Spectroscopic Study of Copper Plasma Produced by Fundamental Nd: YAG Laser by LIBS

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دراسة طيفية لبلازما النحاس التي تم إنتاجها بواسطة ليزر Nd: YAG الأساسي بواسطة LIBS

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ABSTRACT

Background:

The effect of laser wavelength on the analytical results obtained from LIBS by Nd: YAG laser diagnostics to copper element is experimentally investigated by Nd: YAG laser at 1064 nm wavelength. The temperature and density of electrons in copper plasma are calculated under (LTE) conditions.

Materials and Methods:

Various copper transitions were obtained. Identification of transition lines from the spectrum is carried out by comparing spectral lines with NIST atomic database. The results after performing the analysis were compared with (NIST) database.

Results:

The result showed that the various wavelengths obtained from the copper target tare with significant compatibility with the same wavelengths from the National Institute of Standards and Technology (NIST).

Conclusion:

LIBS technique proved to be a precise and accurate tool for calculating electron temperature and electron number density, the presence of different elements with very low tolerance, and diagnosing their concentrations.

Keywords:

LIBS Technique, Laser ablation, Electron Temperature, Electron Density.

1. INTRODUCTION

LIBS (laser-induced breakdown spectroscopy) is widely used for qualitative and quantitative elemental analyses of liquids, gases, and solid materials. A high-energy laser beam is focused on the surface of a solid sample in this technique, resulting in the formation of a micro plasma containing atoms, ions, electrons, and excited species. The emission spectrum of the plasma plume provides valuable information for identifying and quantifying the emitting species present in the ablated material[1].

When the plasma cools, these electrons fall from higher to lower energy levels, emitting a plasma spectrum with different wavelengths for each element of the sample. One of the techniques that can produce plasma is a laser. The laser wavelength influences plasma formation, such as laser-plasma interaction and plasma ignition threshold.

LIBS has several advantages, which include little or no sample preparation; minimally invasive; quick analysis time; and ease of use, which make it ideal for analyzing biological samples such as teeth, hairs, cells, and bacteria. This technique has previously been used in the analysis of human fingernail. Dreyfus et al.16 studied the copper plasma using the laser-induced fluorescence (LIF) technique. Subsequently, Lee et al., 2015 used the 193 nm Excimer laser to observe the laser-ablated plasma at a copper target in the air and determined the electron temperature of the plasma. Hafez et al.18 investigated the copper plasma using the Nd: YAG laser at 355 nm and reported the plasma lifetime, plasma velocity, and electron densities. More recently, Man et al.19 reported the line-broadening analysis of the emission produced by laser ablation of Cu metal[2].

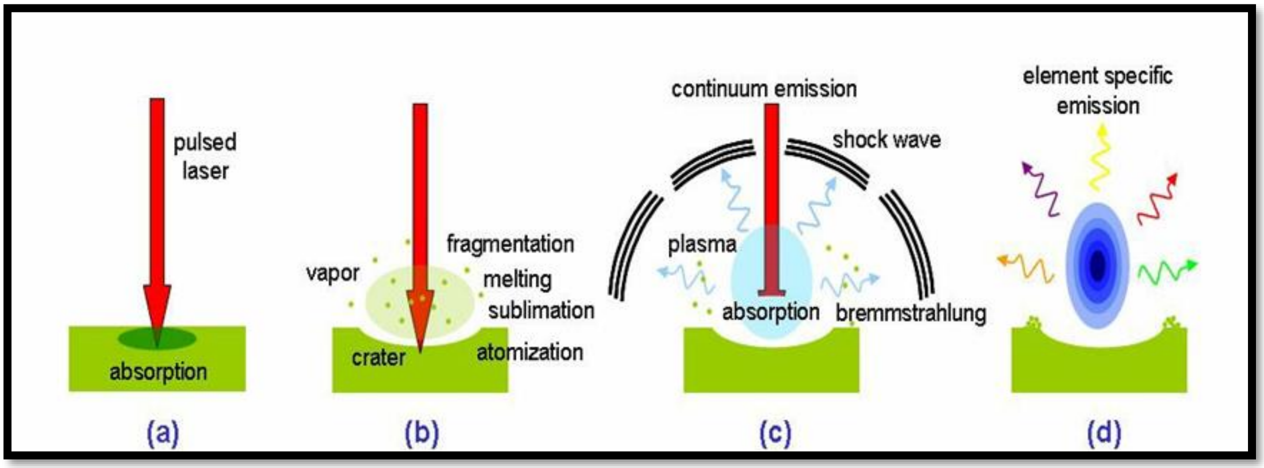

Fig (1) Schematic of the laser – Induced Breakdown Process[3]

2. EXPERIMENTAL SETUP

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The typical LIBS experimental setup used for recording the spectrum of copper sample is shown in Fig. (1) The Q-switched Nd: YAG pulsed laser operating at the wavelength 1064nm with a pulse duration of 10 ns and energy 200mJ with a frequency interval of 1 Hz is used for creating plasma. The laser beam is focused on the sample surface using a 10 cm focal length lens.

The plasma optical emission is collected by optical fiber at a distance 5cm above the plasma at an angle of 45^0 with a laser pulse falling on the sample. A high-resolution Spectrometer was used to receive a plasma emission spectrum of 200-900 nm. The spectrometer must be fast in performance and the response time constant for each moment.

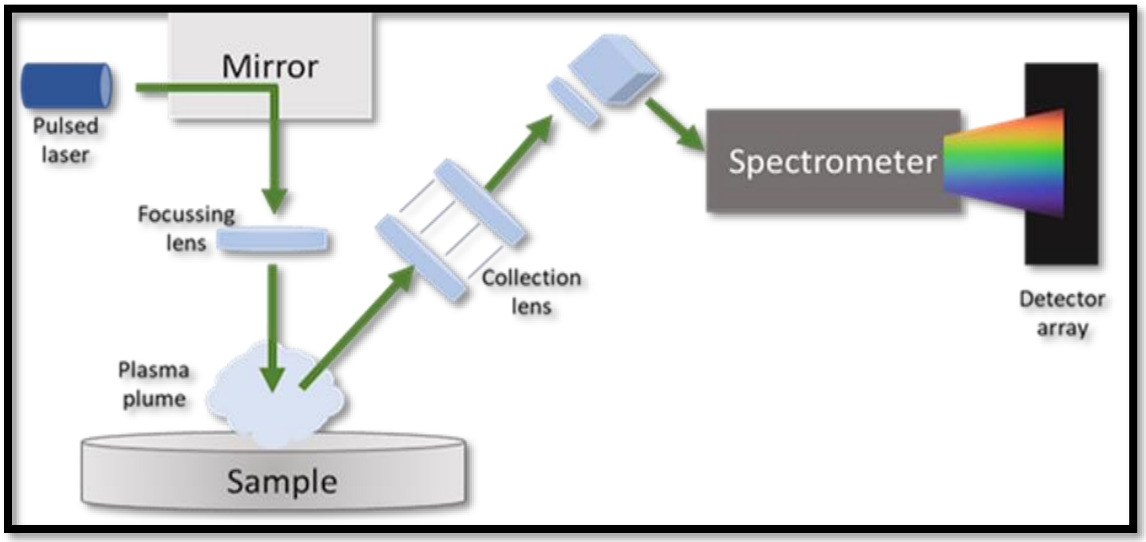

Figure (2) Experimental setup used for the recording of the LIBS spectrum of the elements[4].

2.1 Calculation of Electron Temperature for One and Two Spectral Lines

The plasma temperature is regarded as one of the most important parameters used to characterize the state of the plasma. Accurate knowledge of plasma temperature leads to the understanding of plasma processes such as vaporization, dissociation, excitation, and ionization.

Under the assumption of local thermal equilibrium (LTE), it is possible to investigate the properties of the laser-produced plasma[4]. The plasma temperature of two lines is calculated using the equation[5]:

$$T_e = \frac{(E_2 - E_1)}{K \ln\left(\frac{I_1 \lambda_1 A_2 g_2}{I_2 \lambda_2 A_1 g_1}\right)} \quad \text{......................} \; \textbf{(1)}$$

T_e: electron Temperature
I: line intensity
g_1, g_2: statistical weights

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k: Boltzmann constant
A_{ki}: represents the transition probability
The temperature of a single emission spectrum can be calculated using the equation below[6]:

$$T_e = \frac{(E_2 - E_1)}{k \ln\left(\frac{I\lambda}{A_{ki} g_k}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(2)}$$

2.2 Calculation of Electron Density

Electron density (n_e) is a parameter that describes the number of free electrons per unit volume and is measured in (cm^{-3}). It determines the number of electrons that interact with the laser and is considered an important parameter for describing plasma performance and determining the state of equilibrium. Mc. Whirter's criterion is one of the conditions, which shows that the plasma is at LTE. The relationship can be used to calculate the minimum electron number density required for the local thermodynamic equilibrium (LTE) condition[6].

$$n_e \geq 1.6\ x\,10^{12} (\Delta E)^3\, T_e^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

n_e: electron density in (cm^{-3}) unit
T_e: is the electron temperature in unit K
ΔE: is the energy difference between the states

2.3 Calculation of plasma frequency

The oscillations resulting from the electrons in the plasma are referred to as plasma oscillation, and the frequency of this oscillating motion is called the plasma frequency, which is given by the equation[7]:-

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \varepsilon_0}}$$

ω_p=Plasma angular Frequency
n_e = Electron number density
e = Electronic charge
ε_o = Permittivity of vacuum
m_e = Mass of electron

2.4 Landau Length

It is the amount at which the average Coulomb potential energy of a binary reaction is equal to the average kinetic energy, i.e. it represents the critical length of the binary reaction, and this amount can be used to analyze collision phenomena position correlations in the plasma - and it is determined by the following relationship[8]:

$$l_L = \frac{e^2}{4\pi\epsilon_0 k_B T_e}$$

l_L :-Landau length
ε_0:- Permittivity of free space
K_B :-Boltzmann constant
e:-Charge of an electron
T_e:-Temperatures of the electrons
n_e:- Density of electrons

2.5 Kinetic Energy of Electrons in Plasma

The temperature of electrons in a dynamically balanced system is important compared to the temperature of other particles in the plasma (ions and neutral particles). In the study of the phenomena that occur in the plasma and the kinetic energy of the electrons in the plasma can be calculated after the temperature of the electrons is calculated as in the following equation[9]: -

$$E_K = \frac{1}{2} m v^2 = \frac{3}{2} k_B T$$

k_B:- kinetic energy
v:- electron speed

2.6 Plasma Dissolution Time

The plasma decay time can be calculated according to Maxwell's law and given by the following relation[10]:-

$$\tau_{ee} = 3.16x\,10^4 (\mathrm{E}_e^{\frac{3}{2}})(n_e - 1)$$

E_e:- electron energy (eV)
n_e:- electron density(cm^{-3})

3. RESULTS AND DISCUSSION

A copper target was analyzed by using LIBS; Table (1) shows the Spectroscopic parameters of the observed copper lines sample. The components of this element were spectroscopically examined, and the important parameters that can be determined from laser-produced plasma study are the electron temperature and the electron density.

The electron temperature is particularly important in defining plasma characterization because it describes the relative population distribution of atoms over their energy levels using the Boltzmann law.

The emitted spectrum is examined and recorded by the detector, which displayed a graphical relationship between intensity and wavelength. Figure 1 depicts copper emission lines. When the main copper emission lines were compared to the NIST database, it was clear that there was a good match, as shown in Table (1).

Table (1) Spectroscopic parameters of the observed copper lines sample

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Wavelength 1064nm									
Ion	**λ_{LIBS} nm**	**λ_{NIST} nm**	**Δλ nm**	**I Count**	**A_k s^{-1}**	**g_i-g_k**	**E_i eV**	**E_k eV**	**Transition**
CuII	**492.759**	**492.642**	**0.117**	**1203.2**	**9.0×10^7**	**3 - 3**	**14.340**	**16.856**	**3*d*9(2D5/2)4*d* 2[3/2] 1→ 3*d*9(2D5/2)4*f* 2[3/2]° 1**
CuII	**500.829**	**500.985**	**0.156**	**1324.2**	**5.4×10^7**	**7 - 7**	**14.392**	**16.866**	**3*d*9(2D5/2)4*d* 2[5/2] 3→ 3*d*9(2D5/2)4*f* 2[5/2]° 3**
CuI	**521.484**	**521.820**	**0.336**	**1485.2**	**7.5×10^7**	**4 - 6**	**3.816**	**6.192**	**3*d*104*p* 2P° 3/2→ 3*d*104*d* 2D 5/2**
CuI	**578.368**	**578.213**	**0.155**	**822.8**	**1.65×10^6**	**4 - 2**	**1.642**	**3.785**	**3d94s2 2D 3/2→ 3*d*104*p* 2P° 1/2**
CuII	**655.659**	**655.965**	**0.306**	**1553.2**	**4.9×10^6**	**7 - 9**	**15.067**	**16.956**	**3*d*8(3F)4*s*4*p*(3P°) 1F° 3→ 3*d*9(2D5/2)5*d* 2[9/2] 4**
CuII	**690.414**	**690.261**	**0.153**	**239.4**	**8.0×10^6**	**7 - 7**	**16.975**	**18.771**	**3*d*9(2D5/2)5*d* 2[5/2] 3→ 3*d*9(2D5/2)6*f* 2[5/2]° 3**
CuII	**777.797**	**777.873**	**0.076**	**361.2**	**1.3×10^7**	**5 - 5**	**14.986**	**16.580**	**3*d*9(2D5/2)5*p* 2[5/2]° 2→ 3*d*9(2D5/2)6*s* 2[5/2] 2**

The emission spectra of this element have been recorded and as shown in Figure (1) which describes the relationship between intensity versus wavelength.

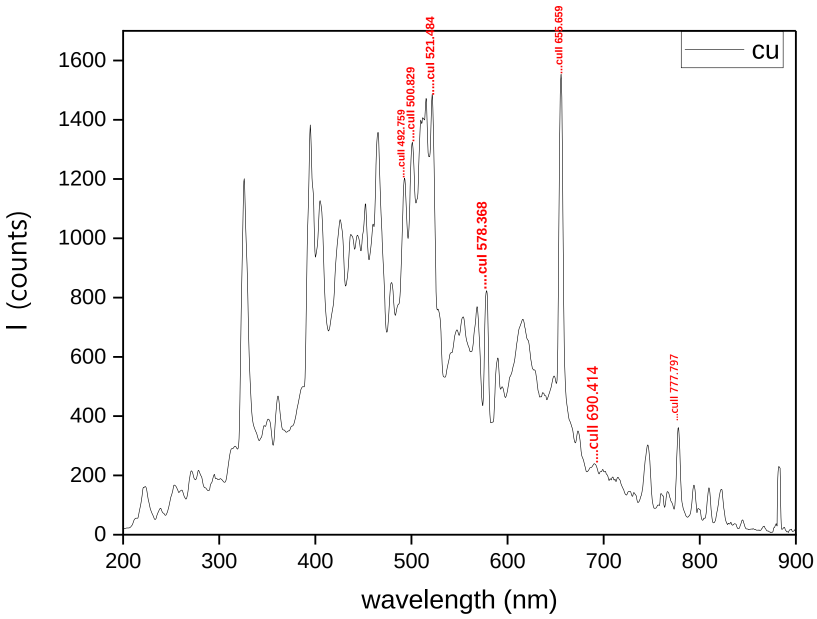

Figure (1) emission spectrum of copper

Table (2) Plasma parameters for the copper element

Th_e (K) electron temperature	N_e (cm^{-3}) electron density	W_p (Hz) Frequency plasma	E_k (eV) kinetic energy	τ_{ee}(s) relaxation time	l_L Landau length
4769.832	$1.76\ x10^{15}$	$3.8\ x10^{8}$	$6.17\ x\ 10^{-1}$	$1.1078\ x10^{-11}$	$3.02\ x10^{-11}$
4524.742	$1.6297\ x10^{15}$	$3.6\ x10^{8}$	$5.85\ x\ 10^{-1}$	$1.13432\ x10^{-11}$	$3.18\ x10^{-11}$
4332.627	$1.4127\ x10^{15}$	$3.4\ x10^{8}$	$5.60\ x\ 10^{-1}$	$1.25264\ x10^{-11}$	$3.32\ x10^{-11}$
12840.630	$1.7843\ x10^{15}$	$3.8\ x10^{8}$	$1.66\ x\ 10^{-1}$	$2.93986\ x10^{-11}$	$1.12\ x10^{-11}$
5818.207	$8.2264\ x10^{14}$	$2.6\ x10^{8}$	$7.52\ x\ 10^{-1}$	$2.88865\ x10^{-11}$	$2.47\ x10^{-11}$
3577.712	$5.5442\ x10^{14}$	$2.1\ x10^{8}$	$4.62\ x\ 10^{-1}$	$2.63324\ x10^{-11}$	$4.02\ x10^{-11}$
3397.988	$3.7774\ x10^{14}$	$1.7\ x10^{8}$	$4.39\ x\ 10^{-1}$	$3.67247\ x10^{-11}$	$4.24\ x10^{-11}$

4. CONCLUSION

LIBS is a spectroscopic technique used to determine electron density and electron temperature. Various experimental conditions such as environment, and laser energy. The laser-produced Cu plasma is studied using a Q-switched Nd: YAG laser at its fundamental wavelength (1064 nm). Plasma emission spectra showing transitions of neutral atoms and singly ionized Cu ions. The intensity of the spectral lines emitted by laser-induced plasma depends largely on the environmental conditions.

Based on the results obtained after inspection and analysis of the samples using the LIBS system and their discussion, it is shown that the LIBS technique performs fast, non-destructive, cheap, and reliable compared to others, and the possibility of studying the performance of the plasma produced by a laser pulse and calculating its parameters (electron temperature, electron density, kinetic energy, Landau length, and relaxation time). LIBS peak intensities can be used to quantify the concentration of trace elements in a sample.

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Conflict of interests

There are non-conflicts of interest.

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الخلاصة

مقدمة:

تم دراسة تأثير الطول الموجي لليزر على النتائج التحليلية التي تم الحصول عليها من LIBS بواسطة Nd: YAG لتشخيص الليزر لعنصر النحاس بشكل تجريبي بواسطة ليزر Nd: YAG عند الطول الموجي 1064 نانومتر. يتم حساب درجة حرارة وكثافة الإلكترونات في بلازما النحاس تحت ظروف (LTE).

طريقة العمل:

تم الحصول على انتقالات نحاسية مختلفة. يتم تحديد خطوط الانتقال من الطيف عن طريق مقارنة الخطوط الطيفية بقاعدة البيانات الذرية NIST. تمت مقارنة النتائج بعد إجراء التحليل مع قاعدة بيانات.(NIST)

الاستنتاجات:

أثبتت تقنية LIBS أنها أداة دقيقة ودقيقة لحساب درجة حرارة الإلكترون وكثافة عدد الإلكترون ، ووجود عناصر مختلفة بتفاوت منخفض للغاية ، وتشخيص تراكيزها.

الكلمات المفتاحية:

تقنية مطيافية الانهيار المستحث بالليزر، الاستئصال بالليزر، درجة حرارة الالكترون، كثافة الالكترون