

# Diagnostic study of Copper plasma in air by laser induced breakdown spectroscopy (LIBS)

Mohammed S.Mahde<sup>1</sup>; Alaa H. Ali<sup>2</sup> ; Mohannad H. Hussein<sup>3\*</sup>

<sup>1</sup>Department of Laser and Opto-Electronic Engineering, University of Technology, Baghdad, Iraq

<sup>2</sup>Department of Materials Research/ Ministry of Science and Technology, Baghdad, Iraq

<sup>3</sup> State Company for Construction Industry/ Ministry of Industry and Minerals, Baghdad, Iraq

\*Email: [mohannad792007@gmail.com](mailto:mohannad792007@gmail.com)

## ABSTRACT

In this work, we study a diagnostic of a copper-plasma in air using a fundamental wavelength of a Nd: YAG laser system. The optical emission spectra of copper-plasma that have been detected using a spectrum analyzer (*Thorlabs GmbH*) have been used to extract the excited plasma temperature via the Saha-Boltzmann method, and measure the electron number density by McWhirter criterion. Measured values of  $N_e$  and ( $T_e$ ) is in the range of (14890.827 K°) and ( $N_e$ ) is ( $2.7 \cdot 10^{15} \text{ cm}^{-3}$ ) at the fundamental wavelength.

**Keywords:** LIBS; Copper-plasma; excited plasma temperature.

## دراسة تشخيصية لبلازما النحاس في الهواء عن طريق طيف الانهيار المستحث بالليزر

في هذا العمل تم تشخيص بلازما النحاس في الهواء باستخدام ليزر النديميوم- ياك النبضي بالطول الموجي الاساسي 1064 nm, وبطاقة 75 mJ. أطيف الانبعاث الضوئي من بلازما النحاس تم الكشف عنها باستخدام المحلل الطيفي, اطيف الانبعاث استخدمت لاستخراج درجة حرارة البلازما وحساب كثافة الاكترون, حيث كانت درجة حرارة بلازما النحاس هي (14890.827 K°), وكثافة الاكترون ( $2.7 \cdot 10^{15} \text{ cm}^{-3}$ )

## INTRODUCTION

The Laser-Induced Breakdown Spectroscopy (LIBS) technique is one of the potentially growing applied techniques used in the field of elemental analysis, because of its simplicity and non-contact nature [1-3]. Which is an analytical promising detection technique for solid, liquid and gaseous samples [4-6] and is based on optical detection of certain atomic and molecular species by monitoring their emission signals from the laser induced plasma [7]. Plasma formed as a result of the focus of lasers intensive on the target surface, due to the interaction of the laser beam with the target material, and that led to the evaporation of the surface layers, the interaction of the laser beam with the evaporated material resulting in an isothermal plasma formation, and expansion and anisotropic adiabatic expansion of the ablated vapour cloud in vacuum [8]. The plasma contains mainly atoms, ions and electrons, and it gives a detailed picture of the basic structure elements [3]. The plasma diagnostics can be done through the measurements of the plasma temperature ( $T_e$ ) and electron density ( $N_e$ ). The plasma temperature determines the strength of the different distribution functions describing the plasma state, while the electron density overall, specifies the state of thermodynamic equilibrium of the plasma [9]. LIBS can be considered technique suitable for a wide range of different applications [10], due to its reliability [11], easy, fast, and in situ chemical analysis with a reasonable precision, detection limits, and cost, and there is no need for sample preparation [12]. Additionally, as is used to identify the the chemical elements [13-15], in soil studies [16], cleaning [17], heritage and culture [18],

measurements of the plasma parameters [19, 20], and Carbon Identify in low-carbon steel [15].

In this work, we study a diagnostic of a copper-plasma in air of a fundamental wavelength, that led to the evaporation and ionization of the sample in the hot plasma, which is analyzed by a spectrometer at a later time. Identify the elements that are unique spectral. We offer report the results of the spectroscopic measurements of the plasma parameters (Plasma temperature and Electron density ) utilizing the spectral lines emitted from the Cu-plasma in air.

## EXPERIMENTAL DETAILS

The experimental arrangement of the LIBS set-up which built in our laboratory shown in Figure 1. A set-up of experimental was designed by a passively Q-switched Nd: YAG laser, of wavelength 1064 nm and pulse duration 9ns was used for LIBS technique used for plasma excitation. It is worth mentioning, there are many lasers used in LIBS technique, except if Nd: YAG laser used a widely because this provides the highest power density [21], and has many applications, for example, laser ablation [22], and laser deposition [23]. The single-shot of laser energie ( 75) mJ was focused onto the Cu sample to a spot diameter of 0.9 mm by a lens of focal length 100 mm, the peak power of the laser pulse is (8.3) MW , and peak-power densities  $1.33 \times 10^9 \text{W.cm}^{-2}$ . The optical emission is collected of Cu sample by a lens of focal length 15 mm and is focused onto optical fiber type (SA,  $50\mu\text{m}/0.22 \text{NA}$ ), which deliver the plasma light to the entrance slit of spectrum analyser, model (Thorlabs GmbH-CCS-100) with (1200 Line/mm) grating and 20- $\mu\text{m}$  slit dimension, which serves to deflect light according to wavelength and then reversed by mirrors, then focuses to the detect and convert optical signals to digital, and then transported the digital signal to the application, which shows us the spectral lines for the sample and then analyzed.

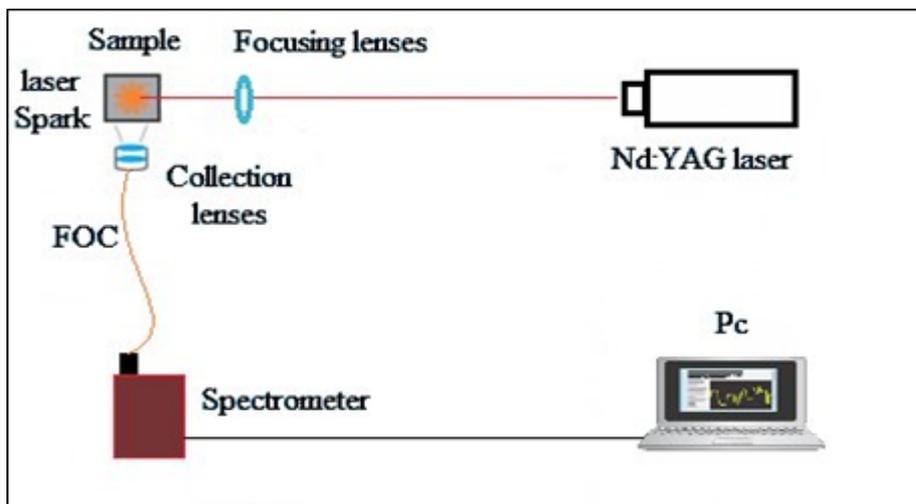
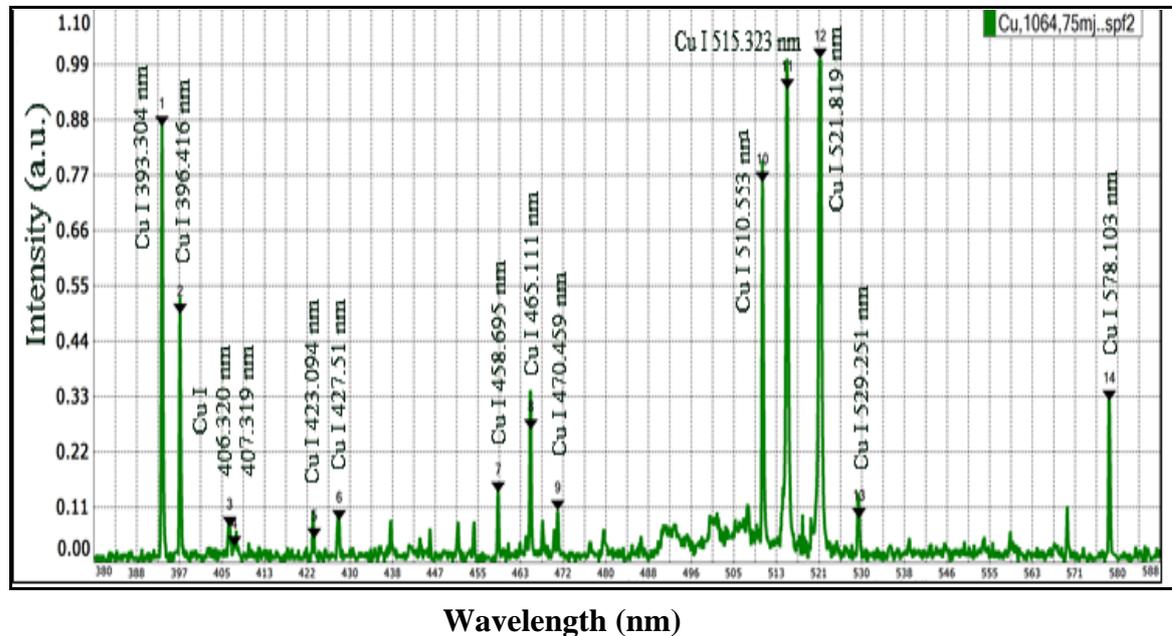


Figure. 1. Schematic diagram of the experimental set-up.

## RESULTS AND DISCUSSION

The emission spectra displayed in the Figure. 2 was recorded using a fundamental wavelength 1064nm of Nd-YAG Laser, with power laser densities  $1.3 \times 10^9 \text{W.cm}^{-2}$ . The

spectra was obtained by data of single-laser-shot under normal atmospheric pressure. The emission spectrum lines consist of neutral and singly ionized spectral lines of transitions of the pure copper element. The wavelengths of all the observed spectral lines along with their relevant spectroscopic data are displayed in Table. 1. Depending on the (*National Institute of Standards and Technology Atomic Spectra Database*) (NIST) [24] and with some of references [25, 26].



**Figure. 2. The emission spectrum generated by the 1064 nm laser on Cu-plasma in air at normal atmospheric pressure in the region from (380-600) nm.**

In LIBS experimental conditions, assuming optically thin plasma and the local thermodynamic equilibrium (LTE) conditions are hold, the reabsorption effects of plasma emission are negligible (i.e. the main ionization process is produced through impact excitation by thermal electrons) [27]. In our experimental conditions, example to a set of emitted spectrum is given in the range from 380 to 600 nm is shown in Figure 2. Shows the strong lines of Copper appear under the above spectrum, from the spectral lines from the sample can determine the atomic constants used to evaluate the plasma temperature and electron densities from the Cu-lines are given above Table. 1. Using the transition  $4p\ 2p \rightarrow 4d\ 2D$  for line Cu I 515.32 nm with  $g_k = 4$ ,  $A_{ki} = 6 \times 10^7\ s^{-1}$ ,  $E_k = 49935.20\ cm^{-1}$ , used to calculate the plasma parameters. The plasma temperature can be estimated by equation below:

$$\ln\left(\frac{I\lambda}{A_{ki}g_k}\right) = -\frac{E_k}{KT_e} + \ln\left(\frac{CF}{U_T}\right) \quad (1)$$

where  $\lambda$  is the wavelength,  $A_{ki}$  is the transition probability,  $g_k$  is the statistical weight for the upper level,  $E_k$  is the excited level energy,  $T_e$  is the temperature,  $K$  is the Boltzmann constants,  $U_T$  is the partition function,  $F$  is an experimental factor and  $C$  is the species concentration.

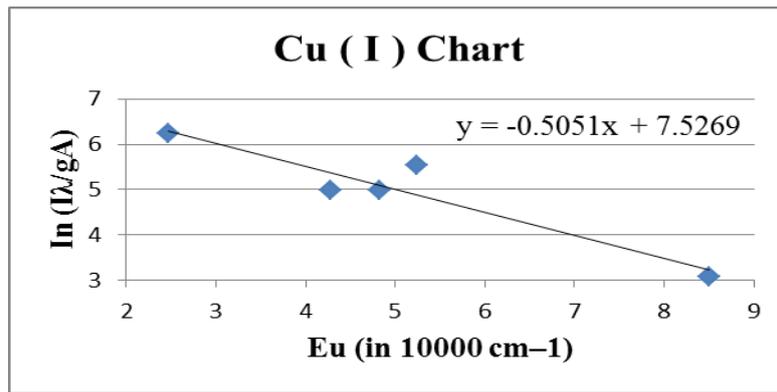
The result  $T_e$  is a straight line with a slope equal to  $(-1/kT_e)$ . The Boltzmann plot for five emission lines [Cu I 406.32, 427.51, 510.32, 515.32 and 521.819 nm] in the single-shot of laser-pulse, the scheme is shown in Figure. 3. The slope of the curve yields a temperature of 14890.827 K° of the Copper sample. The minimum electron density for Local Thermodynamic Equilibrium (LTE), expressed as the **McWhirter criterion** [28], and can be calculated by equation below:

$$N_e \geq 1.6 * 10^{12} . T^{1/2} . (\Delta E)^3 \quad (2)$$

where  $\Delta E$  (eV) is the highest energy transition for which the condition holds, and  $T$  (K) is the plasma temperature. This criterion is a necessary, though insufficient, condition for LTE, and is typically fulfilled during the first stages of plasma lifetime. It is, however, difficult to satisfy for the low-lying states, where  $\Delta E$  is large. However, for any  $N_e$ , it is possible to find high excitation levels where the states are close enough for equation (2) to hold. In the present case  $\Delta E = 2.4$  eV for Cu at 515.324nm (see Table. 1) and its electron density is  $(2.7*10^{15} \text{ cm}^{-3})$ , the plasma is said to be in partial LTE [21, 29].

**Table. 1. The analytical lines of the Cu-pure metal by LIBS technique and identified atomic neutral (I) species.**

Element	$\lambda$	I	gA_u	E_l	E_u
name	(nm)	(relative)	(10 <sup>8</sup> s <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
Cu I	393.304	0.88	9.65E-02	46598.34	72016.76
Cu I	396.417	0.54	8.47E-02	45879.311	71098.17
Cu I	406.32	0.09	1.93E-01	30783.686	55387.67
Cu I	407.319	0.04	6.59E-02	40113.99	64657.8
Cu I	423.094	0.1	1.00E-01	43513.95	67142.7
Cu I	427.51	0.07	2.54E+00	39018.652	62403.32
Cu I	458.695	0.15	1.54E+00	41153.433	62948.29
Cu I	465.112	0.34	3.36E+00	40909.138	62403.32
Cu I	470.459	0.1	4.98E-01	41153.433	62403.32
Cu I	510.554	0.75	7.80E-02	11202.565	30783.69
Cu I	515.323	1	4.14E+00	30535.302	49935.2
Cu I	521.819	1.02	7.33E+00	30783.686	49942.06
Cu I	529.251	0.14	8.72E-01	43513.95	62403.32
Cu I	578.213	0.33	3.80E-02	13245.423	30535.3



**Figure. 3. Boltzmann plot used to determine Plasma Temperature in plasma formed on a Cu (I) sample.**

## CONCLUSIONS

In this work, we have constructed a LIBS system by using a portable commercial Thorlabs spectrometer equipped with ICCD detector to Identify spectral lines emitted from the pure copper sample, the spectral lines were used to evaluate the plasma parameters emitted from the Cu-plasma in air. The plasma temperature and electron density were determined from the plasma formed from the interaction of lasers with the target. Plasma parameters ( $T_e$  &  $N_e$ ) are very important parameters to plasma description and give information about the physical condition that has been identified. The results obtained indicate that the LIBS technique is effective and rapid technique to identify the elements and estimate the plasma parameters which saves a lot of time and efforts.

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## REFERENCE

- [1] A.M.E. Sherbini, "*Measurement of Plasma Parameters in Laser-Induced Breakdown Spectroscopy Using Si-Lines*", WJNSE World Journal of Nano Science and Engineering, 02 (2012) 206-212.
- [2] I.B. Gornushkin, A.Y. Kazakov, N. Omenetto, B.W. Smith, J.D. Winefordner, "*Experimental verification of a radiative model of laser-induced plasma expanding into vacuum*", Spectrochimica Acta Part B: Atomic Spectroscopy, 60 (2005) 215-230.
- [3] F. Capitelli, F. Colao, M.R. Provenzano, R. Fantoni, G. Brunetti, N. Senesi, "*Determination of heavy metals in soils by Laser Induced Breakdown Spectroscopy*", Geoderma, 106 (2002) 45-62.
- [4] F. Vestin, M. Randelius, A. Bengtson, "*Laser-induced breakdown spectroscopy applied on low-alloyed zinc samples*", Spectrochimica Acta Part B: Atomic Spectroscopy, 65 (2010) 721-726.
- [5] L.M. Cabalín, A. González, V. Lazić, J.J. Laserna, "*Laser-induced breakdown spectroscopy of metals covered by water droplets*", Spectrochimica Acta Part B: Atomic Spectroscopy, 74-75 (2012) 95-102.

- [6] Jagdish P. Singh and Surya N. Thakur, **"LASER-INDUCED BREAKDOWN"** Elsevier B.V, 2007.
- [7] M. Hanif, M. Salik, M. A. Baig, **"Diagnostic Study of Nickel Plasma Produced by Fundamental"** (1064nm) and Second Harmonics (532nm) of an Nd: YAG Laser, Journal of Modern Physics, 03 (2012) 1663-1669.
- [8] N.M. Shaikh, S. Hafeez, B. Rashid, S. Mahmood, M.A. Baig, **"Optical emission studies of the mercury plasma generated by the fundamental, second and third harmonics of a Nd: YAG laser"**, Journal of Physics D: Applied Physics, 39 (2006) 4377.
- [9] H.R. Griem, **"Plasma spectroscopy"**, McGraw-Hill, New York, 1964.
- [10] B. Kearnton, Y. Mattley, **"Laser-induced breakdown spectroscopy: Sparking new applications"**, Nat Photon, 2 (2008) 537-540.
- [11] X. Shen, **"Laser-induced breakdown spectroscopy with improved detection sensitivity, selectivity, and reliability"**, University of Nebraska - Lincoln,( 2009).
- [12] F. Anabitarte, A. Cobo, J.M. Lopez-Higuera, **"Laser-Induced Breakdown Spectroscopy: Fundamentals, Applications, and Challenges"**, ISRN Spectroscopy, pp.1-12 (2012).
- [13] R. Noll, **"Laser-induced breakdown spectroscopy fundamentals and applications"**, in, Springer, New York, (2012).
- [14] V. Piñon, M. P. Mateo & G. Nicolas., **"Laser-Induced Breakdown Spectroscopy for Chemical Mapping of Materials"**, Applied Spectroscopy Reviews, 48 (2013) 357-383.
- [15] Mohammed S. Mahdi, Alaa H. Ali, Mohanad H. Hussein, **"Using Laser-induced Breakdown Spectroscopy Technique to Identify the Low-Carbon Steel in the Industrial Alloy"**, Asian Journal of Applied Science and Engineering, 3 (2014) 50-56.
- [16] Walid T, Y. Mohamed, A. Askar, **"Study of the Matrix Effect on the Plasma Characterization of Heavy Elements in Soil Sediments using LIBS with a Portable Echelle Spectrometer"**, Progress in Physics, Vol.1 (2007).
- [17] Colao F.F, R.; Lazic, V.; Morone, A.; Santagata, A.; Giardini, A., **"LIBS used as a diagnostic tool during the laser cleaning of ancient marble from Mediterranean areas"**, Applied Physics A Materials Science And Processing, 79 (2004) 213-220.
- [18] Xu H.L, G. Méjean, W. Liu, Y. Kamali, J.F. Daigle, A. Azarm, P.T. Simard, P. Mathieu, G. Roy, J.R. Simard, S.L. Chin, **"Remote detection of similar biological materials using femtosecond filament-induced breakdown spectroscopy"**, Applied Physics B, 87 (2006) 151-156.
- [19] Gondal M.A., Y.W. Maganda, M.A. Dastageer, F.F. Al Adel, A.A. Naqvi, T.F. Qahtan, **"Detection of the level of fluoride in the commercially available toothpaste using laser induced breakdown spectroscopy with the marker atomic transition line of neutral fluorine at 731.1nm"**, Optics & Laser Technology, 57 (2014) 32-38.
- [20] A. M. El Sherbini, Abdel-Nasser Aboufotouh, Farid F. Rashid, Sami H. Allam, Ahmed M. Al-Kaoud, Ashraf El Dakrouri, Tharwat M. El Sherbini, **"Spectroscopic measurement of Stark broadening parameter of the 636.2 nm Zn I-line"**, Natural Science, 05 (2013) 501-507.
- [21] A. Miziolek, V. Palleschi and I. Schechter, **"Laser-Induced Breakdown Spectroscopy (LIBS) : Fundamentals And Applications"**, Cambridge, UK; New York (2006).
- [22] A.Q.D. Faisal, Z.N. Jameel, A.A. Moosa, **"Preparation of Silver and Gold Nanoparticles By Using Nd-YAG Pulse Laser Ablation"**, Eng. & Tech. Journal, Vol.32,Part (B), No.1, (2014) 138-144.
- [23] H.S. Tareq, **"Deposited Nanostructure Cds Thin Film by Using Pulse Laser Deposition Technique for Fabrication of Heterojunction Solar Cell"**, Eng. & Tech. Journal , Vol.32,Part (B), No.2, (2014) 313-320.
- [24] Kramida A., Ralchenko, Yu., Reader, J., and NIST ASD Team **"NIST Atomic Spectra Database (ver. 5.1)"**, in, National Institute of Standards and Technology, Gaithersburg, MD. , [Gaithersburg, Md.], (2013).<http://www.nist.gov>
- [25] Robert P.L.S. L. Kurucz, Claas Heise , Jim R. Esmond **"Atomic Line Data,Kurucz CD-ROM No (Smithsonian Astrophysical Observatory, Cambridge)"**, 23 (1995).  
<http://www.cfa.harvard.edu>

- [26] Garcimuño M., D.M. Díaz Pace, G. Bertuccelli, "***Laser-induced breakdown spectroscopy for quantitative analysis of copper in algae***", Optics & Laser Technology, 47 (2013) 26-30.
- [27] Mohamed W.T.Y., "***Study of the Matrix Effect on the Plasma Characterization of Six Elements in Aluminum Alloys using LIBS With a Portable Echelle Spectrometer***", PROGRESS IN PHYSICS, 2 (2007) 42-49.
- [28] Gaudioso R., M. Dell'Aglio, O. De Pascale, G.S. Senesi, A. De Giacomo, "***Laser induced breakdown spectroscopy for elemental analysis in environmental, cultural heritage and space applications: a review of methods and results***", Sensors, 10 (2010) 7434-7468.
- [29] Yamanouchi K., M. Nisoli, W.T. Hill, "***Progress in Ultrafast Intense Laser Science VIII***", Springer, (2012).