ELEMENTAL MAPPING OF FRUIT PEEL SAMPLES USING LASER ABLATION

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has emerged as a potent device for studying the interaction of laser beams with materials and has gained significant interest in recent years. This technique allows for fast and contactless analysis of almost any type of material, making it highly versatile and adaptable to diverse analytical problems. Fruits are one of the most commonly produced agricultural products, resulting high level of waste from the juice processing industry. The outer layer of the fruit peel is used in a variety of commercial applications such as food, soft drinks, candy flavors, and as a biomass energy source and adsorbent material. In this study, we observed Carbon (C), Iron (Fe), Magnesium (Mg), Vanadium (V), Calcium (Ca) and Lead (Pb) as trace elements in all samples. We analyzed the data of some emission lines such as C-I (193.09 nm), Mg-II (279.55 nm), Fe-II (229.28 nm), and Mg-II (280.27 nm). Additionally, we have determined the density of electrons in the orange peel sample which is varied from 4.45×10^{17} cm^{-3} to 5.90×10^{17} cm^{-3} with an energy variant from 80 mJ to 190 mJ. However, it is well-known that the value of electron number density (N_e) in the surrounding area of the target sample was at a minimum and increased with increasing energy. We estimated the weight percentage of each element present in the orange sample peel using the CF-LIBS method and found that iron (Fe) has the highest concentration.

Keywords: Laser-induced breakdown spectroscopy (LIBS), analytical problems, CF-LIBS method

1. INTRODUCTION:

Laser-induced breakdown spectroscopy (LIBS) is a robust and advantageous analytical method that can be used to determine the elemental composition of various types of samples, including all three states of matter [1]. This technique operates effectively at atmospheric pressure, making it a convenient choice for many applications [2]. In 1962, Brench and Cross were the first to suggest the concept of laser-induced breakdown spectroscopy (LIBS), as shown in Figure 1 [3]. –Laser-induced breakdown spectroscopy (LIBS) did not gain widespread usage until the 1980s, due to limited awareness and inferior performance compared to other analytical techniques at that time [4]. However, the development of high-power lasers improvements in detector technology, and reduced cost have significantly increased its application in recent years [5].

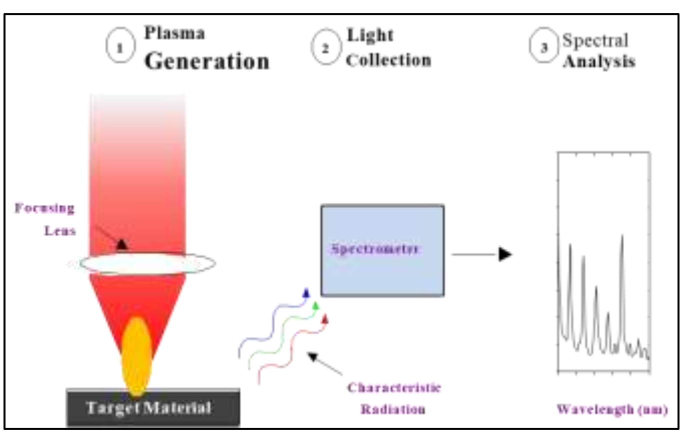


Figure 1. Indication of Laser induced breakdown spectroscopy (LIBS) method.

This laser pulse generates a plasma plume, which consists of a highly excited mixture of ions, atoms, and electrons, on the surface of the sample [6]. The emitted light from the plasma is then collected and analyzed to determine the elemental composition of the sample [7]. The plasma emits characteristic spectral lines that correspond to the elemental composition of the sample [8]. These spectral lines can be detected and analyzed to identify the elements present in the sample (as shown in figure 1) [9].

This study aims to investigate the potential of Laser Induced Breakdown Spectroscopy (LIBS) for the analysis of Citrus fruit peel powder samples, with a specific focus on determining the concentration of elements present in the samples [10]. Citrus farming has achieved some of the greatest commercial and industrial agricultural achievements in history, and the peel waste from citrus and other species is a rich source of bioactive substances such essential oils, flavones, polyphenols, and pigments [11,12].

Furthermore, utilizing citrus peels in traditional ways can aid in mitigating pollution issues arising from the inappropriate disposal of such waste [13]. Further, an investigation is required to determine the in vivo bioavailability and real advantages of these peel extracts obtained from citrus peel [14]. Common mineral contents in fruits include calcium (Ca), carbon (C), iron (Fe), magnesium (Mg), sodium (Na), carbon (C), and zinc (Zn), among others [15]. LIBS has the competency to detect, classify, and compute the chemical structure of a given material [16].

2. METHODS AND MATERIALS

To prepare the sample for LIBS (Laser-Induced Breakdown Spectroscopy) analysis, the following three steps were followed:

i. Cleaning the apparatus: All the equipment and apparatus used in the sample preparation process were thoroughly washed with acetone. This step ensures the removal of any contaminants or residues that may interfere with the analysis and ensures a clean working environment.

ii. Mixing wax and dried fruit peel powder: A maximum of 3 grams of wax was mixed with 10 grams of dried fruit peel powder in a mixture machine, specifically the swing Mill HK-40. This step involves combining the wax and dried fruit peel powder to create a homogenous mixture. The purpose of adding wax could be to facilitate the formation of pellets or to improve the stability and cohesiveness of the sample during analysis.

iii. Pressing the mixture: The mixture of wax and dried fruit peel powder (10 grams) was then pressed using a hydraulic pressure machine. A force of 16×10^4N was applied during the pressing process. This step involves compressing the mixture to form solid pellets or discs. The applied pressure helps in achieving the desired pellet shape and density, ensuring uniformity and reproducibility during LIBS analysis.

3. EXPERIMENTAL SETUP

A typical LIBS experimental setup consists of several components, as illustrated in Figure 2 The setup involves a Q-switch Neodymium Yttrium Aluminum Garnet (Nd: YAG) laser that operates at a wavelength of 532 nm and has a pulse duration of 5 ns, a repetition rate of 10 Hz, and an energy of 400 mJ. A 3D rotator is used to mount the material, which rotates to expose a new surface area to each laser shot. When the laser beam hits the material, a plasma plume is created, which emits radiation, which is then detected by a LIBS 2000+ spectrometer from Ocean Optics, Inc. The spectrometer is equipped with a high-OH optical fiber that is fixed normal to the expansion of the plasma and can detect all radiation within the range of 180 to 660nm. The experimental setup for LIBS involves the synchronization of the Q-switch Nd: YAG laser and the LIBS 2000+ detection setup. An optical cable is used to collect the emitted radiation for qualitative and quantitative analysis, and the data collected is transferred to a computer using OOI LIBS software. The optical setup employed in LIBS experiments provides a precise and reliable method for conducting spectroscopic analysis of materials (Figure 2).

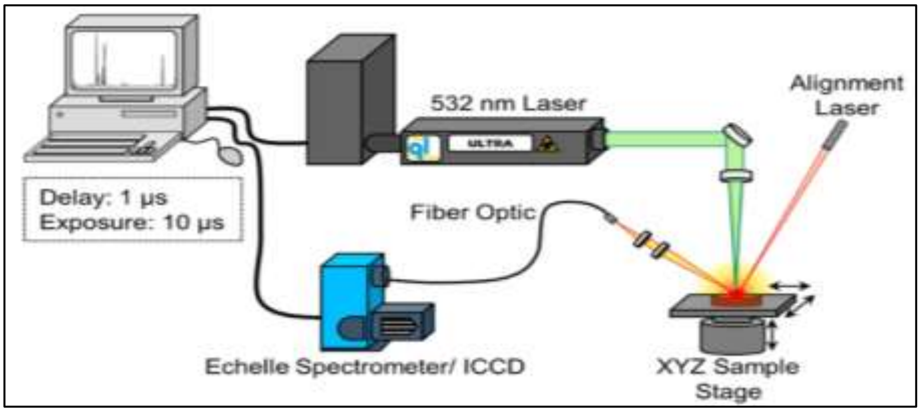
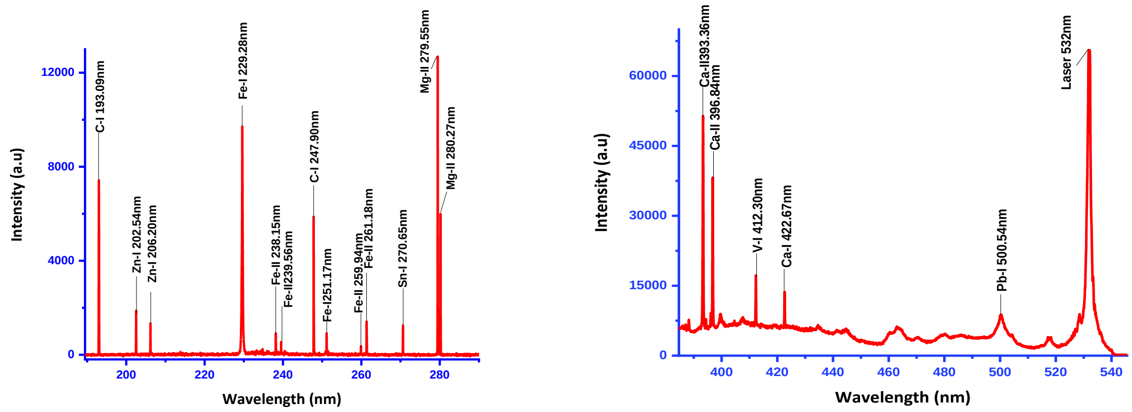


Figure 2. Experimental system of LIBS.

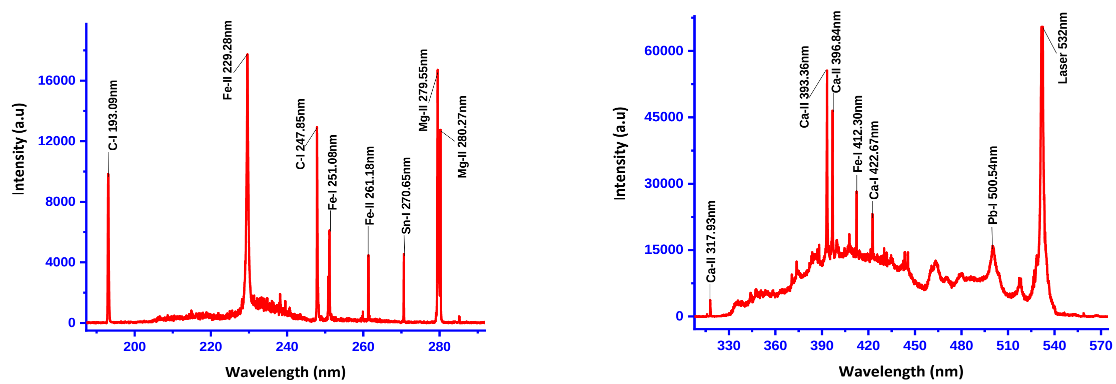
4. RESULT AND DISCUSSION

Three fruits peel sample (Apple, orange and lemon) are chosen which are widely used every day. Moreover, fruits are essential parts of our life, which are rich of vitamin source like iron, magnesium, carbon and calcium to meet healthy life. In this case, mostly common fruits waste is discarded and can much pollution in environment in Pakistan, Citrus fruits are a rich source of folic acid, potassium, pectin, and vitamin C, as well as a range of active phytochemicals. The detected transition lines for the elements were cross-checked against existing research articles and also compared with the NIST database [17].

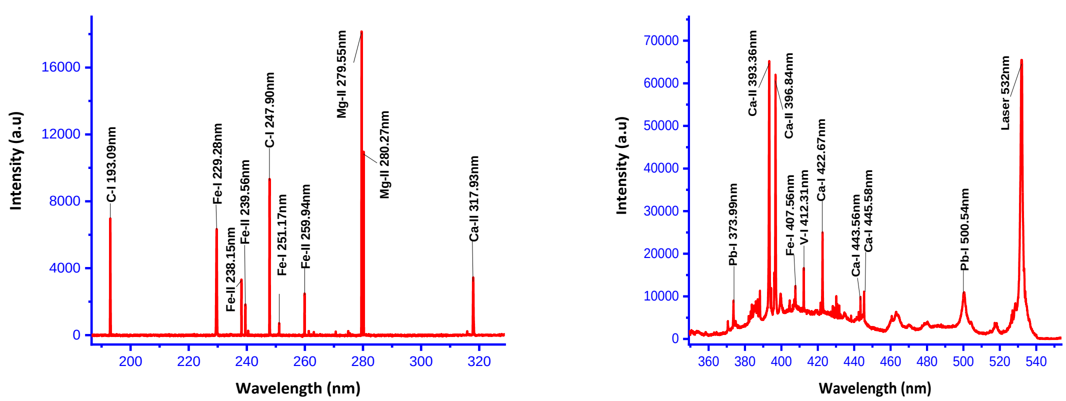
In this work it has been studied emission spectra of all three sample plasmas. To gain more detailed understanding, the whole spectrum is sub divided into smaller portion as shown in figure 3.



(a)Apple sample



(b)Lemon sample



(c)Orange sample

Figure 3. Spectrum of a) apple, b) lemon and c)orange.

The figure 3.(a) shows apple peel spectrum, which consists of neutral Carbon (C-I) at (193.09 and 247.90) nm, neutral Zinc (Zn-I) at (202.54 and 206.20) nm, neutral iron (Fe-I) at (229.28 and 251.08) nm, ionized iron (Fe-II) at (238.15, 239.56, 259.94, and 261.18) nm, neutral Tin (Sn-I) at 270.65 nm and ionized Magnesium (Mg-II) at (279.55 and 280.27) nm. Moreover, it is observed ionized Calcium (Ca-II) at (393.36 and 396.84) nm and neutral Vanadium (V-I) at 412.31 nm, neutral Calcium (Ca-I) at (422.67) nm and neutral Lead (Pb) at 500.54 nm are also present in apple sample.

The figure 3.(b) shows lemon peel spectrum, which consists of neutral Carbon (C) at (193.09 and 247.85) nm, ionized Iron (Fe) at (229.28, 251.08 and 261.18) nm, neutral Tin (Sn-I) at (270.65) nm and ionized Magnesium (Mg-II) at (279.55 and 280.27) nm. Further, ionized Calcium (Ca-II) at (317.93, 393.36 and 396.84) nm, neutral Calcium (Ca-I) at (422.67) nm, neutral Iron (Fe-I) at (412.30) nm and neutral Lead (Pb-I) at (500.54) nm.

The figure 3.(c) shows orange peel spectrum, which consists of neutral Carbon (C-I) at (193.09 and 247.90) nm, neutral iron (Fe-I) at (229.28 and 251.08) nm, ionized Iron (Fe-II) at (238.15, 239.56 and 259.94) nm, ionized Magnesium (Mg-II) at (279.55 and 280.27) nm and ionized Calcium (Ca-II) at (317.93) nm. Moreover, ionized Calcium (Ca-II) at (393.36 and 396.84) nm, neutral Iron (Fe-II) at (407.56) nm, neutral Calcium (Ca-I) at (422.67, 443.56, and 445.58) nm, neutral Lead (Pb-I) at (373.99 and 500.54) nm, and neutral Vanadium (Sn-I) at (412.31) nm.

4.1. ELECTRON NUMBER DENSITY OF ORANGE PEEL SAMPLE PLASMA

To determine whether the local thermodynamic equilibrium (LTE) is achieved in laser ablation, the number density of electrons is a crucial parameter that needs to be measured. There are various methods to calculate electron number density, and one of the simple ones is line broadening, specifically stark broadening, which occurs due to the interaction between the radiating species and the columbic field of electrons and ions. In laser ablation, determining electron number density is essential for determining plasma plume parameters, we have used following equation to calculate electron number density [17].

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

In this study, the electron density (N_e) of Orange peel sample powder was estimated using the impact parameter of Ca-II (393.36 nm), which was measured by applying the Lorentz line shape giving the width (total width at maximum half). The electron density was found to be 4.45×10^{17} cm^{-3} at an energy of 80 mJ and around 5.90×10^{17} cm^{-3} at an energy of 190 mJ. The graph of electron number density versus energy (80-190) mJ is shown in figure 4 and 5.

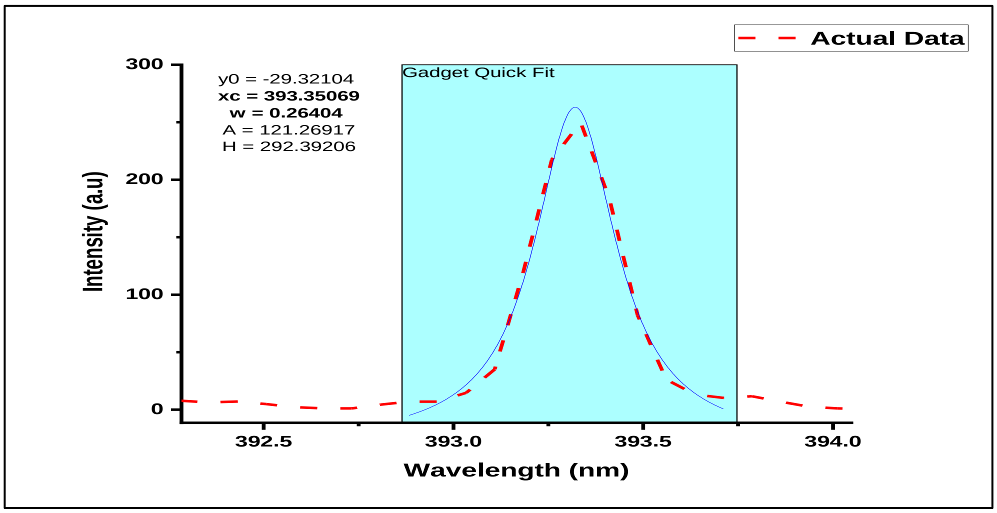


Figure 4. The stark broadening line profile of Ca-II 393.36 line showing width of transition line FWHM $\lambda_{1/2(Stark)}$.

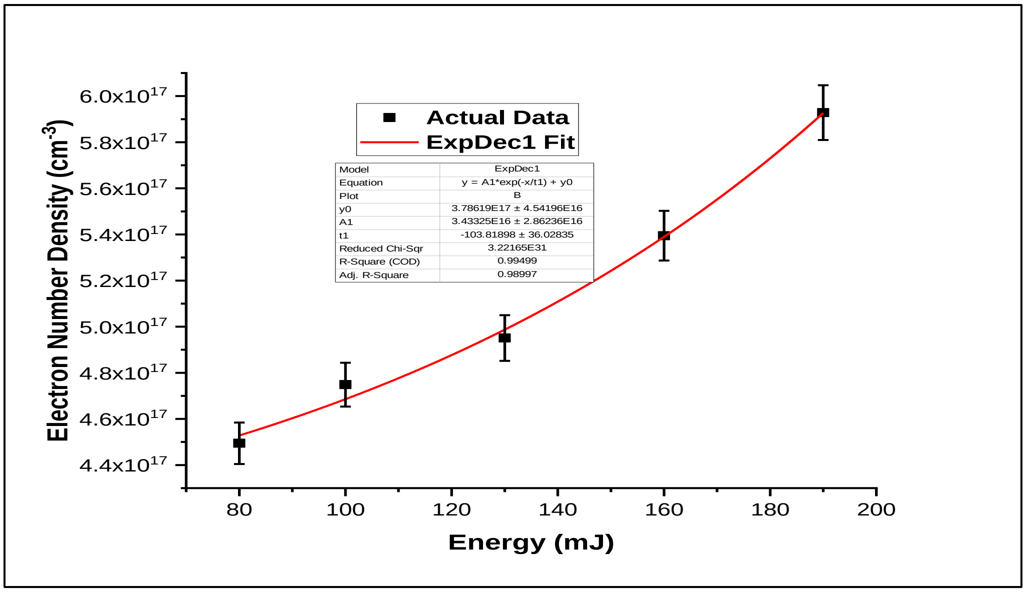


Figure 5. Variation of electron number density of orange peel sample along with increasing energy from 80 mJ to 190 mJ.

WEIGHT PERCENTAGE OF ELEMENTS IN SAMPLE PLASMA

The calibration-free laser-induced breakdown spectroscopy (CF-LIBS) technique is employed in this study to determine the weight percentage of various elements present in Orange peel. This is a convenient and straight forward method for quantifying the elements of interest without requiring any calibration standards. The CF-LIBS technique assumes that the plasma is in local thermodynamic equilibrium (LTE) and can perform quantitative measurements accordingly.

The number density of elements (neutral atoms) is given by the relation[18]:

$$FC_s^z = I^{ki} \left(\frac{U_s\,(T)}{A_{ki} g_k}\right)\ e^{(E_k/kT)} \tag{2}$$

The number density of elements (ionized atoms) is given by the relation:

$$FC_s^{z+1} = I^{ki} \left(\frac{U_s\,(T)}{A_{ki}\,g_k}\right)\ e^{E_k/kT} \tag{3}$$

Where,

- C^Z stands for the concentration of neutral species
- C^{Z+1} stands for the concentration of ionic species
- I_{ki} stands for an Integrated intensity of transition line
- g_k stands for the statistical weight
- A_k stands for the transition probability
- E_k stands for upper level energy
- T stands for the plasma temperature
- U^Z stands for the Partition function
- K_B stands for the Boltzmann constant, respectively.

The work that determines the excitation temperature in electron volts for neutral or ionized transitions of emitting species is known as the partition function Z(T), which can be obtained from the NIST database. The combined concentration of neutral and ionized elements is calculated by adding their individual densities.

$$C_{Total} = C^Z + C^{Z+1} \tag{4}$$

If the equation mentioned above is used to calculate concentration of Ca, Mg, Fe, and C in fruit peel samples, it is possible to determine the weight percentage of each element present in the sample.

$$C^{Ca}\% = \frac{C^{Ca}_{Total} \times (Atomic\ weight\ of\ Ca)}{C^{Ca}_{Total} + C^{Fe}_{Total} + C^{Mn}_{Total} + C^{Mn}_{Total} + C^{Mg}_{Total} + C^{Na}_{Total} \times (At{:}wt{:}\ of\ \ elements)} \times 100 \tag{5}$$

The weight percentage of Calcium, Magnesium, Iron and Carbon present in the Orange (figure 6) Fruit peel sample were determined by calculating their respective concentration using the equation mentioned earlier.

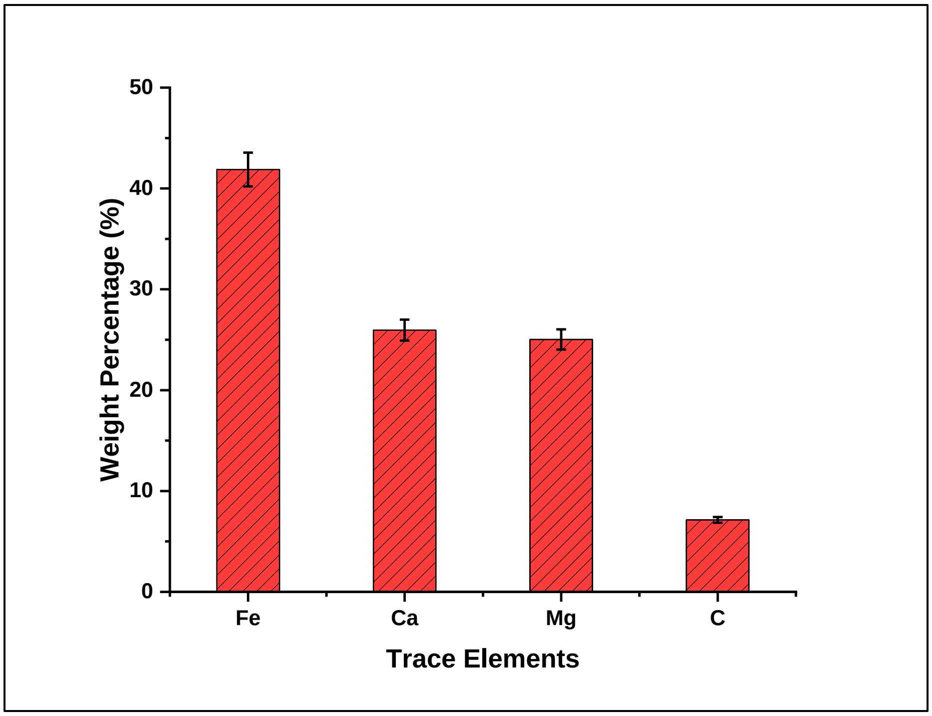


Figure 6. The weight percentage of Iron (Fe), Calcium (Ca), Magnesium (Mg), and Carbon (C).

5. CONCLUSION

Recent years have seen a substantial increase in interest in laser-induced breakdown spectroscopy (LIBS) as a useful technique for examining how laser beams interact with various materials. Using Laser Ablation, We have observed the wavelength of elements, transition lines of Carbon(C), Iron (Fe), Vanadium (V) Calcium (Ca), Lead (Pb) and Zinc (Zn). The variation of intensity of some emission lines such as C-I 247.90 nm, Mg-II 279.55 nm, Fe-II 229.28 nm and Mg-II 280.27 nm data analysis are present. Furthermore, in orange peel sample the density of electrons was observed to vary from 4.45×10^{17} cm^{-3} to 5.90×10^{17} cm^{-3} with an energy variation from 80 mJ to 190 mJ. It is observed that the value of the electron number density (N_e) decreases as laser energy decreases and its value increases with increasing energy. Using the CF-LIBS method, the weight percentage of each element in the orange sample was determined, and it was found that iron (Fe) is present in high concentration in the orange peel.

Fruit residues, which are readily available and inexpensive, have the potential to be valuable nutraceutical resources. These residues are typically considered waste and discarded, but they can provide low-cost and nutritionally beneficial dietary supplements.

Declarations

Ethical Approval

There are no ethical issues involved in this study.

Funding

Not applicable.

Availability of data and materials

All data is available in the manuscript.

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