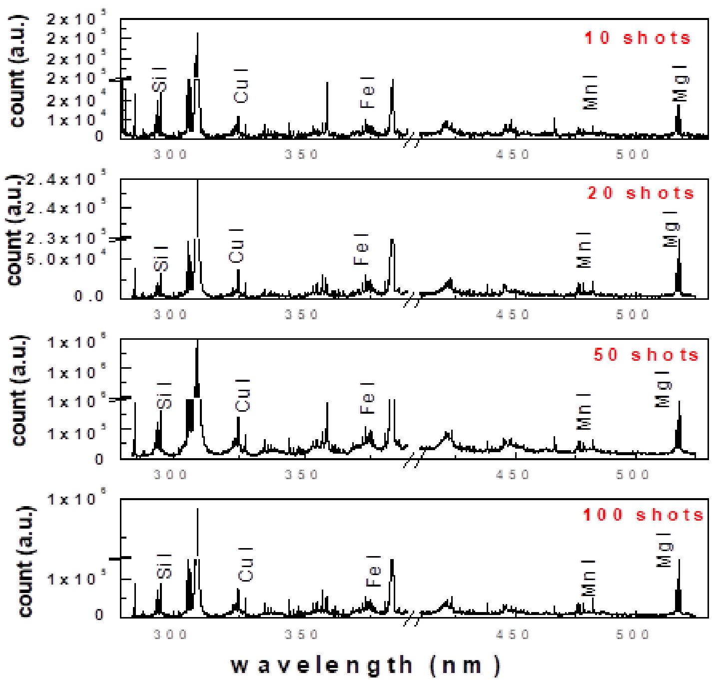

Figure 2: Typical emission spectrum observed at various accumulation levels on an ICCD camera.

Paper ID: ES24529122016 DOI: https://dx.doi.org/10.21275/ES24529122016

Table 1

Element	λ (nm)	LOD for 1064nm [7]	LOD for 532 nm [8]	Improvement percent
Cu I	324.72	44	13	70.4%
	327.39	54.9	18	67.2%
	510.55	58.7	22.5	61.6%
	515.36	43.6	56.9	----
	521.85	36.9	21.8	40.9%
Mg I	517.26	73	8.2	88.7%
	518.36	39	7.4	81. %
Si I	288.15	70	76	----
Cr I	520.84	81	11.6	85.6%
Fe I	344.06	55.3	23.8	56.96%
	375.82	259	29.6	88.5%
Mn I	478.35	68	57	16.1%
	482.34	65	52	20%

In this part of the experimental work, we attempt to determine LIBS plasma parameters. These parameters must be controlled during the experiment to fix the analytical conditions. Many traditional methods are considered for controlling the parameters of laser-induced plasmas. Of these, optical emission spectroscopy (OES) is used extensively [9-15]. OES is based on the study of the spectral distribution of line intensity and broadening in emission spectra. The equilibrium distributions for kinetic energy, excitation energy, and ionization energy are represented by Maxwell, Boltzmann, and Saha equations respectively. It may occur that there is an equilibrium distribution for one of these forms of energy but not for the others [16]. Thermodynamic arguments require that for equilibrium to hold, for every photon emitted by the system, a photon of the same energy must be absorbed, and for every excitation by electron collision, there must be a de-excitation by electron collision. In practice, however, photons do leak out from the plasma, no matter how large or dense the plasma is; otherwise, the plasma cannot be observed. Thus, the condition of near thermodynamic equilibrium requires that such losses be small compared to the total energy.

The determination of electron temperature and number density relies on the analysis of relative atomic and ionic line intensities using Boltzmann and Saha-Boltzmann plot techniques [17, 18]. The validity of these techniques is contingent upon certain assumptions, most notably the presence of local thermodynamic equilibrium (LTE) conditions and optically thin plasma. In order to satisfy the LTE condition, the system must exhibit minimal variations, ensuring that the establishment of kinetic balances occurs more rapidly than the changes in the plasma [19]. The attainment of LTE conditions in laser-induced plasmas is heavily influenced by experimental factors, including pressure, duration and intensity of laser radiation, as well as the thermo-physical properties of the target material [20, 21].

Recalling the criterion for a minimum electron density suggested by both Griem [22] and Fujimoto and McWhirter [23], which can be summarized as [24]:

$$N_e \geq 10^{17} Z^7 \left(\frac{k_B T_e}{E_H^Z}\right)^{1/2} \left(\frac{E_1 - E_2}{E_H^Z}\right)^3 \quad (1)$$

Where, Z is the effective charge seen by the bound electron, E_1, E_2 are the transition energy levels and is the ionization energy of hydrogen or corresponding hydrogenic ions, A simplified version of equation (1) can bewritten as [25];

$$N_e = 1.6\times10^{12}\sqrt{T_e}\,(\Delta E)^3 \quad (2)$$

Where N_e is in cm^{-3}, T_e is in Kelvin, and ΔE is the transition energy in eV.

However, the LTE criterion is easily met for electron densities greater than approximately 10^{17} cm^{-3} in typical laser-induced plasmas [24]. Evaluating equation (2) for the plasma conditions generated by infrared and visible laser wavelengths in the present Al alloy plasma confirms that the LTE criterion holds true.

As previously mentioned in LIBS, the assessment of self-absorption is another essential factor for utilizing spectral lines as diagnostics for LIBS plasma. However, the evaluation of self-absorption is based on the branching ratio of appropriate multiplet lines [26-28].

Temperature Measurements

In this study, we utilize the Oxygen spectral lines [26, 28] as well as the Mn I spectral lines introduced by Stavropoulos et al. [29] as thermometric spectral lines. These lines are employed to determine the plasma temperature through the application of the Boltzmann plot method. Specifically, we examine the plasma temperature under optimal conditions for Laser-Induced Breakdown Spectroscopy (LIBS), which involves the use of two laser wavelengths: the fundamental wavelength at 1064nm and the second harmonic wavelength at 532nm. The excitation temperature can be accurately obtained by measuring the intensity of the aforementioned spectral lines, assuming that the energy level populations conform to the principles outlined by the Boltzmann

Paper ID: ES24529122016 DOI: https://dx.doi.org/10.21275/ES24529122016

distribution law. For full LTE the intensity of the spectral line is given by:

$$I_{ij} = \frac{L}{4\pi} h\nu\, g_i\, A_{ij} \frac{N_\circ}{U(T)} \exp\left\{ -\frac{E_i}{k_B T_{exc}} \right\} \tag{3}$$

Where L is the plasma length, N_o is the number density of atoms in the ground state, U(T) is the partition function, T_{exc} is the excitation temperature ≈ electron temperature, E_i is the excitation energy of the upper level.

Figure (3) shows examples of the emission spectra of Mn I and O I lines for different laser wavelength and at LIBS condition stated above.

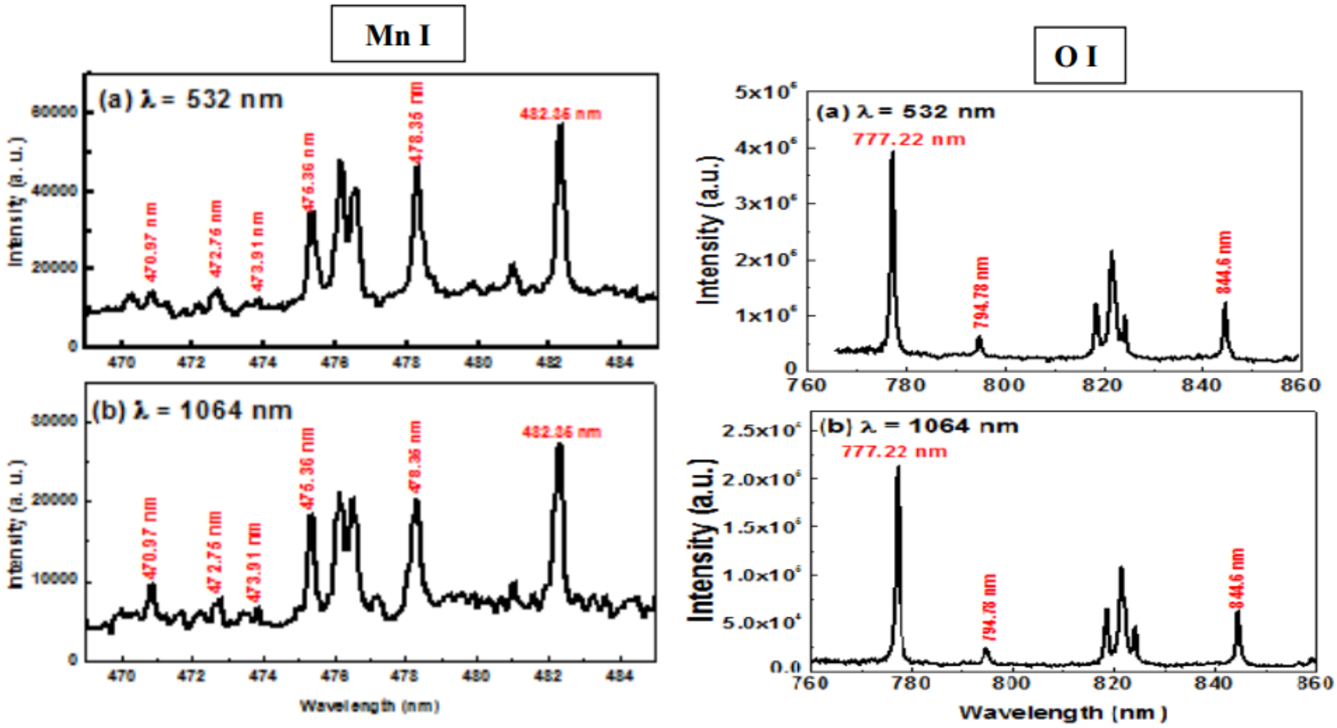

Figure 3: Emission spectral lines of Mn I, O I generated by both laser wavelengths at improved LIBS condition.

Density Measurements

Stark broadening method has been employed for electron density measurements**.** The electron number density n_e for non-hydrogenic ions calculation based on the quadratic Stark broadening of a line expressed as the FWHM in nanometers $\Delta\lambda_{stark}$ is given by:

$$\Delta\lambda_{1/2}(\mathring{A}) = 2w\left(\frac{n_e}{10^{16}}\right) + 3.5A\left(\frac{n_e}{10^{16}}\right)^{1/4}\left[1 - 3/4\, N_D^{-1/3}\right] w \left(\frac{n_e}{10^{16}}\right) \tag{4}$$

Where w is the electron impact width parameter or Stark width parameter, A is the ion broadening parameter, and N_D represents the number of particles in the Debye sphere. The second term in Eq. is normally neglected due to the negligible contribution of ion-broadening under typical LIBS conditions, hence:

$$\Delta\lambda_{stark} = 2w\left(\frac{n_e}{N_e^{ref}}\right) \tag{5}$$

Where w is the half width half-maximum Stark parameter at the reference density N_e^{ref}.

The use of hydrogen lines for electron number density determination, particularly, the lines in the Balmer series, is a well-established plasma diagnostic method. The electron number density can be determined by using H_α line:

$$n_e(cm^{-3}) = N_e^{ref}\left(\frac{\Delta\lambda_{H_\alpha}}{\alpha_{1/2}}\right)^{3/2} \tag{6}$$

Where $\Delta\lambda_{H\alpha}$ is the line width of the H_α line in nm and $\alpha_{1/2}$ is the Stark constant at the reference density N_e^{ref}.

The analysis of the line profile was conducted in the following manner. First, the instrumental profile was convoluted with a Lorentzian function of varying width. This convoluted profile was then fitted to the experimental profile using a least-square fitting procedure. Through this fitting process, the collisional contribution to the width of the line profile was determined. Multiple spectral lines were utilized to calculate the electron density, including the Stark FWHM of the Ha line and several non-hydrogenic lines (O I, Al II, and Si I) [28]. Figure 4 displays the Ha line along with its least square fits for both laser wavelengths under LIBS conditions.

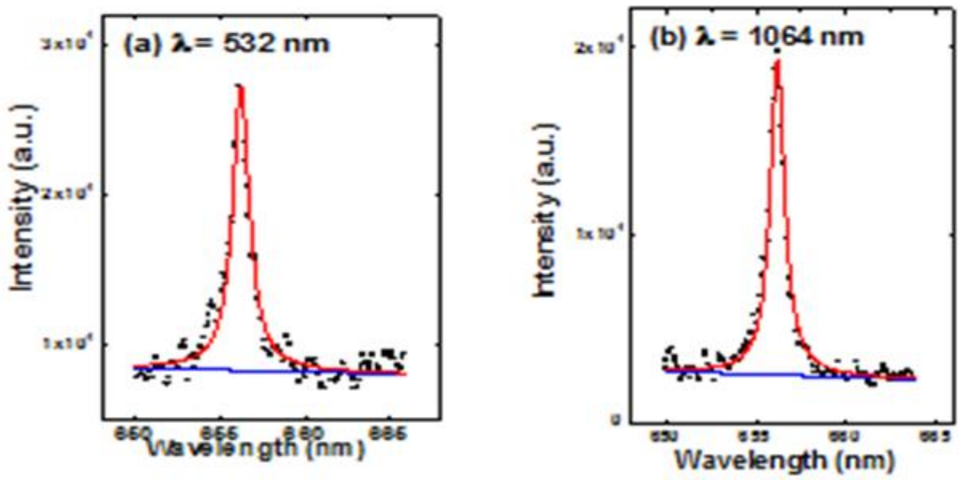

Figure 4: Sample of H_α line with its least square fits for both laser wavelengths at LIBS condition.

Table 2 displays the average plasma temperature and density under the optimized conditions for LIBS. It is evident from the table that the plasma temperature aligns with the findings from previous research [28], for both laser wavelengths used in the optimized plasma for LIBS analysis. Furthermore, the determined density affirms that the generated plasma operates within the local thermodynamic equilibrium (LTE) regime.

Table 2

Parameter	Fundamental laser (1064nm)	Second harmonic (532nm)
kT_e (eV)	1.0 ± 0.07	0.85 ± 0.08
N_e (cm^{-3})	$(0.90 \pm 0.15) \times 10^{17}$	$(1.22 \pm 0.06) \times 10^{17}$

4. Conclusion

The plasma temperature for the optimized plasma used in LIBS analysis is 1eV and 0.85eV for 1064nm and 532nm laser wavelengths. This finding closely aligns with the temperature values associated with other spectrochemical analytical techniques and excitation sources, such as Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) [30-32]. In addition to the plasma temperature, the determined density also indicates that the plasma generated is in Local Thermodynamic Equilibrium (LTE).

Acknowledgment

Thank you Prof. Th. El-Sherbiny and Prof. S. Allam (praying to God for mercy and forgiveness for him) and colleagues in the laboratory of Lasers and New Materials, Department of Physics, Faculty of Science, Cairo University, Cairo, Egypt for supporting the current work. We also extend our sincere thanks to Dr. A. A. Abdel-Wahab, and Prof. F. M. Abdel Rahim and Prof. Abd ElDaim Nossair from the Faculty of Science, Al-Azhar University, Assiut Branch, Egypt, for their valuable comments and discussions. Sincere thanks to Prof. N. Can Dept. of Physical Sciences, College of Science, Jazan University, Saudi Arabia for revising this manuscript.

References

[1] E. Heidecker, J.H. Schafer, J. Uhlenbush, W. Wiol, J. Appl. Phys. 64, 2291, (1988).

[2] Z. Andreic, V. Henc-Bartolic, H.J. Kunze, Phys. Scr. 47, 405, (1993).

[3] D.E. Kim, K.J. Yoo, H.K. Park, K.J. Oh, D.W. Kim, Appl. Spectrosc. 51, 1, (1997).

[4] E. Tognoni, V. Palleschi, M. Corsi, G. Cristoforetti, Spectrochim. Acta Part B 57, 1115, (2002).

[5] P. Fichet, P. Mauchien, J.-F. Wagner, C. Moulin, Anal. Chim. Acta 42(9), 269, (2001).

[6] D. A. Cremers, L.J. Radziemski, "Chapter 1: *"Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications"*, Eds. A. W. Miziolek, V. Palleschi, and I. Schechter, Cambridge University Press: New York, pp. 1-39 (2006).

[7] H. Hegazy, E. A. Abdel-Wahab, F. M. Abdel-Rahim, S.H. Allam, and A. M A. Nossair , Applied Physics B: Lasers & Optics 115, 173-183 (2014).

[8] H. Hegazy, E. A. Abdel-Wahab, F. M. Abdel-Rahim, S.H. Allam, and A. M A. Nossair, Arab Journal of Nuclear Science and Applications 47(3), 80-92 (2014).

[9] S.S. Chu, M. Ye and C.P. Grigoropoulos, "*Spectroscopic Characterization of Laser-Induced Titanium Plume*", Proceedings 5th ASME_JSME, ASME_JSME, San Diego, California, USA, March 15-19, 1-5 (1999).

[10] X.T. Wang, B.Y. Man, G.T. Wang, Z. Zhao, B.Z. Xu,Y.Y. Xia, L.M. Mei and X.Y. Hu, Appl. Phys. 80-3, 1783-1786 (1996).

[11] B.Y. Man, Appl. Phys. B 67, 241-245 (1998).

[12] M.H. Hong, Y.F. Lu, T.M. Ho, L.W. Lu and T.S. Low, "*Plasma diagnostics in KrF excimer laser deposition of Ti thin films*" in: D. Shu-Sun and S.L. Wang (Eds.), "*Laser Processing of Materials and Industrial Application II*", Proceedings of SPIE 3550, SPIE441 (1998).

[13] F. Fuso, L.N. Vyacheslavov, G. Masciarelli and E. Arimondo, J. Appl. Phys. 76-12, 8088-8096 (1994).

[14] O.A. Bukin, I.V. Bazarov, N.S. Bodin, A.A. Il'in, V.D.Kiselev, E.A. Sviridenkov, V.I. Tsarev and A.Yu Major, Quantum Electron. 28-8 685-688 (1998).
[15] S. Yalcin, D.R. Crosley, G.P. Smith and G.W. Faris, Appl. Phys. B, 68, 121-130(1999).
[16] S.N. Thakur, *"Atomic Emission Spectroscopy"* in: Jagdish P. Singh and Surya N. Thakur, Laser-Induced Breakdown Spectroscopy, Elsevier press, Amsterdam (2007).
[17] H.R. Griem, "*Plasma Spectroscopy*", McGraw-Hill Book Company, New York (1964).
[18] R.H. Huddlestone and S.L. Leonard, "*Plasma Diagnostic Techniques*", Academic Press, New York - London (1965).
[19] J.A. Van der Mullen, Physics Reports of Physic Letter, PRPLCM 191 (2 and 3) 109-220 (1990).
[20] D.B. Chrisey and G.K. Huber, "*Pulsed Laser Deposition of Thin Films*", Wiley Inter-Science Publication, New York (1994).
[21] A. De Giacomo, V.A. Shakhatov and O. De Pascale, Spectrochimica Acta Part B 56, 753-776(2001).
[22] H.R. Griem, Phys. Rev. 131, 1170-1176 (1963).
[23] T. Fujimoto and R.W. McWhirter, Phys. Rev. A 42, 6588-6601(1990).
[24] P.K. Diwakar and D.W. Hahn, Spectrochimica Acta Part B, 63, 1038–1046 (2008).
[25] A. Thorne, U. Litzen and S. Johansson, "Spectrophysics: *Principles and Applications*", Springer, New York (1999).
[26] H. Hegazy, Applied Physics B: Lasers & Optics 98, 601-606 (2010).
[27] H.-J. Kunze, in *3rd Workshop on Plasma and Laser Technology, Ismailia, Egypt, 1993*, edited by Ph. Mertens (Forschungszentrum Jűlich GmbH, 1994), pp. 31–46.
[28] H. Hegazy, E. A. Abdel-Wahab, F. M. Abdel-Rahim, S.H. Allam, and A. M A. Nossair, Eur. Phys. J. D. 68: 107 (2014).
[29] P. Stavropoulos et al., Spectrochimica Acta Part B 59, 1885-1892 (2004).
[30] R. E. Wolf, Ph.D. thesis, Research Chemist, USGS/CR/CICT, (2005).
[31] J. B. Olsen, J. H. Macedone and P B. Farnsworth, J. Anal. At. Spectrom., 21, 856-860 (2006).
[32] P. Serapinas, J. Salkauskas, Z. Ezerinskis and A. Acus, Spectrochimica Acta Part B 65, 15–23 (2010).