Calculation of the Coupling Coefficient of Electrons in Laser Induced Plasma for Samples of Writing Ink Elements Using LIBS Technique

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Abstract

The technique of laser breakdown spectroscopy (LIBS) was employed for samples of writing inks under the influence of a Nd:YAG laser pulse 1064 nm with a pulse duration of 10 ns on different targets of writing ink models. The plasma parameters were also calculated, which are the temperature and density of electrons, assuming local thermodynamic equilibrium conditions (LTE) and using a spectral detector model (View spectra 2100) for the spectral range (200nm - 900nm). The results showed differences in the values of the pairing coefficient of electrons in the plasma. Produced due to the laser pulse used as well as in the plasma parameters mentioned, which can be applied in plasma spectroscopy for forensic sciences in detecting forgery in documents and tracking the performance and phenomena of the plasma formed due to the laser pulse.

Key Words: LIBS Technique, Electrons Pairing Coefficient, Plasma Parameters, Electron Temperature, Electrons Density.

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Introduction

The Laser Induced Breakdown (LIBS) technique is a quick analytical tool that can be used to show the components of the material components in their solid, liquid and gas states (Vander Wal, 1999; Williams, 2018). And to know the chemical structures of materials where a laser pulse is used to form plasma on the surface of the target sample. LIBS) for examining different materials, including inks used in the writing process, thin films, biological sciences, various forensic sciences, the environment, and others due to the advantages that they are characterized by being quick to perform and non-destructive as the samples do not need prior preparation during the analysis and examination process (Mahdee, 2016).

The process of plasma formation is the basic principle of this spectroscopy, where when the laser pulse is directed at the surface of the target material so that it is sufficient to form an ionized plasma, and with more absorption of the laser energy by the process of the Bremsstrahlung Inverse, which causes an increase in the ionization process.

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And this process is renewed and as a result leads to collapse ionization because the increase in the ionization rate leads to an increase in the absorption processes of the laser energy, which in turn causes an increase in the ionization rate, until it reaches the dark plasma state of the laser and the material is protected from it at the critical plasma density, and then the laser will be reflected by Plasma and this in turn leads to the beginning of the expansion of the plasma and this expansion will reduce the density of electrons and then the laser will be able to pass through the plasma and thus heat the surface of the material and by continuing these periodic processes until the time of the end of the laser pulse. Affects energy transfer (Ferreiraa, 2011; Godoi, 2011).

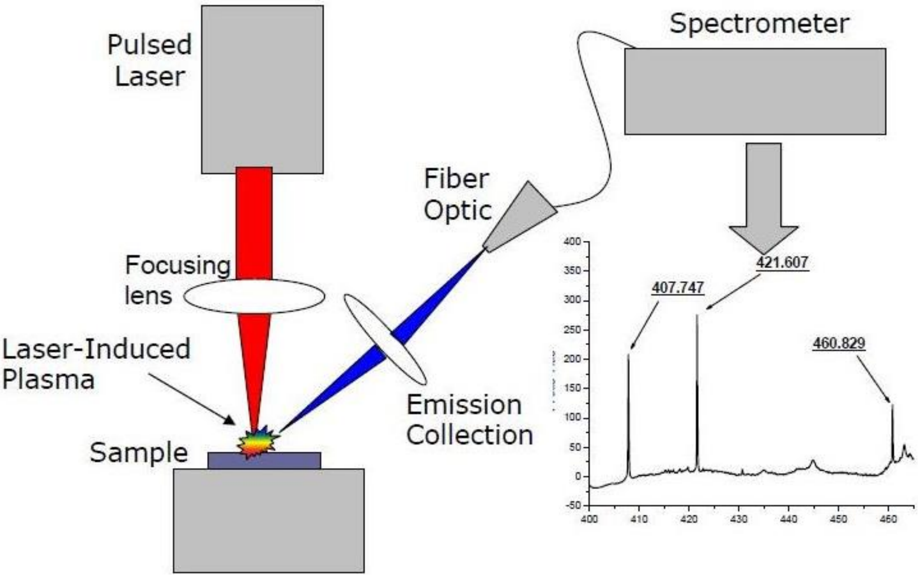

Figure 1. LIBS technique (Jiang, X., 2012).

When the plasma decays, the electrons will move to lower energy levels. This transition results in a spectrum with different wavelengths for each element of the target material. These wavelengths are received by an optical fiber, which in turn transmits them to the spectroscopic analyzer to be analyzed, where each chemical element is linked with its own emission spectrum, therefore, the separation and study of these wavelengths is to know their chemical composition (Jiang, X., 2012).

Calculating the Temperature of Electrons

Assuming the state of local thermal equilibrium (LTE), it is possible to study the properties of the laser produced plasma and determine the temperature for it, where the plasma temperature is measured in Kelvin or electron-volt units. The plasma can be calculated using the following equation (Hussain, T., 2016).

$$\ln\left(\frac{I\lambda}{A_{ki}\; g_k}\right) = -\frac{E_k}{K_B\, T_e} \qquad (1)$$

Where E_k represents energy of the upper plane, I spectral intensity, Aki transition probability, gk statistical weight, and K_B Boltzmann constant.
By determining the temperature of the electron, the number of free electrons per unit volume can be calculated, which is called the electron density, which is important to describe the performance of the plasma (Milan, M., 2001).

Calculating Density of Electrons

The electron density is called the number of free electrons per unit volume and is measured in (cm^{-3}), and it determines the number of electrons that interact with the laser and is an important parameter to describe the performance of the plasma and determine the state of equilibrium. The density of electrons is described using the Mc Whirter's criterion and is given by the following relationship (Miziolek, A.W., 2006).

$$n_e \geq 1.6\times10^{12}\, T_e^{1/2}\, \left(\Delta E\right)^3 \qquad (2)$$

where n_e is the electron density, T_e is the electron temperature, and ΔE is the energy difference between two levels.

The Pairing Coefficient of Electrons in the Plasma

It is the ratio between the average potential energy and the average kinetic energy of the particles in the plasma **(Koreisha, S., 2006).** [13]:

$$\Gamma = \frac{\langle E_p \rangle}{\langle E_c \rangle} \qquad (3)$$

Where: $\langle E_p \rangle$ represents the average potential energy of the interaction of a particle with a neighboring particle. And $\langle E_c \rangle$: average kinetic energy.

The pairing coefficient equation for electrons is given:

$$\Gamma_{ee} = \frac{e^2}{K_B T_{re}} \qquad (4)$$

where e: electronic charge, K_B: Boltzmann constant, T: temperature.

The value of the coupling coefficient determines the behavior of the particles and the kinetic energy of the plasma, re: the radius of the electron sphere, which is the amount that characterizes the average distance between two electrons inside the plasma.

$$r_e = \sqrt[3]{\left(\frac{3}{4\pi n_e}\right)} \qquad (5)$$

Where: n_e: represents the electron density, r_e: the radius of the electron sphere.

Results and Discussion

In this work, samples of writing inks were taken, which are shown in Table No. (1) for the purpose of performing a spectroscopic analysis of its elements and measuring the temperature and density of electrons and the absorption coefficient of the reversal of the braking radiation. The chemical elements included in the components of the ink were selected (Ti, K, Na, Ga, Cu, F, S, Si) from the samples mentioned in Table No. (1).

Table 1. Samples examined in the study.

Sample	Brand	Color	Type	Source
1	Sigma	blue	dry	**India**
2	Smart	blue	dry	**India**
3	Rebnok glaria	blue	dry	**India**
4	Nataraj	blue	dry	**India**
5	Linc Axo	blue	dry	**India**
6	Montex Elite	black	dry	**India**
7	Idea office	blue	dry	**China**
8	Montex LCD	blue	dry	**Germany**

The emission spectrum of these elements was obtained as shown in Figures (3), (4), (5), (6), (7), (8), (9), (10). Which describes the relationship between intensity versus wavelength.

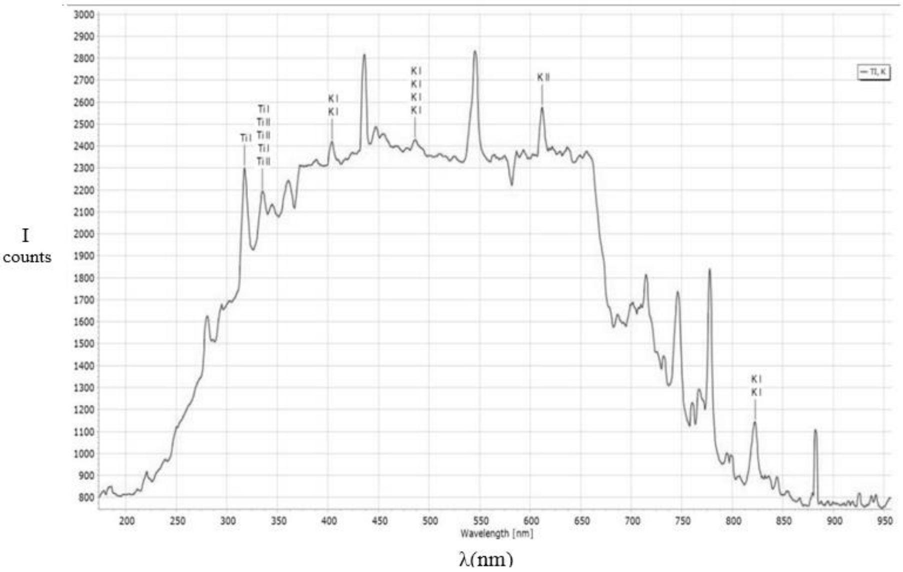

Figure 2. Emission spectrum of sample No. (1).

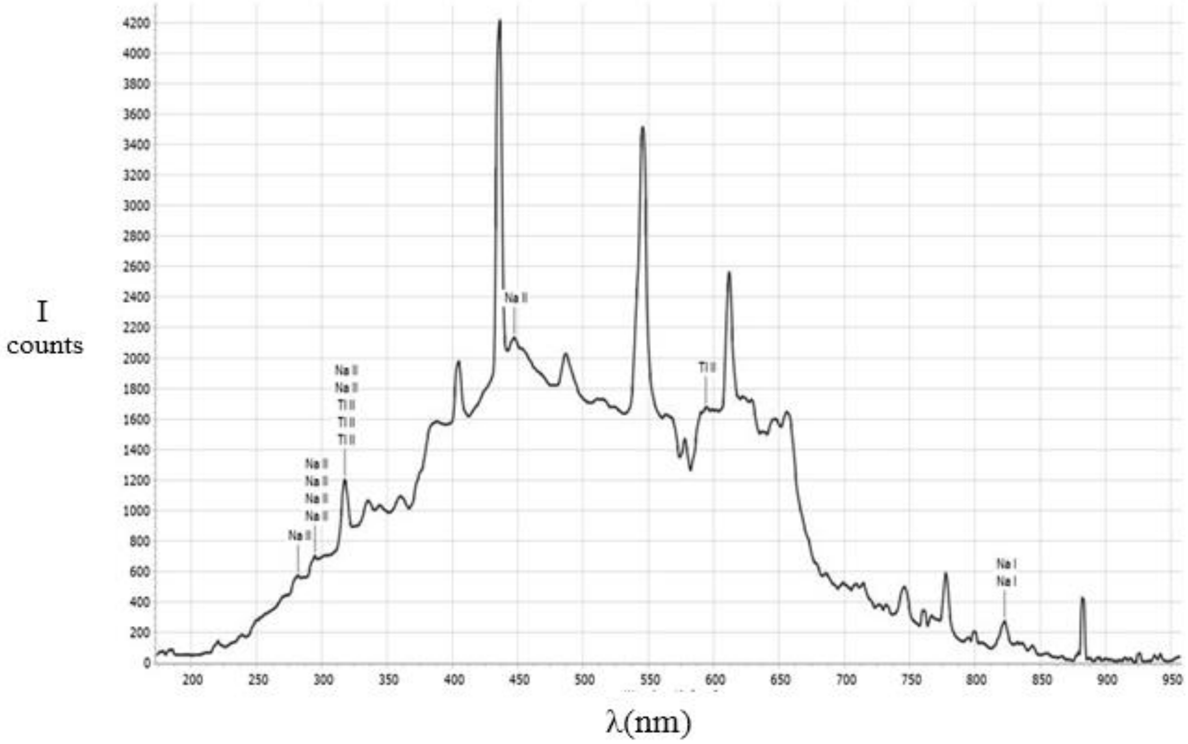

Figure 3. Emission spectrum of sample No. (2).

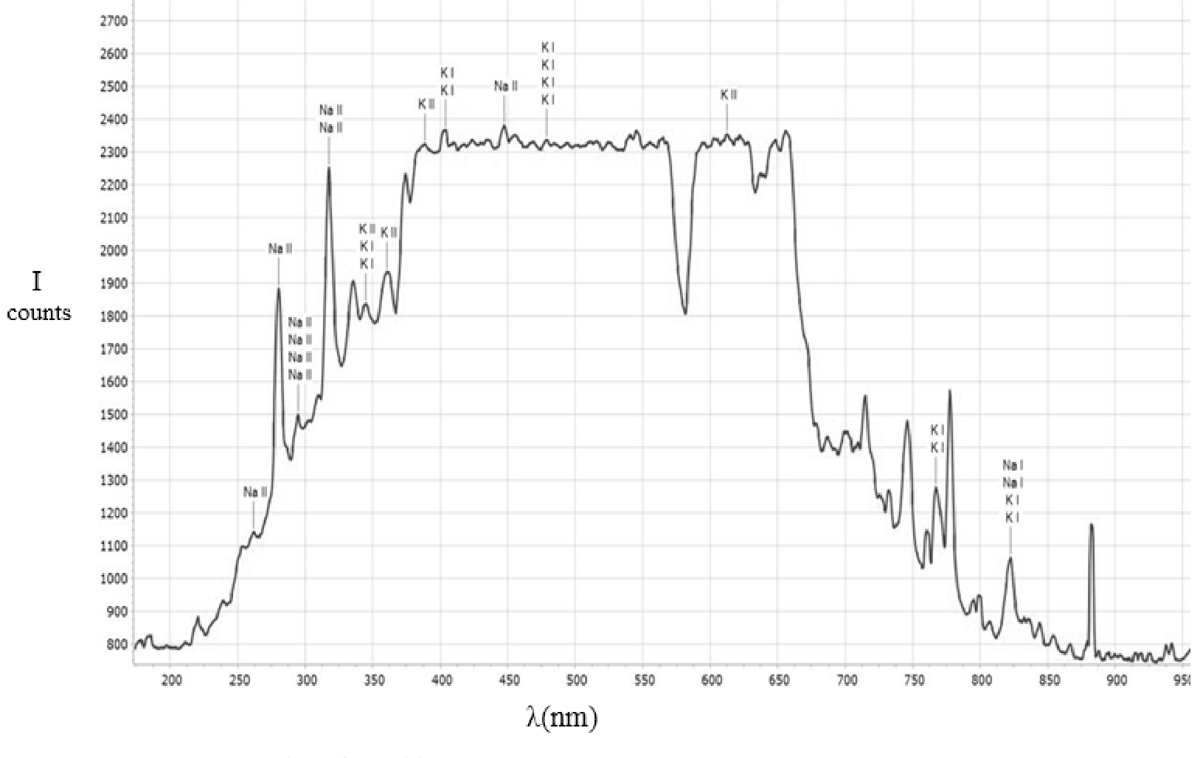

Figure 4. Emission spectrum of sample No. (3).

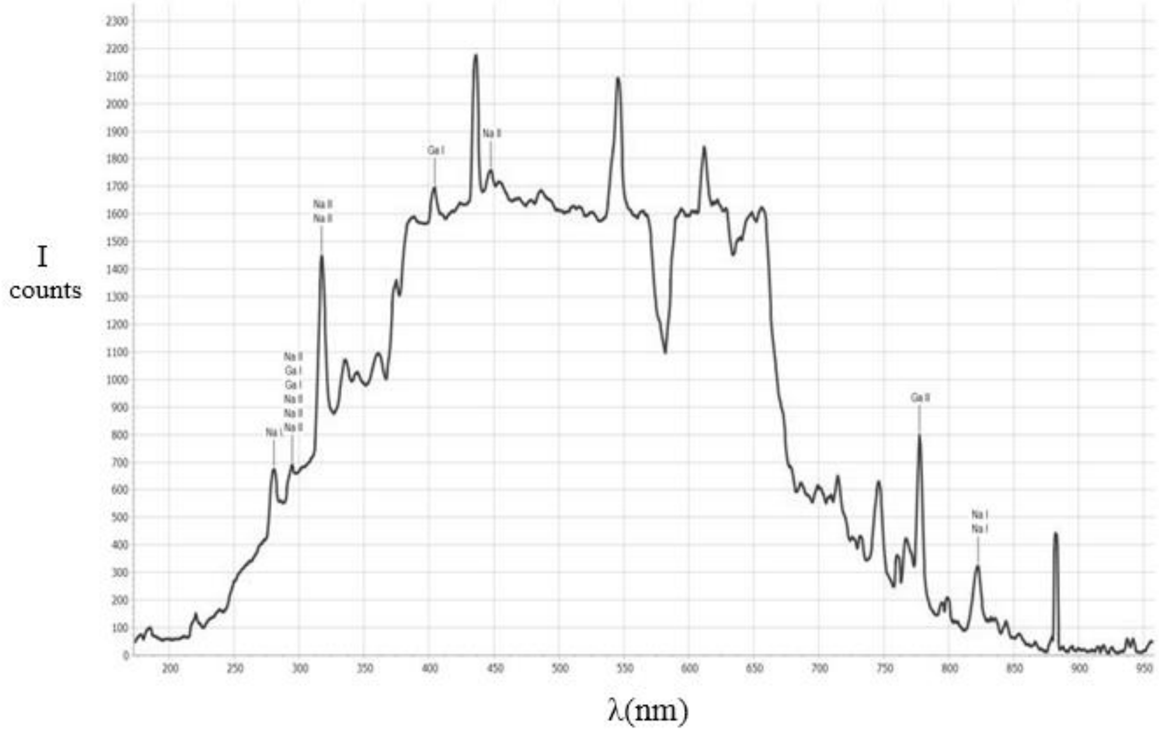

Figure 5. Emission spectrum of sample No. (4).

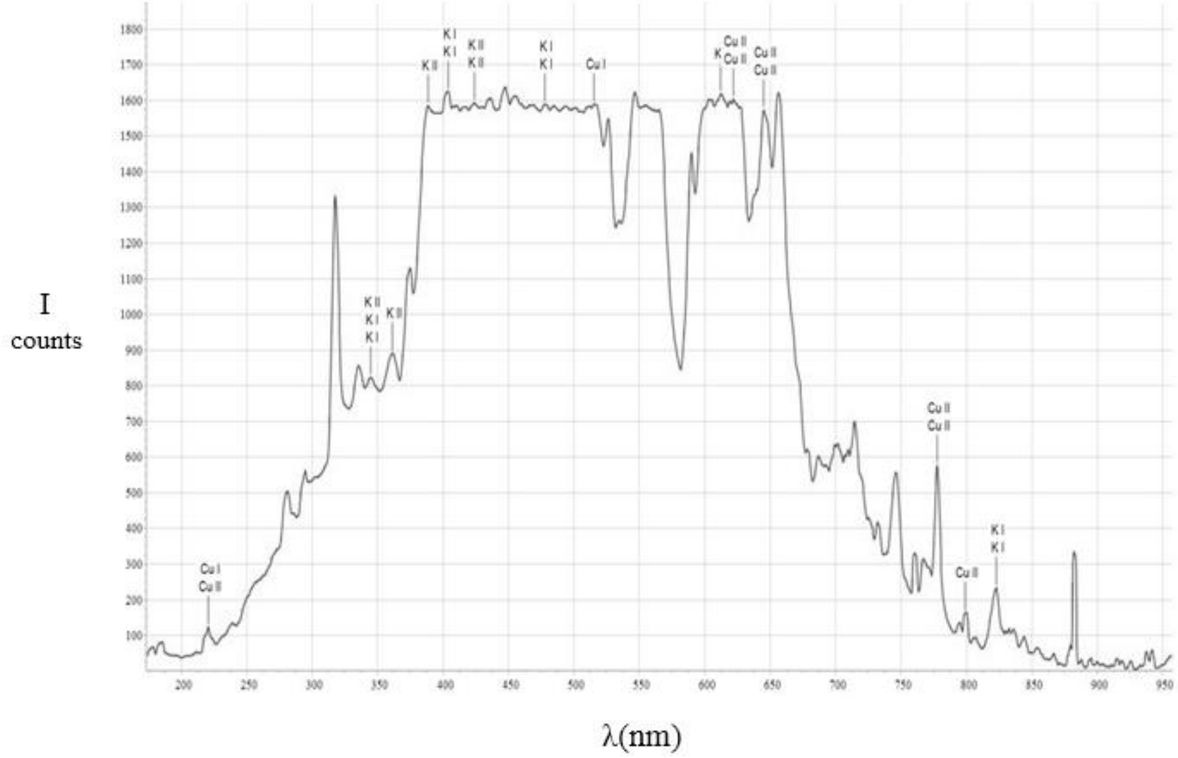

Figure 6. Emission spectrum of sample No. (5).

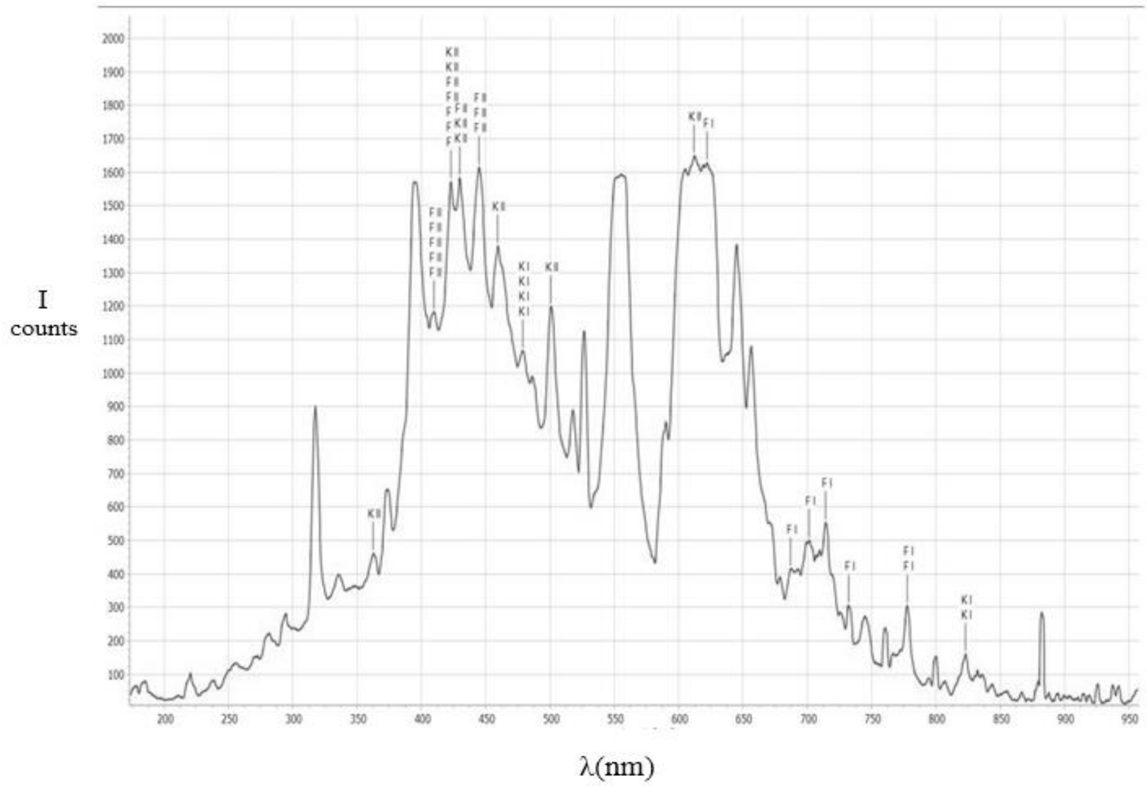

Figure 7. Emission spectrum of sample No. (6).

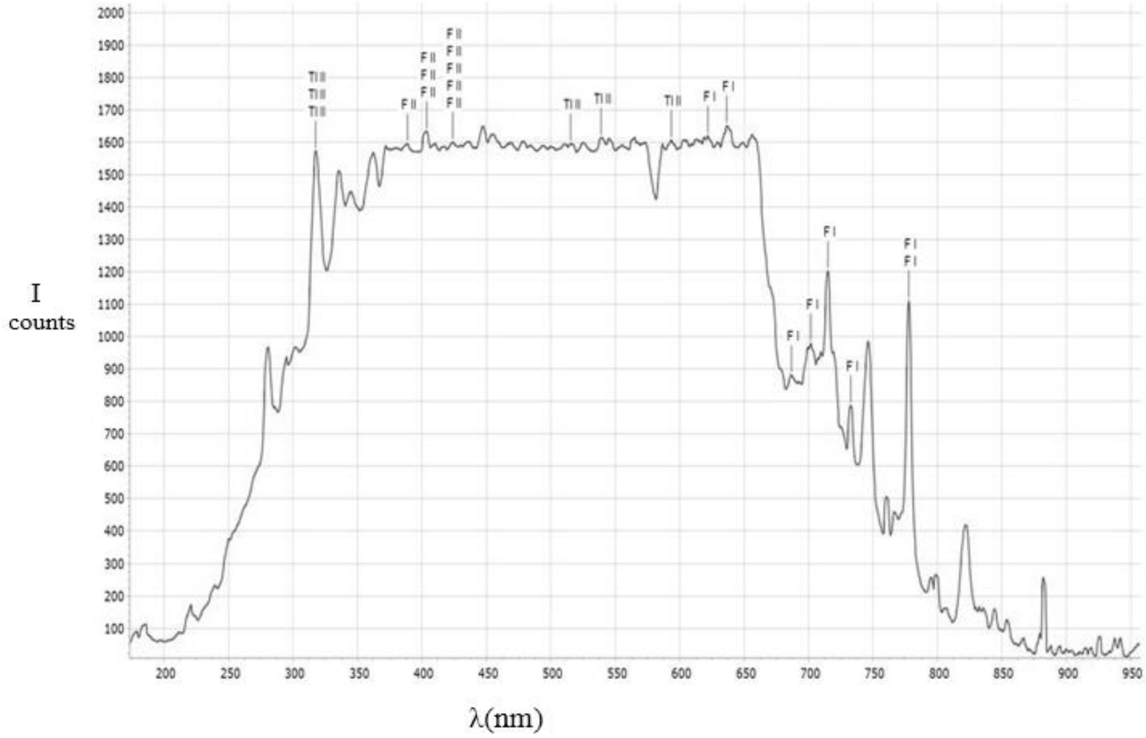

Figure 8. Emission spectrum of sample No. (7).

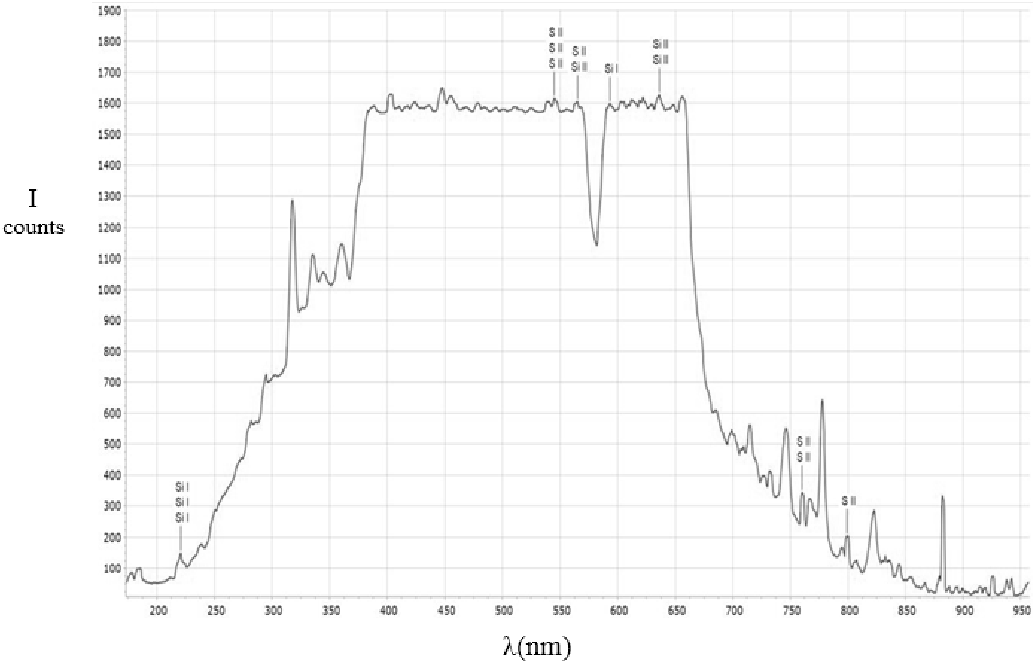

Figure 9. Emission spectrum of sample No. (8).

Table (2) shows the main emission lines for the sample elements whose data were recorded in this study using the NIST spectroscopy database (NIST At., 2019). Which determines the type of spectral line, energies, statistical weight, and transmission probability.

Table 2. Data of the spectral emission lines for the examined elements in the study.

No.	Ion	λ $_{\text{LIBS}}$ (nm)	λ $_{\text{NIST}}$ (nm)	I (Counts)	A_{ki} (s^{-1})	g_k Upp.	E_l (ev)	E_u (ev)
1	Ti I	317.51	317.55	2301.0	1.4E+08	9	2.134	6.034
1	KI	486.30	486.34	2427.9	3.6E+08	2	1.017	4.165
2	Ti I	317.57	317.55	1200.8	1.7E+08	9	2.134	6.034
2	Na I	819.46	819.48	274.64	5.1E+07	6	2.104	3.616
3	K I	825.06	825.01	1062.1	6.4E+07	6	2.669	4.172
3	Na I	819.42	819.48	1062.1	5.1E+07	6	2.104	3.616
4	Na I	819.47	819.48	323.48	5.1E+07	6	2.104	3.616
4	Ga II	779.20	779.22	789.48	7.1E+07	9	13.355	14.940
5	Cu I	515.31	515.32	1588.6	6.0E+07	4	3.785	6.191
5	K I	825.02	825.01	233.35	6.4E+04	6	2.669	4.172
6	K I	825.01	825.01	160.1	6.4E+04	6	2.669	4.172
6	F I	712.75	712.78	552.66	5.0E+08	2	13.025	14.764
7	Ti II	539.12	539.12	1613.5	1.2E+08	8	5.567	7.866
7	F I	780.00	780.02	1110.3	2.5E+07	4	5.280	6.960
8	S II	545.90	545.91	1613.9	5.9E+08	3	8.045	10.125
8	Si II	637.10	637.13	1627.2	6.8E+08	2	8.121	10.060

The T_e electron temperature, the electron density n_e and the pairing coefficient of electrons in the plasma Γ_{ee}. were calculated For these elements using equations (1), (2), (4) and (5). As shown in Table (3).

Table 3. Shows the parameters of the plasma, the electron temperature, the electron density and the pairing coefficient of electrons in the plasma and for all the elements examined from the samples.

No. Sample	Ion	T_e (K)	n_e (cm^{-3})	r_e (cm)	Γ_{ee}
1	Ti I	9395.91	9.20E+15	2.96E-06	5.17E-06
1	KI	7536.9	4.33E+15	5.49E-06	5.03E-06
2	Ti I	8439.56	8.72E+15	2.96E-06	5.19E-06
2	Na I	5816.18	4.22E+14	3.85E-06	2.99E-06
3	K I	7959.54	4.85E+14	3.80E-06	3.35E-06
3	Na I	7158.0	4.68E+14	3.75E-06	2.89E-06
4	Na I	5951.3	4.27E+14	3.78E-06	2.76E-06
4	Ga II	18777.5	8.83E+14	5.93E-06	5.11E-06
5	Cu I	12461.4	2.49E+15	5.18E-06	4.81E-06
5	K I	7012.1	1.44E+15	5.68E-06	5.08E-06
6	K I	4536.7	1.16E+15	5.76E-06	5.05E-06
6	F I	2185.9	1.24E+15	1.63E-06	1.13E-06
7	Ti II	13028.9	2.22E+15	5.79E-06	5.47E-06
7	F I	17008.0	9.89E+14	1.84E-06	1.18E-06
8	S II	15449.6	1.79E+15	2.04 E-06	1.82E-06
8	Si II	9630.2	1.66E+15	3.13E-06	2.84E-06

Through the calculated values above, the difference between the temperature and electron density of the sample elements can be observed, as well as the difference in the values of the pairing coefficient of electrons in the plasma formed by the laser pulse. The most important factor in these differences is the amount of the electronic sphere radius in the plasma and the energy of the laser pulse. These values distinguish between the components of the samples and detect forgery impurities in the quality of the ink material used in the documents, whether it is added to the original material, and this is due to the plasma performance and the basic parameters of the plasma. This work can study the performance of the laser produced plasma.

Conclusion

Through the results that were measured after examining the samples of writing ink, which were of different types and origins using LIBS technology, we conclude the following:

- The results showed the differences in the values of the pairing coefficient of electrons in the generated plasma due to the laser pulse and that it depends on the temperature and electronic density of the generated plasma.
- The main parameters of the plasma calculated in this work, which are electron temperature, electron density, were consistent with most of the internationally agreed results.
- The results showed that the amount of the pairing coefficient of electrons in the generated plasma is directly related to the radius of the electron sphere in the plasma.
- It has been shown in the work of the LIBS technique that it is effective and good in determining the presence of elements for writing ink materials without affecting or damaging the sample, as the emission spectrum of the elements of those samples was found and the relationship between wavelength and intensity for those elements was found.
- It turns out that the pulsed laser is an important tool in agitating and irritating materials to obtain plasma because of the objective results shown and compatible with most of the global results.
- The analytical results and the calculated and recorded values have shown that it is a good method in detecting and studying writing inks, which can be employed in the field of forensic evidence to detect forgery in documents and papers.
- The differences in the calculated values of the pairing coefficient of electrons in the plasma are useful in studying the performance of the plasma formed due to laser energy, and analyzing and studying the ionization and excitation processes of the material.

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