Numerical Study of Argon Spectra Using Libs Technique

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The aim of this work is to present numerical study of the experimental spectra of plasma containing argon. This study is concerned with electronic transitions from atom and ion of argon in plasma. The plasma is generated after steaming the sample by laser induced breakdown spectroscopy LIBS. Our calculation is based on line intensity ratio method to obtain the theoretical spectra and to estimate the electron temperature. The obtained results are compared to the experimental spectral database of LIBS. The results of our numerical study have shown an agreement with the already published experimental results.
Keywords: Numerical Study, Argon Spectra, LIBS Technique.

1. Introduction

The techniques of plasma diagnostics are important in plasma physics which are used to describe the state of plasma and to obtain information about the nature of plasma, such as electron temperature, plasma potential, and density of the plasma. Several studies have been carried out on this subject [1–7] Some works used the theoretical methods to study the atomic spectra which is based on the estimation of electron temperature or density of the plasma by optical emission spectroscopy, Langumir probe, Stark broadening, Boltzmann plot method, and Saha-Boltzmann equation method. In some previous studies the experimental methods have adopted for different types of analysis. Among these methods we can mention spectrometry in the visible or near infrared, XRF, or spectroscopy of laser-induced plasma LIBS [8–18].

Laser Induced Breakdown Spectroscopy known as LIBS is one of the most used techniques in recent developments. The advantages of LIBS technique are high sensitivity for multi-elemental analysis and detection for light and heavy elements. Moreover,the detection of

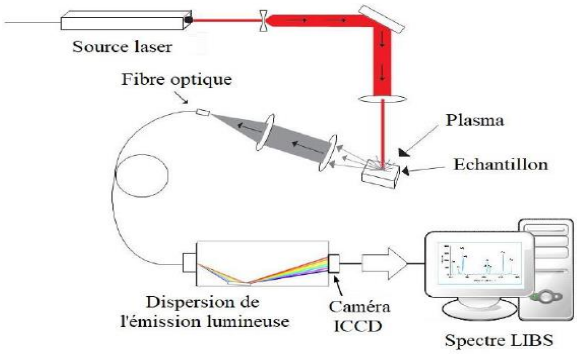
sample by LIBS is simple and a nondestructive because it does not need complex sample pretreatment. LIBS analysis of soil contributed to several important aspects of the soil. LIBS is also, an analytical pulsed laser-based technique [19–24].
In this paper, the simulation of spectra resulting from the laser sublimation plasmaof argon was carried out by using the numerical model that describe the experimental spectrum resulting from laser generated plasma containing Argon.

2. Moexperimental Description
The scheme is shown in figure 1. The system consists of the following main parts:

- Laser source commonly Nd:YAG or other type of laser.
- Surface of the sample.
- Spectrometer with optical fiber collected by ICCD camera.
- The collected data is stored by computer.

The principle of the LIBS spectroscopy is that the laser is focused onto the surface of a soil sample, where it is vaporized. Later on, the laser contributes to the excitation and ionization of the vapor that develops above the surface of the sample that causes the production of a micro-plasma in which all the present atoms are excited by colliding with the free electrons of the plasma and radioactively after the laser pulse as well. The plasma continues to expand in the atmosphere wetting. The atoms and ions inside it are then separated by emitting distinct radiation which is transmitted by optical fiber to a spectrophotometer where it is distributed into a spectrum of lines in the [200 - 900nm] spectral range. These lines, which represent the initial composition of the analyzed sample, are allowed to be exploited [25, 26].

Figure 1 – Schematic description of experimental setup



3. Theoretical Description
Theoretically, we will draw the spectra resulting from the argon sample using a numerical program in the Fortran language based on the atomic physical database and the following equations:

- The Maxwell's law
- The Boltzmann's law
- The Dalton law
- The electric neutrality law

- The law of conservation of matter

Our program considers all the broadening lines possible: Doppler, natural, effect Stark, Van der Waals collision, instrumental broadening and Voigt Profile. Spectroscopic methods are used in this program. The recommended data are as follows:

- Minimal and the maximal wave lengths
- Number of the point representing the spectra
- Van der Waals Constant and atomic mass of etch element in the medium
- Experimental width: Gaussian or Lorentzian shape
- Input files of the atomic databases of each element

The database gives the concerned energy levels of each element with the statistical weights associated, the transition wavelengths and the radiated transition probabilities.
To calculate the theoretical spectra, the databases from atomic physics for all the elements that may exist in the medium have been set up sample along with possible impurities (O, H,C, N).

4. Results and Discussion

The experimental results of typical emission spectra by using LIBS technique of argon plasma in the spectral range of $200 - 900$nm to ArI and ArII are presented in figures 2 and 3. It is worth mentioning that we only analyze the portion specified in the frame that is within the spectrum range [424, 436nm] that is shown in figure 3. We have twolines with high intensity compared to the rest of the other spectral lines, the line with the greatest intensity is located in the range [425, 428nm], while the second is located between [429, 432nm].

Figure 2 –

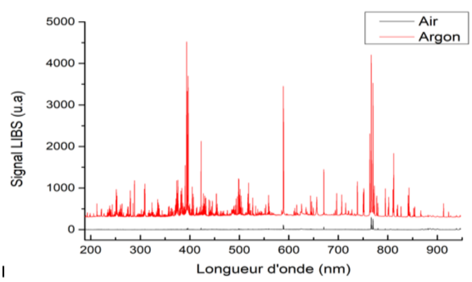
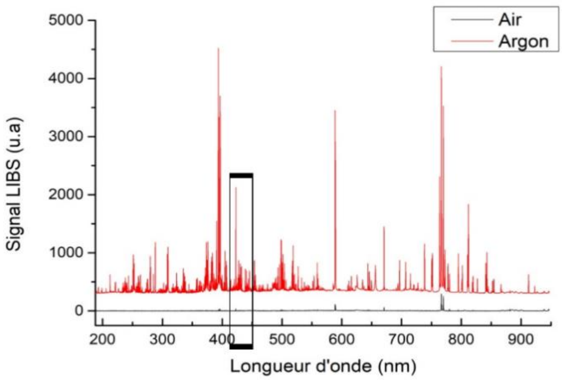


Figure 3 –



The numerical results of spectra of ionized argon and the potential impurities are illustrated in figures 4, 5 and 6. Based on the international database of atomic physics NIST, we find out that all the numerical results of spectra computed, through the use of FORTRAN code, are situated within the spectra range 424 to 436nm .

Figure 4 –

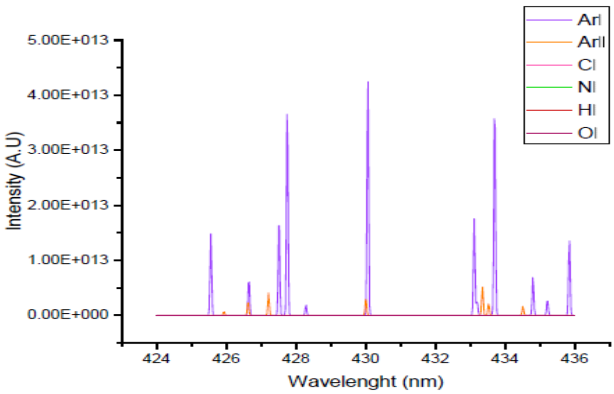


Figure 5 –

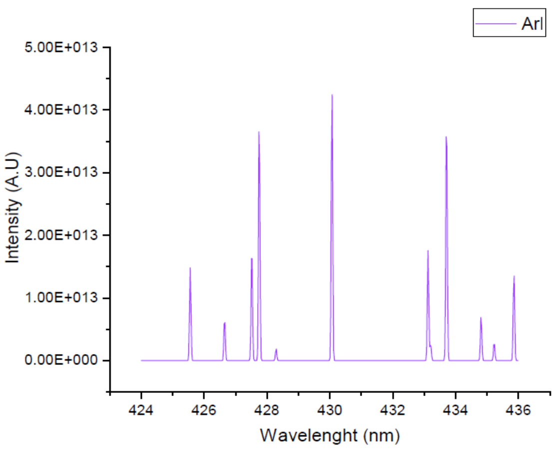
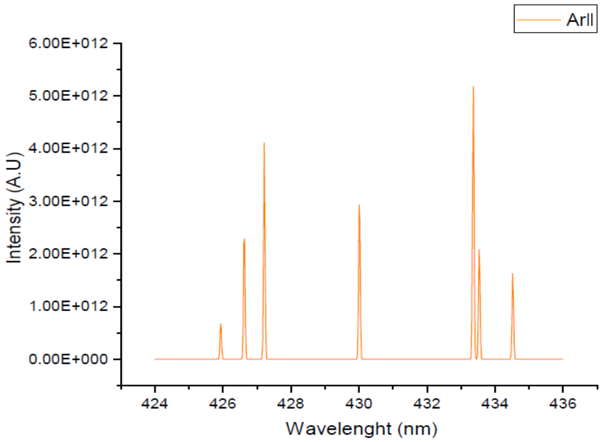


Figure 6 –



- As we can see in figure 4 all lines appeared in the spectrum have been identified as neutral argon ArI and ionized argon ArII spectra. When comparing ArI and ArII in figures 5 and 6 show the following result lines of ArI appear obviously in the spectrum, while they barely appear in ArII.
- Intensity of lines in ArI is much higher than that in ArII. The general increase of the intensity of the lines in ArI can be attributed to the increase in the rate of excitingcollision, therefore, the probability of exciting collisions of electrons with ArI is higher than that in ArII. Consequently, most of ArI lines appear clearly in the spectrum.
- A comparison between the intensities of the argon lines theoretically and experimentally in the spectral range of 424 − 436nm indicates a rational agreement of the intensities of the argon lines ArI theoretical and experimental.
- To estimate the electron temperature T_e in plasma at the local thermal equilibrium LTE, different methods are available out of which the most commonly used are line ratio method and Boltzmann plot method.

4.1. Line-Ratio Method

This method is based on relative intensities of two spectral lines of the same atomic species and it is preferred since it provides the possibility of the evaluation of the electron's temperature without knowing the number density of the atomic species.

$$R = \frac{I_2}{I_1} \quad (1)$$

$$\frac{I_2}{I_1} = \frac{g_2.A_2.\lambda_1}{g_1.A_1.\lambda_2} exp\left(\frac{E_1 - E_2}{k_B T}\right) \quad (2)$$

$$K_B T = \frac{E_1 - E_2}{\ln\left(R\frac{g_1.A_1.\lambda_2}{g_2.A_2.\lambda_1}\right)} \quad (3)$$

Where I_1, λ_1, g_1 and A_1 are the total intensity (integrated over the profile), the wavelength, the statistical weight and the transition probability, respectively of one line with E_1 its excitation energy. The corresponding quantities for the other line are I_2, λ_2, g_2 , A_2 and E_2 [27, 28].

4.2. Boltzmann Plot Method

An excitation temperature can be deduced from the absolute intensity of the atomic line which corresponds to the transition between the ground state to the excited state, when the population of the atoms is evaluated using the Boltzmann distribution in local thermal equilibrium (L.T.E) [29].

Boltzmann plot is one of the most effective approaches for the estimation of the electron temperature T_e which is represented by the formula [30],

$$\ln\left(\frac{I_{if}.\lambda_{if}}{A_{if}.g_i}\right) = \frac{E_i[cm^{-1}]}{k_\beta T_{ex}[K]} + constant \qquad (4)$$

Where I_{if} is the relative intensity (in arbitrary units) of the emission line between the energy levels i and j, λ_{if} its wavelength, g_i is the degeneracy or statistical weight of the emitting upper level i of the studied transition, and A_{if} is the transition probability for spontaneous radiative emission from the level i to the lower-level j. Finally, E_i is the excitation energy of level i and Boltzmann constant.

Parameters of the argon lines ArI employed for determining T_e are listed in the table 1 [31],

E_i(ev)	g_i	$A_{if}(s^{-1})$	I (u.a)	λ(nm)
11:62359272	3	8x10^{+5}	3.65 x10^{+13}	427:2169
14:50606764	5	3.1x10^{+5}	4.25 x10^{+13}	430:0101

First, we calculate by the equation (1) the ratio between the intensity of the two spectrums depends to a great extent on the selected pairs of lines hardly appears and its intensity is much higher than the intensity of other lines specified in the previous table. After that, we get by the equation (3) the electron temperature T_e = 2.61eV =30243K, this value is roughly identical to the theoretical range between 02 and 03 eV.

5. Conclusion

In this current study, a numerical model to analyze the spectra resulting from the laser sublimation plasma of argon was carried out. Our model calculation was enabled to determine the radioactive elements in the medium. The electron temperature has been estimated using the ratio of the lines intensities technique, and their values have been found to be dependent on the wave lengths of the two chosen lines. A comparison between the estimated electron temperature obtained by line ratio method has been shown a good agreement with the experiment.

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