

Elemental Composition of the Soils using LIBS Laser Induced Breakdown Spectroscopy

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Abstract

Laser induced breakdown spectroscopy (LIBS) technique has been used for the elemental composition of the soils. In this technique, a high energy laser pulse is focused on a sample to produce plasma. From the spectroscopic analysis of such plasma plume, we have determined the different elements present in the soil. This technique is effective and rapid for the qualitative and quantitative analysis of all type of samples. In this work a Q-switched Nd: YAG laser operating with its fundamental mode (1064 nm laser wavelength), 5 nanosecond pulse width, and 10 Hz repetition rate was focused on soil samples using 10 cm quartz lens. The emission spectra of soil consist of Iron (Fe), Calcium (Ca), Titanium (Ti), Silicon (Si), Aluminum (Al), Magnesium (Mg), Manganese (Mn), Potassium (K), Nickel (Ni), Chromium (Cr), Copper (Cu), Mercury (Hg), Barium (Ba), Vanadium (V), Lead (Pb), Nitrogen (N), Scandium (Sc), Hydrogen (H), Strontium (Sr), and Lithium (Li) with different finger-prints of the transition lines. The maximum intensity of the transition lines was observed close to the surface of the sample and it was decreased along the axial direction of the plasma expansion due to the thermalization and the recombination process. We have also determined the plasma parameters such as electron temperature and the electron number density of the plasma using Boltzmann's plot method as well as the Stark broadening of the transition lines respectively. The electron temperature is estimated at 14611 °K, whereas the electron number density i.e. $4.1 \times 10^{16} \text{ cm}^{-3}$ lies close to the surface.

Keywords:

Electron number density; Electron temperature; LIBS; Plasma plume; Spectroscopy;

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a fast and reliable analytical technique. In the past few years, significant advances have been made in the area of LIBS applications to the detection of the heavy and toxic elements present in the food, soil samples affecting humans and animal health. In this work, we have tried to provide comprehensive knowledge and data about the different percentages of the elements present in the soil of Sindh province in Pakistan. In this method, a high-intensity laser pulse from a Q-switched Nd: YAG laser is focused to target sample for the ablation of the sample in the form of the plasma plume [1][2][3].

In the literature, much of the experimental and the theoretical work is reported for this technique [7][8][11][32][38]. This technique (LIBS) exhibits very attractive features and become the most reliable, fast and eco-friendly in the field of materials analysis, process control, environmental monitoring, life sciences and has the capacity of multi-elemental detection, rapid response, very little or no sample preparation, high spectral resolution and high sensitivity [18][25][26][27][30]. Meanwhile, many experimental studies are reported in the literature about the characteristics of the soil plasma. Bublitz et. al. [16] presented the spectroscopic study of soil diagnostics. Sarah et. al. [40] has discussed the characteristics and forensic analysis of the soil sample. Hussain et. al. [43] measured the nutrients in greenhouse soils using Nd: YAG laser. Martin et. al. [36] determined the total carbon and nitrogen in the soil. Bustamante et. al. [24] used Laser induced breakdown spectroscopy for characterization of Ca in a soil depth profile. Xia-Fen Li et. al. [23] determined the temperature and electron number density of soil plasma generated by laser ablation fast pulse discharge plasma spectroscopy (LA-FPDPS) [39][45]. Ciucci et. al. [9] has developed the calibration-free laser-induced breakdown spectroscopy and argued that the plasma temperature and electron number density are the two main parameters for plasma characterization based on the measured plasma temperature and electron number density. Akhtar et. al. [22] has analyzed the elements of Pb and Cu in soil sample using laser-induced breakdown spectroscopy under an external magnetic field. Cao et. al. [10] used pulse laser ablation (PLA) to observe the big second-order non-linear optical response from sapphire substrates deposited ZnO thin films. Sheikh et. al. [34] studied spectroscopic studies of Zn plasma produced in the air through 1064, 532 and 355 nm Q-switched Nd: YAG laser. Saji et. al. [20] studied optical emission spectroscopy of ZnO sample using 355 nm laser from Nd: YAG laser [4][12][14][28][29][37]. In present work, Laser induced breakdown spectroscopic technique has been utilized for soil samples collected from the right bank of river Indus of Sindh province of Pakistan. From the spectroscopic analysis of the transition lines, we have found different toxic and nutritious elements present in the soil. We have also estimated the plasma parameters from the recorded emission spectrum.

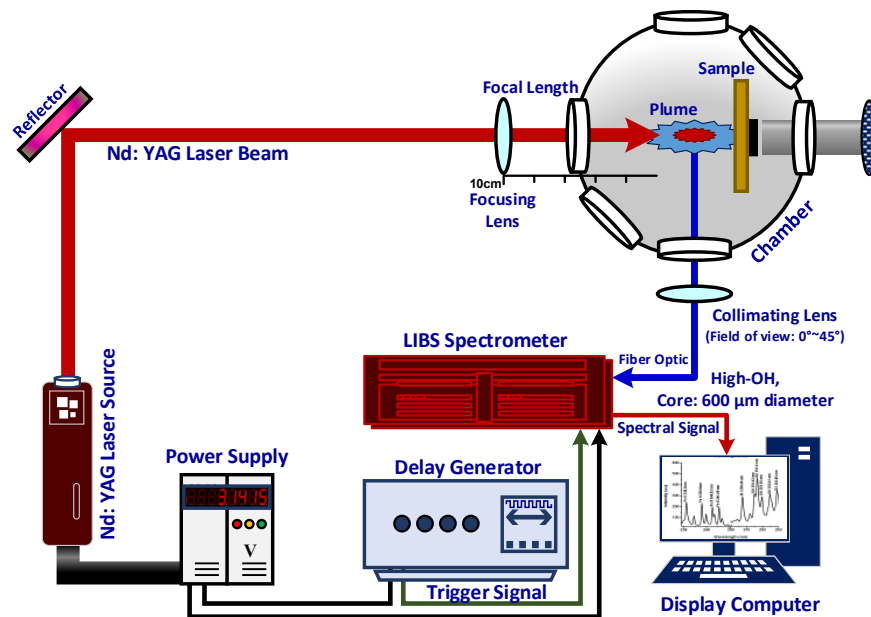


Fig.1. The experimental arrangement of LIBS (Laser Induced Breakdown Spectroscopy) method [20].

2. Sample Preparation

The soil samples were collected from the right bank of river Indus at the three and six inches depth from the wheat cropped field. The soil sample was dried at 100°C up to one hour in the microwave oven.

The samples were then grinded and powdered using Retsch Mortar Grinder RM-200. Then next it was filtered to obtain the required size using Sieving Machine Retsch AS-400. Then 10 gram sample mix with 3 gram wax using Swing mill HK-40.

Then 3 gram of the whole mixed sample was wasted. The net 10 grams were taken for the pallet preparation using Electro-hydraulic press PE-EL. The 10 gram pallets of the sample were hence prepared for LIBS analysis.

3. Experimental Setup

The experimentation bench of Laser induced breakdown spectroscopy (LIBS) was set as shown in Fig.1. This experimental arrangement was adapted from Ref. [20]. For the ablation of the sample, we have used a high power Q -switched Nd: YAG laser pulse operating with 400 mJ at fundamental mode with a pulse duration of 5 ns and repetition rate of 10 Hz.

The laser energy was measured with the energy meter (Nova - Quantel, France). A reflecting glass is used for reflecting the laser beam and a focusing quartz lens of 10 cm focal lengths is used to focus the laser beam on the target material.

The estimated area of the laser spot on the target was approximately $\approx 3.0 \times 10^{-4} \text{ cm}^2$. The target was mounted on the sample stage, which was rotated to provide a fresh surface after each laser pulse to avoid deep crater. The distance between the focusing lens and the sample was less than the focal length of the lens, this prevented any breakdown of the ambient gas (air) in front of the target.

The emission from the plasma plume was collected through an optical fiber (High-OH, Core diameter: 600 μm) with a collimating lens ($0^{\circ}\sim 45^{\circ}$ field of view) placed at a right angle to the laser producing plume. The LIBS2000 detection system is equipped with five spectrometers each having slit width of 5 μm , covering the range between 200 nm ~ 700 nm.

Each spectrometer has a 2048 element linear CCD array and an optical resolution of $\approx 0.1 \text{ nm}$. The LIBS2000 detection system and the Q -switch of the Nd: YAG laser were synchronized. The LIBS2000 system triggered the Q -switch of the Nd: YAG laser and the flash lamp out of the Nd: YAG laser triggered the LIBS2000 detection system through a four-channel digital delay/Pulse generator (SRS DG 535).

The pulse energy of the Nd: YAG laser was varied through the OOI-LIBS software [13]. The output data were averaged for 10 laser shots. The data acquired simultaneously by all the five spectrometers were stored on a PC through the OOI-LIBS software for subsequent analysis.

Table-1. Trace elements found in Soil Sample with various wavelength(s) and concentrations. These include Iron (*Fe*), Calcium (*Ca*), Titanium (*Ti*), Silicon (*Si*), Aluminum (*Al*), Magnesium (*Mg*), Manganese (*Mn*), Potassium (*K*), Nickel (*Ni*), Chromium (*Cr*), Copper (*Cu*), Mercury (*Hg*), Barium (*Ba*), Vanadium (*V*), Lead (*Pb*), Nitrogen (*N*), Scandium (*Sc*), Hydrogen (*H*), Strontium (*Sr*), and Lithium (*Li*).

| Elements | 1 | | | | | 2 | | | | | |
|-----------------|--------------------|--------|--------|--------|---------|-----------------------|--------|--------|--------|--------|--------|
| | Iron (<i>Fe</i>) | | | | | Calcium (<i>Ca</i>) | | | | | |
| Wavelength (nm) | 1. | 238.24 | 274.90 | 406.53 | 492.21 | 502.50 | 315.8 | 397.25 | 443.49 | 558.87 | 616.90 |
| | 2. | 239.61 | 324.95 | 407.37 | 495.95 | 519.27 | 317.9 | 422.67 | 445.59 | 559.44 | 643.90 |
| | 3. | 240.52 | 358.12 | 413.44 | 498.44 | 522.74 | 335.02 | 428.30 | 518.88 | 559.84 | 645.56 |
| | 4. | 241.09 | 386.59 | 414.60 | 499.05 | 523.29 | 364.44 | 429.90 | 526.17 | 560.12 | 646.25 |
| | 5. | 258.64 | 373.71 | 421.75 | 500.18 | 537.14 | 370.60 | 430.25 | 526.42 | 585.74 | 647.16 |
| | 6. | 259.90 | 374.94 | 438.53 | 501.006 | 538.38 | 373.69 | 430.77 | 527.03 | 610.27 | 649.96 |
| | 7. | 260.70 | 376.05 | 487.82 | 501.64 | 540.57 | 393.36 | 431.86 | 534.9 | 612.22 | 714.82 |
| | 8. | 261.18 | 404.58 | 489.37 | 502.22 | -- | 396.84 | 442.54 | 558.19 | 616.12 | -- |

| Elements | 3 | | 4 | | 5 | | 6 | | 7 | 8 | |
|-----------------|------------------------|--------|-----------------------|--------|------------------------|--------|-------------------------|--------|-------------------------|------------------------|--------|
| | Titanium (<i>Ti</i>) | | Silicon (<i>Si</i>) | | Aluminum (<i>Al</i>) | | Magnesium (<i>Mg</i>) | | Manganese (<i>Mn</i>) | Potassium (<i>K</i>) | |
| Wavelength (nm) | 1. | 323.45 | 334.27 | 250.49 | 252.82 | 256.79 | 364.92 | 279.01 | 285.21 | 274.02 | 344.05 |
| | 2. | 323.71 | 336.24 | 251.43 | 252.85 | 257.50 | 358.70 | 279.55 | 516.73 | 274.73 | 372.13 |
| | 3. | 324.05 | 337.35 | 251.61 | 263.12 | 308.21 | 394.40 | 279.77 | 517.26 | 403.28 | 399.18 |
| | 4. | 326.26 | 338.46 | 251.92 | 288.15 | 309.27 | 396.15 | 280.27 | 518.36 | 407.99 | 400.12 |
| | 5. | 332.46 | 521.03 | 252.41 | 319.22 | -- | -- | -- | -- | -- | 532.36 |

| Elements | 9 | | 10 | | 11 | | 12 | | 13 | | |
|-----------------|----------------------|--------|------------------------|--------|----------------------|--------|-----------------------|--------|----------------------|--------|--------|
| | Nickel (<i>Ni</i>) | | Chromium (<i>Cr</i>) | | Copper (<i>Cu</i>) | | Mercury (<i>Hg</i>) | | Barium (<i>Ba</i>) | | |
| Wavelength (nm) | 1. | 357.18 | 361.93 | 425.43 | 428.93 | 324.75 | 327.30 | 398.39 | 614.10 | 553.32 | 440.68 |
| | 2. | 361.04 | 490.44 | 427.48 | -- | 325.22 | -- | 542.52 | -- | 493.40 | -- |

| Elements | 14 | | 15 | | 16 | | 17 | 18 | 19 | 20 | |
|-----------------|-----------------------|--------|--------------------|--------|-----------------------|--------|------------------------|-----------------------|-------------------------|-----------------------|----|
| | Vanadium (<i>V</i>) | | Lead (<i>Pb</i>) | | Nitrogen (<i>N</i>) | | Scandium (<i>Sc</i>) | Hydrogen (<i>H</i>) | Strontium (<i>Sr</i>) | Lithium (<i>Li</i>) | |
| Wavelength (nm) | 1. | 275.63 | 277.85 | 363.95 | 261.43 | 588.99 | 589.59 | 316.09 | 656.42 | 421.42 | -- |

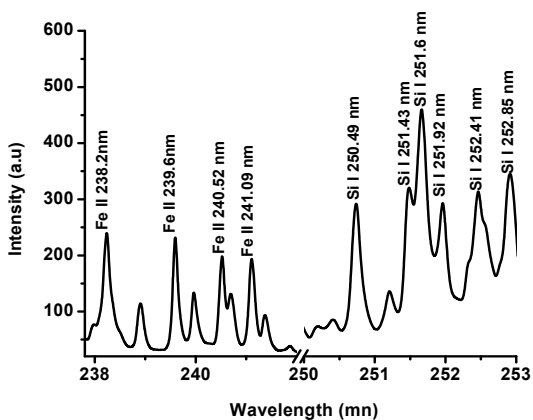


Fig.2 (a): Spectra in the range of 238 nm to 253 nm of Soil sample.

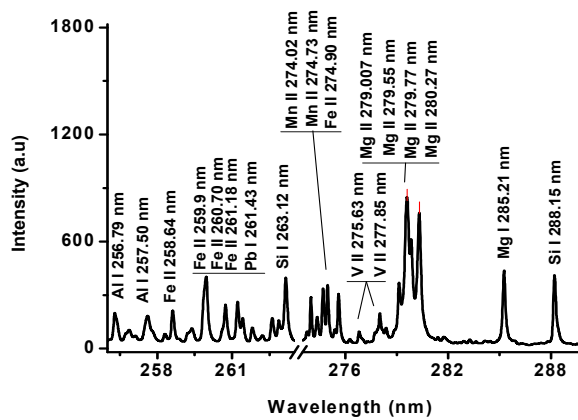


Fig.2 (b): Spectra in the range of 255 nm to 288 nm of Soil sample.

Table-2. Spectroscopic parameters used to calculate electron temperature.

| Wavelength λ (nm) | Statistical Weight | | Transition Probability A_{ij} (s^{-1}) | Upper Level Energy E_k (cm^{-1}) |
|------------------------------|--------------------|-------|---|---|
| | g_k | g_i | | |
| 335.02 | 3 | 5 | 8.90×10^7 | 45050.42 |
| 393.50 | 2 | 4 | 5.88×10^8 | 25414.40 |
| 534.94 | 5 | 5 | 1.08×10^8 | 362893.47 |
| 559.84 | 3 | 5 | 3.30×10^8 | 40719.84 |
| 616.12 | 5 | 5 | 1.60×10^7 | 36575.119 |

4. Results and Discussion

4.1 The Atomic Emission Spectrum of Soil Plasma

In the first set of experiment, we have focused on the elemental composition of the different elements present in the soil. For this purpose, we used the fundamental mode of a Q-switched Nd: YAG laser, having the laser irradiance of $4.5 \times 10^{10} W/cm^2$ was focused on the soil sample placed in air.

The emission spectrum from plasma plume was registered on the PC through OOI-LIBS software. The total range of the spectrum varies from 200~720 nm. The emission spectrum contains Iron (Fe), Calcium (Ca), Titanium (Ti), Silicon (Si), Aluminum (Al), Magnesium (Mg), Manganese (Mn), Potassium (K), Nickel (Ni), Chromium (Cr), Copper (Cu), Mercury (Hg), Barium (Ba), Vanadium (V), Lead (Pb), Nitrogen (N), Scandium (Sc), Hydrogen (H), Strontium (Sr), and Lithium (Li) as shown in Table-1.

A portion of the spectrum from 200~290 nm is shown in Fig.2 (a) and Fig.2 (b). It was observed that the intensity of the Iron and Calcium is dominant as compared to the other elements (Vanadium, Scandium, Hydrogen, Lead, Nitrogen and Strontium) present in the soil.

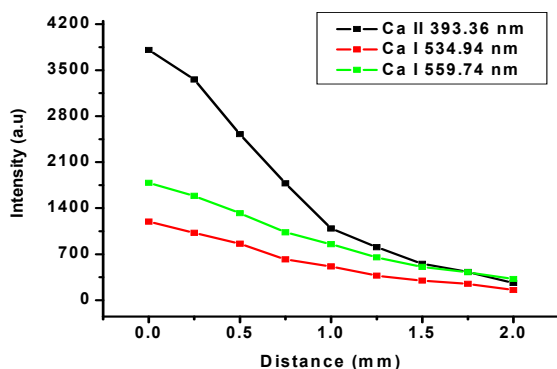


Fig.3. Spatial variation in the signal intensities of Ca-II 393.36 nm, Ca-I 534.94 nm and Ca-I 559.74 nm lines as function of distance (0~2 mm) from soil target surface.

The intensity of the transition line is associated with the population of such exciting level and it is also temperature-dependent of the plasma. The intensity variation of spectral lines is expressed by a relation via Eq. (1) as given below [20][33][34][35].

$$I_{ij} = \frac{h\nu}{4\pi} N_i g_i A_{ij} \quad \dots (1)$$

In the above equation, I_{ij} shows the intensity, N_i shows the number density, g_i denotes statistical weight, A_{ij} shows the transition probability and i and j shows the lower level and upper level respectively.

To study the hydrodynamic nature of the plasma plume expansion, we have recorded the spectrums at different positions along the axial direction of the plasma. The spatial variation of few of the transition lines of Ca-II 393.36 nm, Ca-I 534.94 nm and Ca-I 559.74 nm are shown in Fig.3.

It is shown that close to the surface of the sample at around 0 mm, the intensity of the transition lines are strongest while becoming weakest at a distance of 2 mm from the surface of the sample. This variation has indicated the thermalization and the recombination process of the plasma during its expansion along the axial direction.

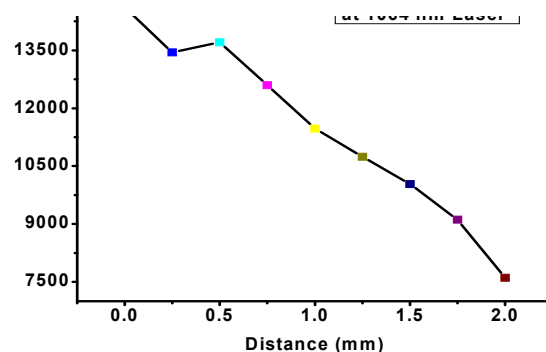


Fig.4. Electron temperature variation of soil plasma along with axial distance (0~2 mm).

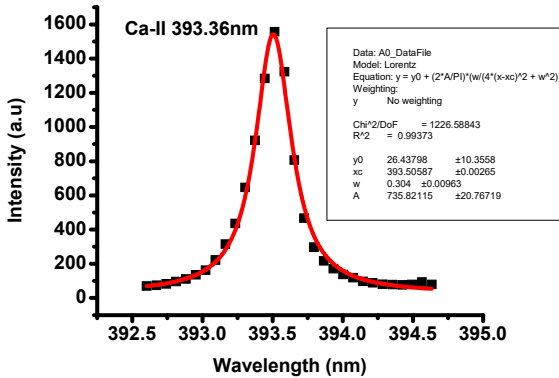


Fig.5. Optical transition line of *Ca-II* 393.36 *nm* the solid line represents the Lorentzian fit whereas dots show actual data.

4.2 The Electron Temperature

Electron temperature is one of the very important parameters for the laser-produced plasma. In this work, the Boltzmann plot method is used to determine the electron temperature from the selected Calcium neutral transition lines. Boltzmann plot method adapted from [31] is given below by Eq. (2).

$$\ln\left(\frac{\lambda_{ki} I_{ki}}{A_{ki} g_k}\right) = \ln\left(\frac{N}{Z}\right) - \left(\frac{E_k}{KT_e}\right) \quad \dots (2)$$

Where, λ_{ki} is the wavelength of the emission transition line, I_{ki} is the intensity of the emission transition line, A_{ki} is the transition probability, g_k is the statistical weight of the upper level, N is the upper-level population, Z is the partition function, E_k is the excitation energy, K is the Boltzmann constant and T_e is the electron temperature. To calculate electron temperature T_e selected neutral Calcium lines 335.02 *nm*, 534.94 *nm*, 585.74 *nm* and 616.12 *nm* respectively, the details of these transition lines are given in Table-2.

A plot of $\ln\left(\frac{\lambda_{ki} I_{ki}}{A_{ki} g_k}\right)$ versus upper-level energy yield a straight line having the slope $-1/KT_e$. The electron temperature is estimated from the slope. In the present experiment electron temperature T_e is estimated as 14611 °K close to the plasma plume (0 *mm*) and 7607 °K at (2 *mm*) away from plasma plume. The overall variation of electron temperature is a decreasing pattern as shown in Fig.4.

4.3 The Electron Number Density

The emission spectrum reveals noticeable line broadening due to the phenomenon of the ‘‘Doppler Effect’’ and ‘‘Stark Effect’’ etc. In the laser-produced plasma under the assumption of the local thermodynamic equilibrium (LTE), the Stark line broadening is the primary mechanism influencing these emission spectra [15][19][41][42].

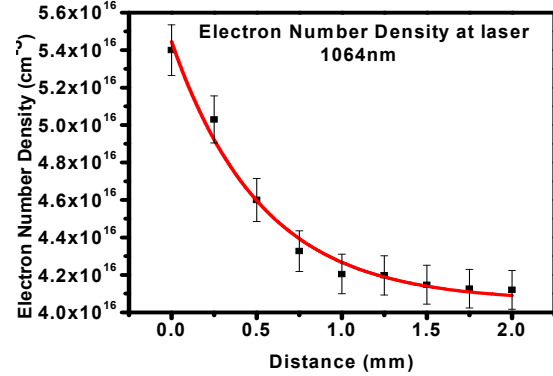


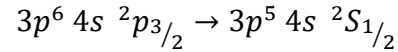
Fig.6. Electron number density variation of soil plasma along with axial distance (0~2 *mm*).

The electron number density, related to the Full-Width Half Maximum (FWHM) of the Stark broadened lines is given by an expression [6][17].

$$\Delta\lambda_{1/2} = 2\omega\left(\frac{N_e}{10^{16}}\right) \quad \dots (3)$$

Whereas $\lambda_{1/2}$ is FWHM, ω is the impact parameter which can be determined from the literature [5][21][44], N_e is the electron number density.

To get the FWHM of the Stark broadened lines, we have fitted the Lorentzian fit on the singly ionized Calcium line at 393.36 *nm* is identified as follows and shown in Fig.5.



The calculated value of the electron number density close to the surface approximately at 0 *mm* distance is about $5.5 \times 10^{16} \text{ cm}^{-3}$ and it decreases up to $4.1 \times 10^{16} \text{ cm}^{-3}$ at 2 *mm* distance along the axial direction. The decreasing variation of electron number density is due to multiple reasons such as the recombination of plasma etc. The variation of electron number density along with distance is shown in Fig.6.

5. Conclusion

We have studied the elemental characterization of the laser-produced plasma of the soil samples taken from nearby to the Indus River Sindh Pakistan. We have determined Iron (*Fe*), Calcium (*Ca*), Titanium (*Ti*), Silicon (*Si*), Aluminum (*Al*), Magnesium (*Mg*), Manganese (*Mn*), Potassium (*K*), Nickel (*Ni*), Chromium (*Cr*), Copper (*Cu*), Mercury (*Hg*), Barium (*Ba*), Vanadium (*V*), Lead (*Pb*), Nitrogen (*N*), Scandium (*Sc*), Hydrogen (*H*), Strontium (*Sr*), and Lithium (*Li*) elements present in the soil. The concentration of the Iron and Calcium is maximum as compared to the other elements.

We have also observed some heavy elements in the soil. The intensity of transition lines is higher close to the target surface and becomes weaker as the detector moves away from the target surface.

Meanwhile, we have also determined the plasma parameters such as electron temperature and the electron number density using the Boltzmann plot method and the Stark broadening of the transition lines respectively. The electron temperature varies from 14611°K to 7607°K at a different axial distance from 0 mm to 2 mm from target sample, whereas the electron number density varies from $5.5 \times 10^{16} \text{ cm}^{-3}$ to $4.1 \times 10^{16} \text{ cm}^{-3}$ at the distance of about range 0 mm to 2 mm away from the target surface.

The maximum value of electron number density is close to the target surface at 0 mm and follows decreasing when plasma getting expansion from away the target surface. The intensity, as well as the shift in transition lines decreases due to plasma recombination.

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