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Analysis Study of Plasma Parameters of Calcium Ion in Black Seed by Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract: ***This study was conducted to find out the effect of physical factors such as temperature and humidity on the black seed, based on folk medicine accounts that recommend chewing the black seed and moistening it with saliva. to take advantage of its nutritional properties [1]. Laser induesd breakdown spectroscopy technique were used to analyze black seed components that were exposed to heat and humidity to varying degrees and at different times and were purchased in the local market for the 2019 harvest. Using a laser (Nd: YAG) with a wavelength of 1064 nm with a pulse energy of 120 mJ, a width of 10 ns and a frequency of 10 Hz, the plasma used in the system was generated in a quasi-experimental method based on the idea that the plasma is homogeneous. Electron density and plasma temperature was calculated applying Saha-Boltzmann equation and Boltzmann plot method. The generated plasma was concentrated on the surface of the black seed powder and paste and the essential micronutrients were determined in the carbon black seeds.spectroscopic study was performed using calibration free LIBS procedure. The relative concentration for (Ca) in black seeds were obtained. The results showed that the black seed was not affected by humidity and temperature factors due to the stability of the presence of elements in it with the difference of the relative concentration of some elements. In black seed kernels , Ca is more, but Na is less. With different macronutrient ratio of potassium, iron, sulfur and sodium.***

Keywords: Nigella sativa, black seed, Black Cumin, Laser-induced breakdown spectroscopy (LIBS), Plasma

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) [8], a good analysis technique for non distructive testing (NDT), It has several advantages: high speed and can only be used for multi-component analysis. The main physical process that LIBS technology is the formation of high-temperature plasma, induced by a short laser pulse, focused on the sample's surface to ablate a tiny fraction of it into a plasma, a particular state of matter characterized by high temperature and strong ionization [4].

The minimal sample is required and the destruction of the sample is minimal and inexpensive and can be used in Wide range of materials with no pre-treatment or test preparation, Flexible.This technique is based on the generation of plasma that is induced on a sample by laser. When the laser pulse terminates, the plasma starts to cool. During the plasma cooling process, the electrons of the atoms and ions at the excited electronic states fall down into natural ground states, causing the plasma to emit light with discrete spectral peaks. The emitted light from the plasma is collected and coupled with an ICCD/spectrograph detector module for LIBS spectral analysis.Used to determine the original composition of a sample [2].it have used in Expansion to a wide range of applications, namely the processing of industrial materials, Analyze monuments and works of art and identify radioactive and hazardous materials, environmental [3].

2. Plasma Characterization

2.1 Measurement of Plasma Temperature

The temperature of the plasma is estimated by the relative emission intensities of the spectral lines. And using the theory of atomic structure and spectra [1], and the Boltzmann diagram [1, 12]. The separation of the wavelengths of the lines used must be very small to avoid corrections to the relative response of the detector and to increase the accuracy, a large number of spectral lines must be used to determine the temperature of the plasma relative to a given spectrum and the energy separation in the higher excited state should be as large as possible to get accurate results and that the lines are optically thin and therefore equation (1) gives the temperature of the plasma in the case of 'an LTE approximation [1, 2].

$$\ln\left(\frac{I_k \lambda_k}{g_k A_k}\right) = -\frac{E_k}{K_B T} + \ln\left(\frac{F}{p}\right) \quad (1)$$

Where I, λ, A, g are the spectral intensity, wavelength, transition probability and statistical weight of the upper state respectively.

E_k is the energy of the upper level; K_B is the Boltzmann constant, T is the temperature and b is a constant coefficient of all the ionic lines considered. In a few cases, g, f and Ek can be obtained from the Handbook of Spectral Constants, Chemistry and Physics.

From the diagram of the right logarithmic terms of equation (1) as a function of Eu, we obtain a straight line whose slope is equal to 1 / BcT. So we can get the temperature of the plasma from the slope of the straight lineα [1, 2].look figure 11.

$$T = \frac{1}{K_B \alpha} \quad (2)$$

2.2 Measurement of Electron Density

The electron density using atom and ion spectral lines emitted from the plasma is determined by employing the Saha–Boltzmann equation for the line intensities of the species in two consecutive charge states Z and Z + 1 of a particular element as [2.13]

$$N_e = 2\left(\frac{2\pi m_e k}{h^2}\right)^{\frac{3}{2}} T^{\frac{3}{2}} \left(\frac{I\lambda}{A_{ij} g_i}\right)_{atom} \left(\frac{A_{ij} g_i}{I\lambda}\right)_{ion} \quad (3)$$

3. Materials and Methods

3.1 Samples Preparation

Samples were purchased from seeds of N. sativa. From the local market, the 2019 harvest. The black seed is a small pill that contains fatty compounds surrounded by scales when exposed to direct plasma impulses that lead to burning it and not benefiting from the nutrients it contains [4].

To prepare the samples, 150 grams were taken and soaked in water to obtain different degrees of humidity (50 grams per sample 26.2%, 30%, 41.5% for the duration 5, 10, 15 minutes), use of a device (BENETECH GM 1363B - hygrometer and temperature) to measuer humidity and temperature [5].

It was crushed and squeezed to get its nutritional juice as an emulsifier, then was squeezed and squeezed with constant pressure of 400 kg / cm so that the oily substance and nutritional value does not come out, and also density of the material affects the LIBS signal. then was converted into a circular disc containing black and white dots.After that, the material was transferred to a furnace at a temperature of 100 degrees to see the effect of the temperature at different times 5, 10 and 15 degrees Celsius.

This process was repeated to prepare samples at different temperature of corresponding humidity and time.

3.2 The Experimental Setup

LIBS instrumentation:
An optical system was formed so that the external lights do not affect the plasma and obtain a light overlay.The setup of the LIBS experiment shown in Figure 1 consisted of:

*** Laser:**
neodymium-doped yttrium aluminum garnet (Nd:YAG) Laser with a wavelength of 1064 nm has pulse energy 120 mJ a pulse width of 10 nanoseconds and a frequency of 10 Hz was used.

*** Focusing, Collection and Spectrometer system:**
A LIBS 2000+ peripheral optical spectrometer equipped with a CCD detector, a bundle of optical fibers, a lens, a translation stage and a computer was used. The laser light is focused by a compact lens with a focal length of 10 cm and is located 5 cm from the surface of the sample [6]. The experiments were performed under normal air pressure and room temperature. Light is collected from the fine plasma by an optical fiber, which is positioned at an angle of 45 degrees to the laser beam. The other end of the optical fiber is connected to a LIBS 2000 + 0.1 nm spectrometer. Then the spectral signal is stored on a computer and analyzed with the ThorLabs.

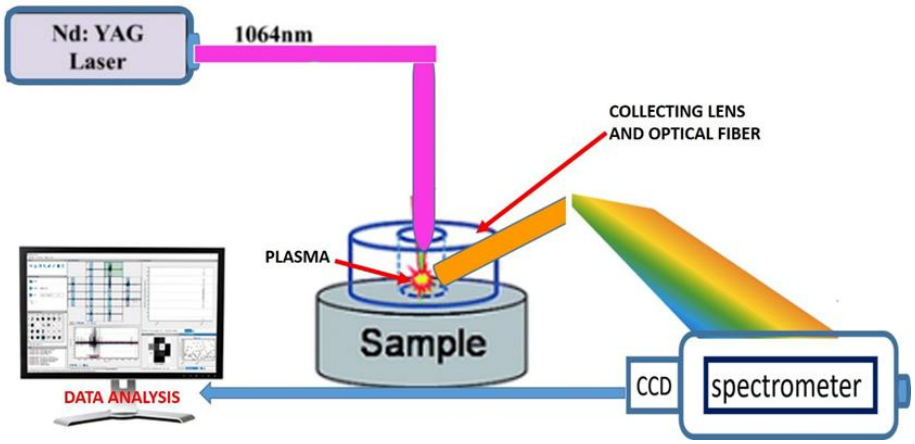

Figure 1: Experimental Setup of LIBS

3.3 The Experimental Procedure

After the samples were prepared using pressurized pellet technology and exposing them to the required humidity and temperature (sample preparation method above), the sample was transferred to the system after placing a name on each sample that was exposed to the laser beam from the plasma generator and it is one 5 cm away from it and the time of each pulse was 10 nanosec. At a frequency of 10 Hz, the pulse energy was 120 mJ, The detector was gated in synchronization with the laser pulse. then the data was collected and transferred to the computer through a USB

connection using an application from Thorlabs OSA. Then the steps mentioned above were repeated for other samples of different times to show what is happening in the sample [7, 9]. We have recorded the results in the following tables.

4. Results and Discussion

4.1 Spectral Analysis

The LIBS spectrum consists of spectral lines that provide information about the components of the sample. A typical laser-induced plasma spectrum was generated by 10 ns laser pulses focused at 1064 nm with an energy of 120 mJ, and the laser shots were assembled on an ICCD array.

The spectral range of the emission lines of calcium (Ca), iron (Fe), sulfur (S) and potassium (K) from 393 to 660 nm was shown using the black seed sample. In this spectral range it is possible to observe the emission of calcium ion lines (Ca II) at 393.49 nm and 396.97 nm, the lines of (Ca I) at 422.85 and 649.72 nm elements, as well as their spectral parameters are taken from the NIST - Database extracted [9, 11] are given in Table -1. The high density of calcium lines was observed in comparison to the remaining elements, which confirms the richness of the elements black seeds in this element, see Figures (1-9).

Table 1: Spectroscopic data used for the determination ofthe plasma temperature

NO	elements	Wavelength (nm)	Intensity (au)	Relative intensity	A_{ki} X 10^8 s	g	$E_u e.V$
1	Ca II	393.47	0.38401	1	1.35	4	3.15
2	Ca I	422.85	0.2744	0.549206413	2.2	3	2.9
3	K II	430.38	0.072216	0.166391129	0.013	5	20
4	S I	551.07	0.11842	0.35776435	0.73	2	15.8
5	Na II	445.58	0.12363	0.247443108	0.0281	4	3.8

Tables (2-9) show the results of different values of the effect of temperature and humidity on samples using libs spectroscopy. Figures (1-9) list the results of the search for the element included in the composition of the samples after the influence of temperature and humidity on them.

Table 1: The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 5 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.38401	Ca II
2	396.97	0.31483	Ca II
3	422.85	0.22164	Ca I
4	430.38	0.072216	K II
5	443.59	0.087064	Ca I
6	445.58	0.10361	Na II
7	504.35	0.067689	Si II
8	526.98	0.07969	Ca I
9	558.95	0.089439	Ca I
10	589.15	0.17838	Na I
11	612.46	0.08906	Ca I
12	616.49	0.11646	Ca I
13	644.22	0.077131	Ca I
14	646.56	0.068338	Ca I

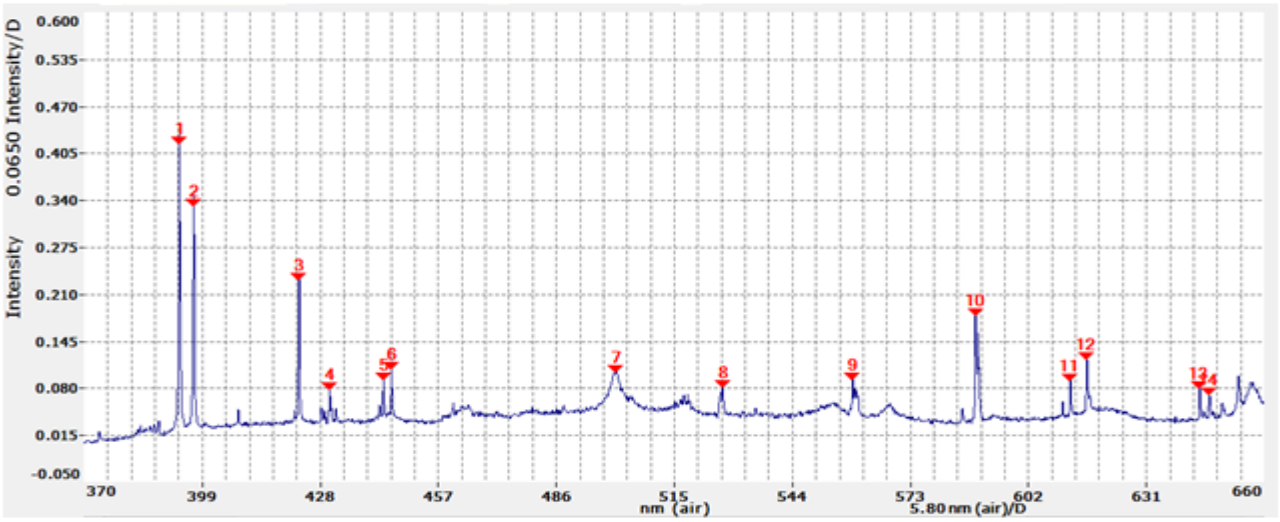

Figure 2: LIBS spectrum of sample (S1) at 26.2% -5min

Table 2: The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 10 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.5066	Ca II
2	396.97	0.40996	Ca II
3	422.86	0.27583	Ca I
4	445.58	0.17296	Na II
5	509.51	0.0955	K I
6	526.99	0.12954	Ca I
7	558.97	0.14502	Ca I
8	589.15	0.14287	Na I
9	616.5	0.18483	Ca I
10	644.22	0.11951	Ca I
11	646.56	0.068338	Ca I
12	649.73	0.098941	Ca I

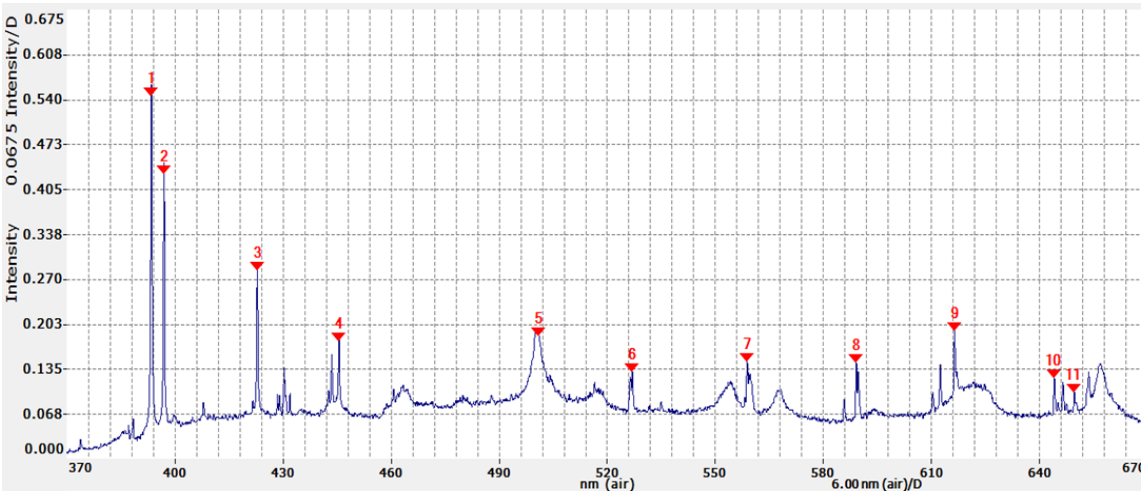

Figure 3: libs spectrum of sample (S1) at 26.2% -10min.

Table 3: The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 15 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.49	0.35004	Ca II
2	396.97	0.2772	Ca II
3	422.85	0.21531	Ca I
4	430.38	0.067612	K II
5	445.57	0.087933	Na II
6	526.99	0.068482	Ca I
7	589.14	0.11586	C II
8	612.47	0.068237	Ca I
9	616.5	0.089925	Ca I

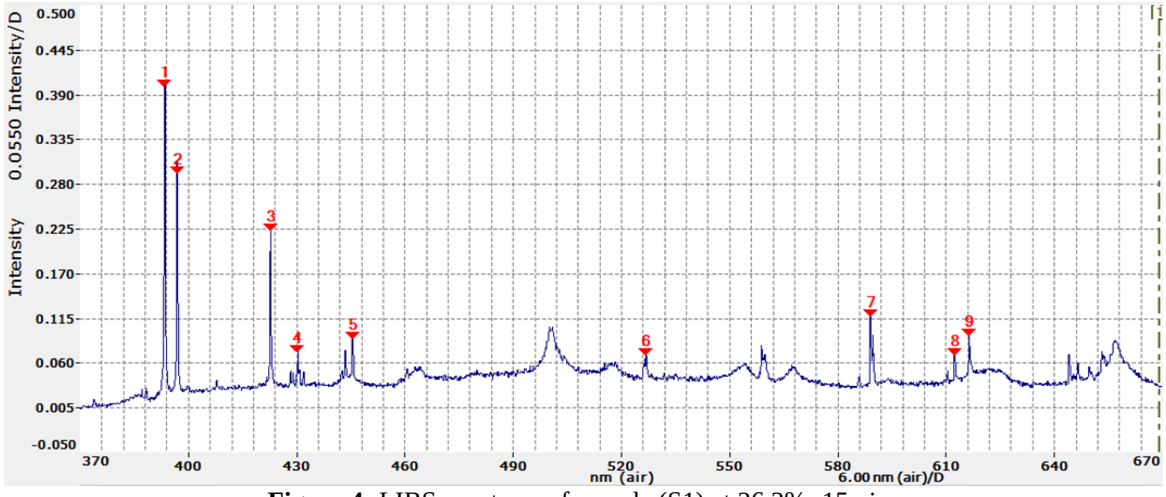

Figure 4: LIBS spectrum of sample (S1) at 26.2% -15min.

Table 4: The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 5 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.29089	Ca II
2	396.97	0.24071	Ca II
3	407.91	0.063125	Y I
4	422.85	0.15336	Ca I
5	431.92	0.051122	O II
6	443.59	0.092827	Ca I
7	445.58	0.10366	Na II
8	589.14	0.083702	C II
9	616.5	0.089925	Ca I
10	649.66	0.075544	Ca I

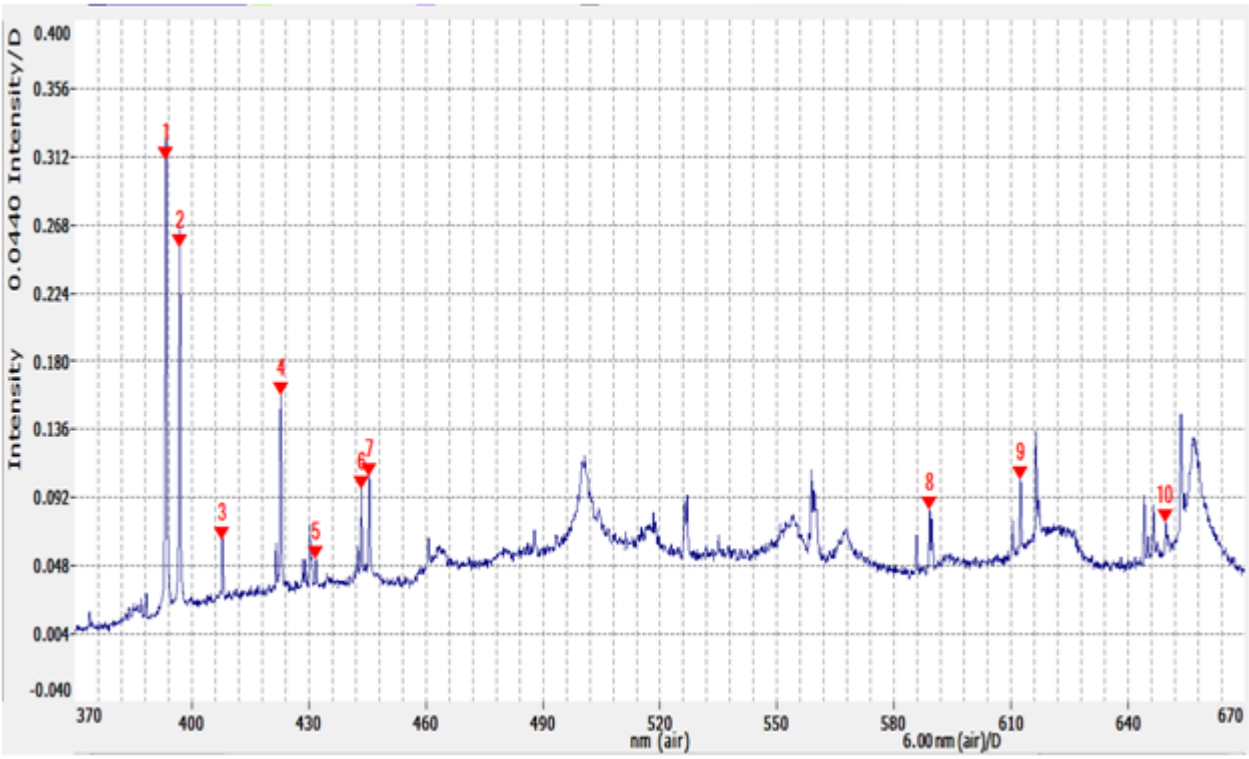

Figure 5: LIBS spectrum of sampled (S2).at 30% -5min

Table 5: The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 10 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.60566	Ca II
2	396.97	0.47882	Ca II
3	407.9	0.11122	Y I
4	422.84	0.28706	Ca I
5	430.38	0.12245	K II
6	506.69	0.10464	Ti I
7	526.99	0.11925	Ca I
8	558.96	0.13588	Ca I
9	589.15	0.16389	Na I
10	616.49	0.16176	Ca I

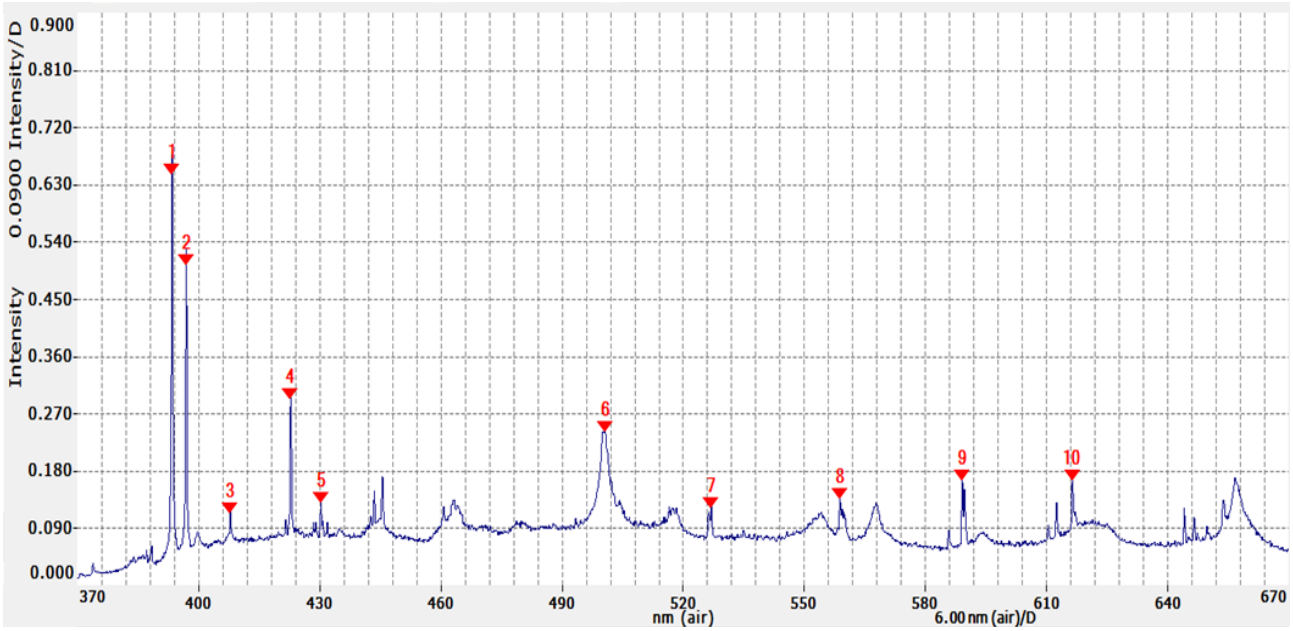

Figure 6: LIBS spectrum of sample (S2) at 30% -10 min.

Table 6: The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 15 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.49054	Ca II
2	396.97	0.39236	Ca II
3	422.85	0.25232	Ca I
4	428.43	0.080626	Ti I
5	445.58	0.15521	Na II
6	527	0.11528	Ca I
7	558.96	0.13102	Ca I
8	589.14	0.11677	C II
9	612.46	0.13328	Ca I
10	646.56	0.10228	Ca I

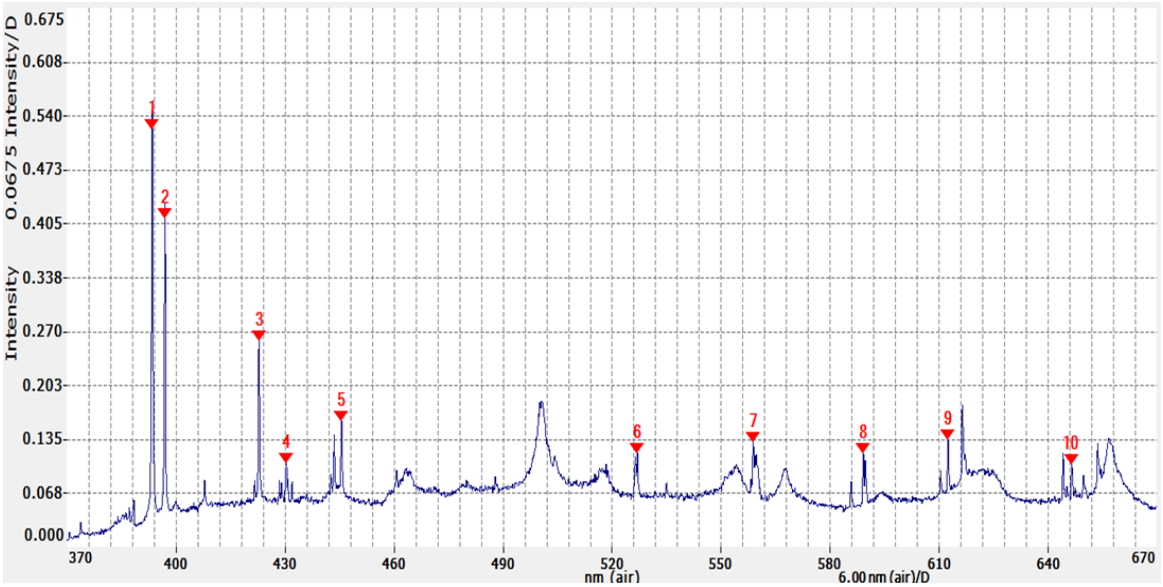

Figure 7: LIBS spectrum of sample (S2) at 30% -15min.

Table 7: The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 5 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.49963	Ca II
2	396.97	0.39214	Ca II
3	422.85	0.2744	Ca I
4	430.37	0.091486	K II

5	443.59	0.10747	Ca I
6	445.58	0.12363	Na II
7	460.73	0.083134	K II
8	504.23	0.086495	Si II
9	527	0.093873	Ca I
10	558.96	0.11604	Ca I
11	612.47	0.11655	Ca I
12	616.49	0.15655	Ca I
13	644.22	0.10019	Ca I

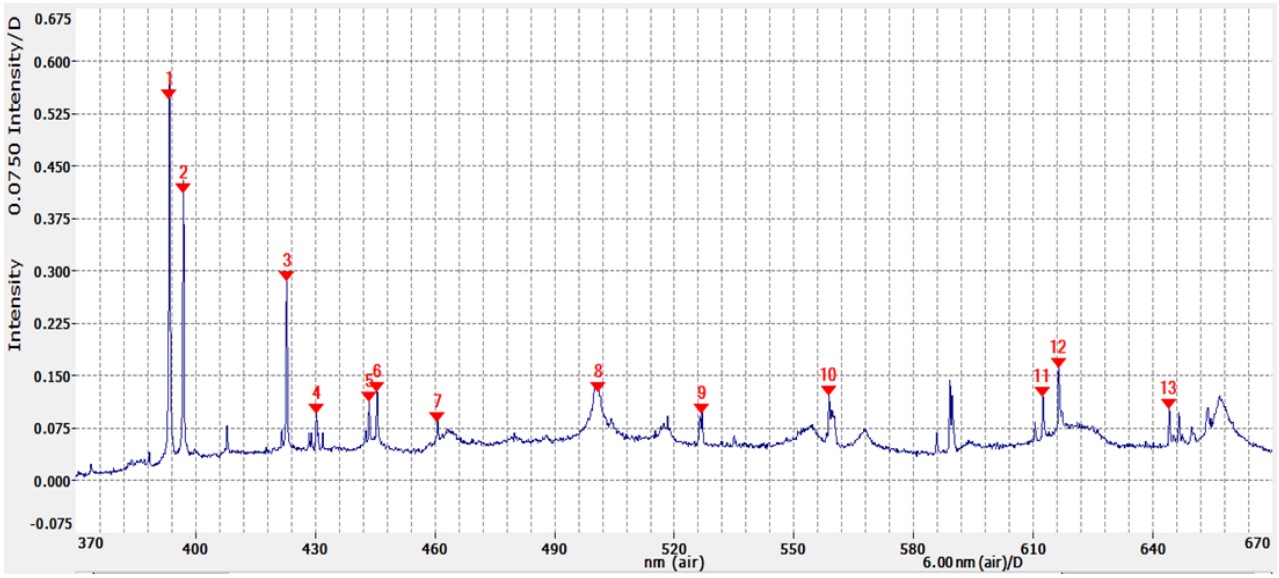

Figure 8: LIBS spectrum of sample (S2) at 41.5% -5 min.

Table 8: The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 10 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.79453	Ca II
2	396.97	0.66147	Ca II
3	422.85	0.38067	Ca I
4	516.51	0.16207	Fe I
5	527	0.16851	Ca I
6	558.98	0.18764	Ca I
7	589.16	0.16048	C II
8	646.56	0.14739	Ca I
9	649.68	0.13275	Ca I

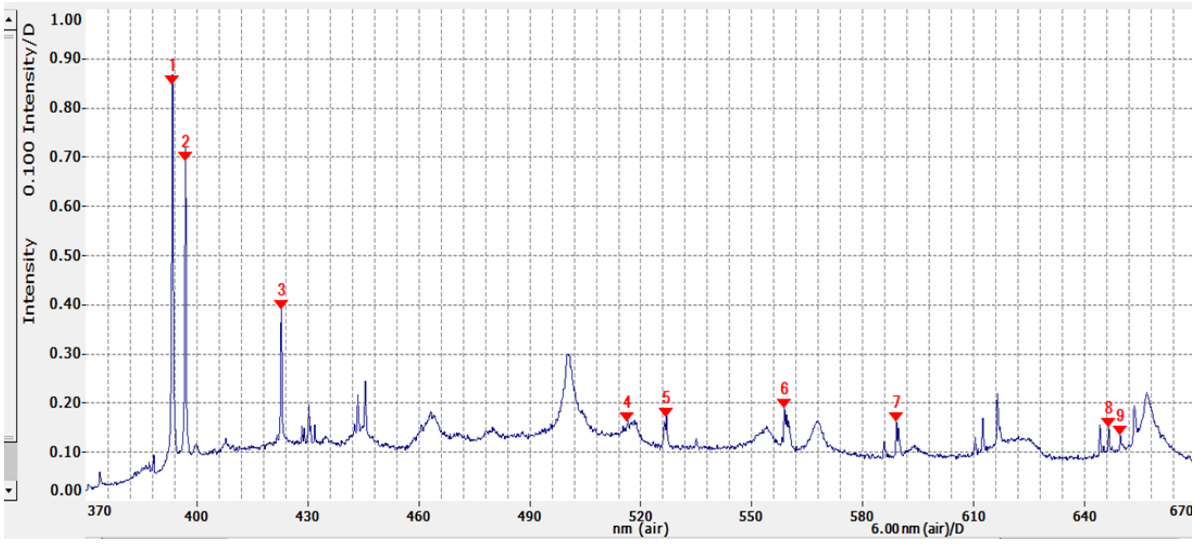

Figure 9: LIBS spectrum of sample (S2) at 41.5% -10 min.

Table 9: The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 15 minut			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.49	0.331	Ca II
2	396.97	0.26837	CaII
3	422.85	0.22024	Ca I
4	551.07	0.11842	S II
5	589.15	0.17469	Na I
6	649.72	0.11144	Ca I

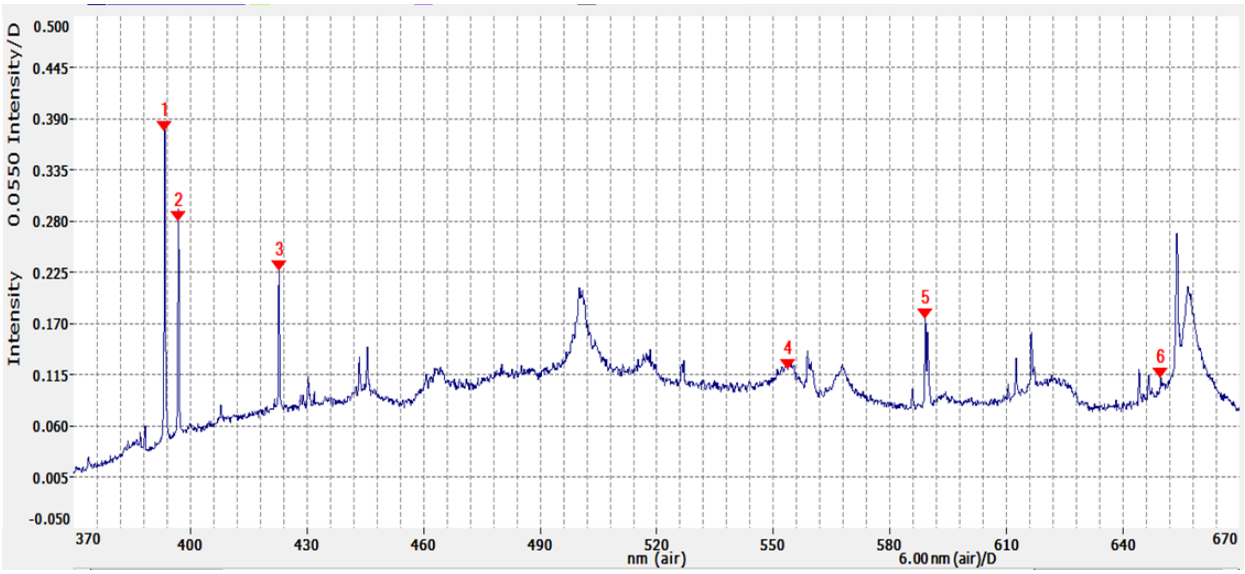

Figure 10: LIBS spectrum of sample (S2) at 41.5% -15min.

The emission spectra of the respective elements were obtained as complete as in Figures 2-10. Seven major micronutrients were found in the three types of black seed samples (mainly Ca, Na, Fe, Si, Ti, S and K).

4.2 Selection of the spectral line

To determine the temperature of the plasma and the electron density, the chosen spectral line must be isolated from the spectra and have a good profile. Because these parameters depend on the integrated density of the spectral lines. By analyzing temperature, electron density, and concentration, spectral data was taken from the NIST (National Institute of Standards and Technology) (Atomic Spectra Database) (http: http://www.nist.gov/srd/index.htm.). Neutral and simple ionization ions are the main source of finite element lines.

4.3 Boltzmann Plasma Method Plasma Temperature (T)

If the plasma is in LTE, then the population density of the atomic and ionic states will be described by the Boltzmann distribution. By measuring the relative intensity of the line, it is possible to estimate the temperature of the electron across the slope of a straight line in the Boltzmann diagram. Plasma temperature was calculated according to the equation (1, 2) (Andrzej et al., 2006).

Table 10: The electron density calculated using Saha-Boltzmann equation for the samples

Element	Plasma temperature (K)	Electron density (/cm3)
Ca I	3354.2	2.34 x10^{18}
Ca II	2655.4	2.91 x10^{18}

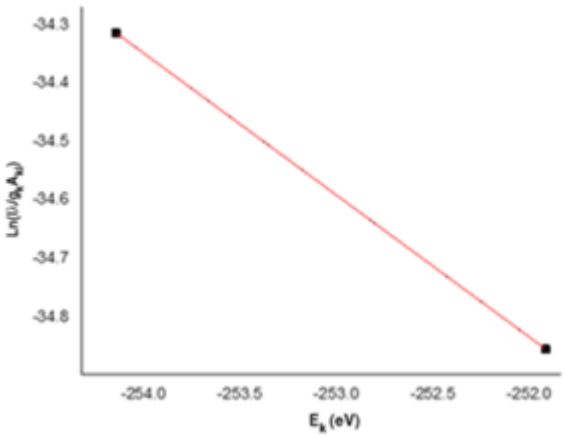

Figure 11: Boltzmann plot made using two Cu I lines, considering the intensities

5. Conclusions

LIBS technology has been applied to black seeds to identify specific micronutrients. Major, minor and trace elements (Ca, Na, Fe, Si, Ti, S and K).were identified and counted. A procedure based on the Saha-Boltzmann multi-element diagram was used, allowing the temperature and electron density to be determined. Based on our study, the concentration of calcium in black seeds is very high. On the contrary, it contains less sodium. The other micronutrients are almost the same in all types. Due to the high concentration of calcium in the black seed, the black seed has better nutritional content in terms of the presence of

calcium.LIBS technology is seen to be a fast and attractive tool to identify micro-nutrients in cereal crops.

Through the results of the observation and discussion, we found that the black seed was not significantly affected by the humidity and temperature factor, as it can thus be preserved in different storage conditions and makes it not affected by the climatic conditions.

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