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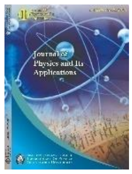

Enhancement of Laser-Induced Breakdown Spectroscopy (LIBS) Sensitivity Using Electric Fields: A Study on Non-Metal Samples

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has proven to be a versatile and effective technique for elemental analysis across a variety of fields, including geology, archaeology, materials science, nuclear power, and medicine. This study focuses on the application of an external electric field to enhance the performance of LIBS, specifically for non-metal samples such as black coral. By introducing an electric field and varying laser energy levels, the effects on plasma generation and emission intensities were investigated. The experimental results demonstrate that applying an electric field significantly enhances spectral intensity, with notable improvements in the Carbon (C I) emission line at 247.8 nm. The enhancement was observed to be nonlinear, with significant increases only when the electric field strength exceeded 200 V/cm. Laser energy was also found to play a critical role, with carbon signals only detectable at energies above 20 mJ, and optimal results achieved at 50 mJ. These findings highlight the combined effect of laser energy and electric field strength in enhancing LIBS sensitivity, particularly for detecting trace elements in organic samples. This approach offers a simple, efficient, and effective method to improve LIBS performance, with potential applications in fields such as fossil age determination and other analytical studies requiring high sensitivity.

1. Introduction

LIBS has emerged as a versatile and efficient tool for elemental analysis across a wide array of applications, including geology [1,2], archaeology [3,4], materials science [5], nuclear power plant [6,7] and medicine [8,9]. Its capability to perform rapid, in situ, and minimally invasive analyses has positioned it as a valuable technique for detecting elemental compositions. By utilizing laser pulses to create plasma, LIBS enables the identification of chemical elements through the emitted light, making it particularly suitable for scenarios requiring small sample sizes and minimal preparation [10].

Despite its advantages, LIBS faces challenges in detecting trace elements, particularly at very low concentrations (below 10 ppm). Addressing this limitation has been a focal point of recent research, with various strategies explored to enhance sensitivity and detection limits. Techniques such as dual laser pulses [11-13], magnetic field confinement [14,15], gas application on the sample [16], a combination of dual lasers and magnetic field [17,18] and electric field [19] have demonstrated promising results. Among those techniques, electrical field is the simple method because of less preparation, no extra sample pretreatment and it does not affect the sample position.

Studies from Ahmed et al. shows that with external electric field, limit detection of metal such as copper, silver and gold are improved. The setup of the electric field is rather simple with the introduction of two metal electrodes that are connected to external high-power supply. And the electrodes are put in front of the sample that will not interfere or modify the sample.

In this paper, we will focus on studying the effect of electric field in signal enhancement of LIBS. The study will analyze the effects of electric field parameters on plasma generation and emission characteristics. The plasma effect under different values of electrical field and different laser energy are studied. The samples used in this experiment are non-metal as it the study that Ahmed does is a metal sample.

2. Experimental setup

To investigate the influence of an applied electric field, the experimental setup is arranged as shown in Fig. 1. An Nd:YAG laser (355 nm wavelength) is employed, with its output energy adjustable from 15 mJ to 70 mJ. This laser is used to ablate the sample and produce plasma. The beam is focused onto the sample using quartz lenses with a focal length of 150 mm. The sample itself is mounted on a holder connected to a DC motor, allowing it to be rotated so that fresh areas of the sample surface are continually exposed. The sample is place in the atmospheric environment.

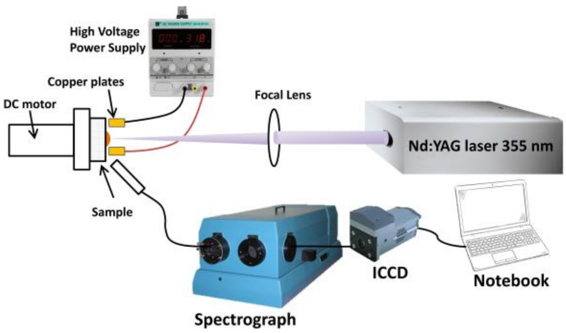

Fig. 1: Diagram of the experimental setup with two copper electrodes to produce an electric field

In front of the sample, two copper plates are positioned with a 10 mm gap between them, forming the region where the plasma interacts with electric field generated from the copper plates. The electric field is generated by connecting the copper plates with a power supply capable of delivering 0–400 V, resulting in an electric field ranging from 0 to 400 V/cm applied to the plasma. To maintain their position and ensure a consistent gap, both copper plates are secured within a specially designed electrode holder.

Fig. 2 illustrates the design of the electrode holder, indicating where both copper plates are positioned. The figure shows the exploded and assembly view of the design. The holder is made of insulation material to prevent electric interference. The holder consists of three main components: the base, the bottom electrode holder, and the top electrode holder. The base serves as a support structure that elevates the entire electrode assembly in line with the position of the sample. The bottom electrode holder secures one of the copper plates and is equipped with a sliding mechanism that allows the electrode's position to be adjusted front-to-back for precise alignment. The top electrode holder, supported by two vertical pillars, holds the other electrode in place. The top electrode can be slide up and down to adjust the gap between the electrode.

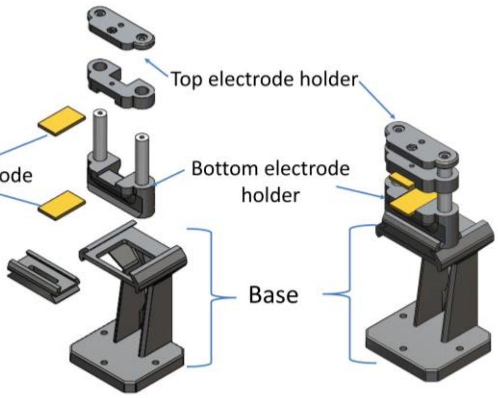

Fig. 2: Exploded and assembled view of specially designed electro holder that consists of three main parts which are top electro holder, bottom electro holder and the base

This electrode holder is placed in front of the sample to position the copper electrode in front of the sample and generate electric field that confined the plasma emissions. An optical fiber will be placed near the sample to collect the plasma emissions. The fiber will be used to capture the ablated plasma that is confined between the electrodes. This fiber will be connected to a spectrometer (McPherson 2061 model) equipped with an intensified CCD (ICCD) camera (Andor iStar intensified CCD) to detect the wavelengths and intensities of the emissions. The data obtained will be recorded by a computer and processed using specialized software.

The sample used in this experiment is black coral, selected as a non-metal sample due to the lack of studies on the effects of electric fields on non-metallic materials. This experiment aims to investigate the carbon content within the black coral. Carbon serves as a key indicator for organic samples, as other organic elements, such as nitrogen and oxygen, are often present in the surrounding air. The experiment will consist of three series of tests. The first series is to test the effect of electric field in the sample. The second series involve applying a fixed electric field of 400 V/cm while varying the laser energy to examine its effect and determine the optimal laser energy for ablation. Once the suitable laser energy is identified, subsequent tests will be conducted under varying electric field intensities to evaluate their influence on the sample.

3. Experimental Result and Discussion

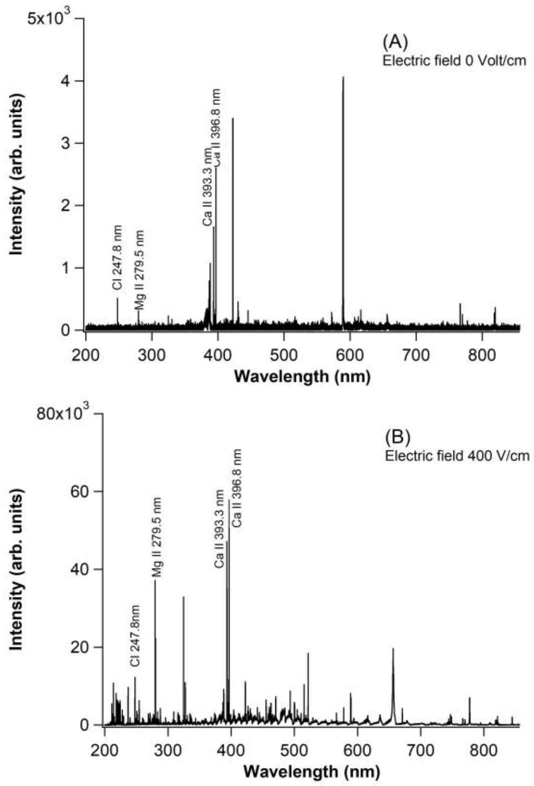

Fig. 3: Emission spectra of black coral obtained using a Nd:YAG laser at 355 nm with an energy of 50 mJ under atmospheric air conditions (1 atm), recorded using a spectrometer with a time delay of 1 µs and a time width of 30 µs. (A) Spectra without an electric field and (B) spectra with an applied electric field.

Fig. 3 shows the full spectral results of black coral within the wavelength range of 200–800 nm, comparing conditions with and without an applied electric field (400 V/cm and 0 V/cm, respectively). The spectra reveal a significant signal enhancement under the electric field. For example, the intensity of the Ca II 396.8 nm spectral line increases from 2600 at 0 V/cm to 54,000 at 400 V/cm, reflecting a 20-fold enhancement. Similarly, the carbon line (C I 247.8 nm) shows an intensity rise from 500 at 0 V/cm to 12,280 at 400 V/cm, corresponding to a 24-fold enhancement. These observations demonstrate that the electric field enhances spectral signals, with varying levels of enhancement observed across different spectral lines.

In order to observe the effect of laser energy to the enhancement, we apply different energy to the sample under the effect of electric field 400 V/cm. The result is shown in Fig. 4, where we can see that there is an increment of C I 247.8 nm intensity with increment of laser energy. We also observe that for laser energy 15 mJ and 25 mJ, there is no carbon signal. This is because the laser has less energy to ablate the carbon atom. Above that energy level we can see that there is increment of signal

The increment in the emission spectral line intensity is due to the higher laser energy given to the sample, this leads to greater material ablation. As more material is ablated, the resulting plasma becomes richer with excited atoms, thereby enhancing the emission intensity. This relationship is evident from the increment of emission intensity with increment of laser energy. However, there exists a threshold energy which the laser energy is insufficient to significantly heat and ablate the sample. This is demonstrated in the cases of laser energy 15 mJ and 25 mJ, where there is no carbon emission is observed due to inadequate ablation.

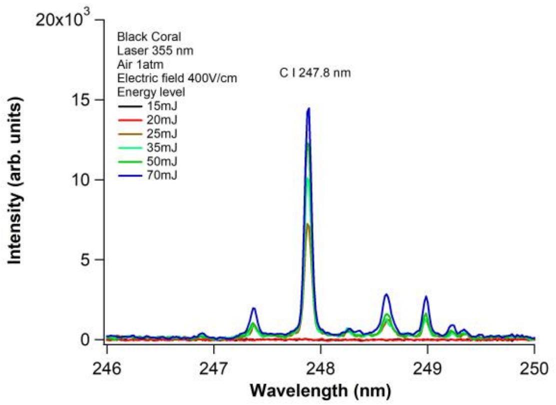

Fig. 4: Emission spectra of black coral obtained using a 355 nm Nd:YAG laser at varying energy levels under atmospheric air conditions (1 atm). The spectra were recorded with a spectrometer using a time delay of 1 μs and a time width of 30 μs. (A)

Fig. 5 show the Intensity of Carbon CI 247.8nm versus laser energy. The figure show that above 20mJ laser energy that we can obtain a signal spectrum of Carbon. Above that we can see that there is enhancement of spectrum. In this case, we choose energy laser of 50 mJ as the optimum energy as energy 70 mJ is too high for practical applications.

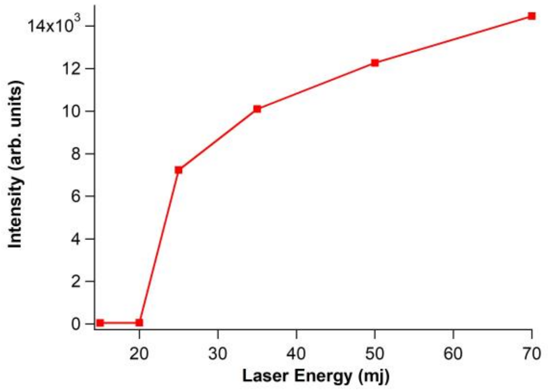

Fig. 5: Graph illustrating the correlation between laser energy and the intensity of Carbon (C I) at 247.8 nm, recorded under atmospheric air conditions (1 atm) with an applied electric field of 400 V/cm, using a time delay of 1 μs and a time width of 30 μs.

We then investigated the effect of varying electric field strengths on carbon intensity. Fig. 6 shows the carbon intensity under different electric field conditions. The results indicate that electric fields up to 200 V/cm do not produce any significant enhancement. However, beyond this threshold, the intensity begins to increase, with higher electric field strengths leading to progressively greater enhancements.

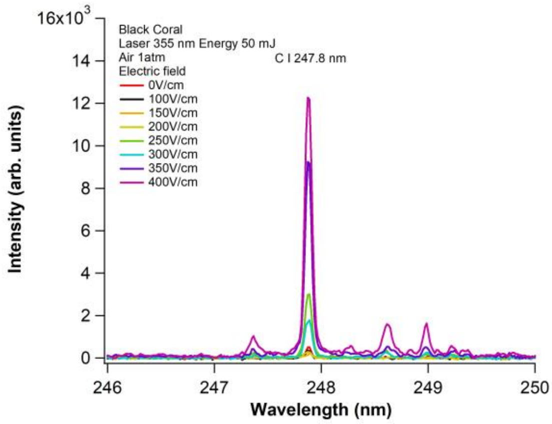

Fig. 6: Emission spectra of black coral obtained using a 355 nm Nd:YAG laser with an energy of 50 mJ, measured under varying electric field values in atmospheric air conditions (1 atm). The spectra were recorded with a spectrometer using a time delay of 1 μs and a time width of 30 μs.

The presence of the electric field affects the characteristics of the plasma generated during laser ablation. With the presence of the electric field, it will accelerate the charged particle ablated from the laser. These charged particles undergo more frequent and energetic collisions with neutral atoms, thereby increasing the rate of excitation and ionization processes. As a result, the population of excited species within the plasma grows, leading to a stronger and more intense spectral emission. Additionally, the electric field can contribute to better confinement of the plasma plume, reducing its rapid expansion and maintaining a higher particle density for a longer duration. This confinement further enhances the probability of radiative transitions, contributing to the observed increase in signal intensity.

Fig. 7 illustrates the relationship between electric field strength (in V/cm) and the intensity of the carbon emission line (C I 247.8 nm) under atmospheric conditions. The graph shows a nonlinear trend, where the intensity remains relatively constant at low electric field strengths (up to approximately 200 V/cm), indicating minimal enhancement in this range. Beyond this threshold, there is a sharp increase in intensity, which becomes more pronounced as the electric field strength increases further.

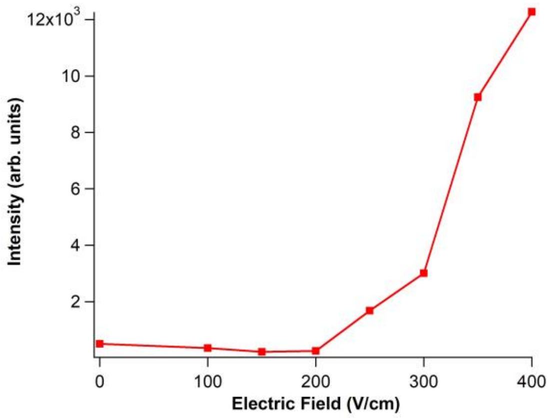

Fig. 7: Graph illustrating the correlation between electric field and the intensity of Carbon (C I) at 247.8 nm, recorded under atmospheric air conditions (1 atm) with laser energy 50 mJ, using a time delay of 1 μs and a time width of 30 μs

At higher electric field strengths, the intensity of the emission rises significantly, suggesting that the applied electric field enhances the plasma properties and improves the emission efficiency. This behavior highlights the potential of the electric field as a tool to increase signal intensity in laser-induced breakdown spectroscopy (LIBS), thereby improving the detection sensitivity for carbon. The steep rise in intensity at higher electric fields emphasizes that we should set the electric field as high as possible.

The results of this experiment demonstrate that the application of an electric field significantly enhances spectral intensity. This approach has the potential to improve the performance of laser-induced breakdown spectroscopy (LIBS), particularly in detecting small concentrations of samples, making it especially valuable for applications such as determining the age of fossils.

4. Conclusion

This study highlights the significant impact of laser energy and electric field strength on the enhancement of emission signals in laser-induced breakdown spectroscopy (LIBS), particularly for black coral samples. The application of an electric field was shown to significantly enhance the intensity of spectral lines, such as C I 247.8 nm, with the enhancement becoming notable only when the electric field strength exceeded 200 V/cm. Beyond this threshold, the signal intensity increased sharply, suggesting that the electric field improves plasma confinement and excitation efficiency. Similarly, the study demonstrated a direct correlation between laser energy and emission intensity, with carbon signals only detected when the laser energy exceeded 20 mJ. The signal intensity increased with higher laser energy, reaching an optimal level at 50 mJ, while 70 mJ, though producing a stronger signal, was considered impractical for routine applications due to excessive energy demands. The combination of a 400 V/cm electric field and 50 mJ laser energy resulted in significant spectral signal enhancement, confirming the effectiveness of this approach in improving LIBS sensitivity. These findings underline the importance of optimizing both electric field strength and laser energy to enhance detection sensitivity, demonstrating the potential of electric fields as a simple and efficient tool for improving LIBS performance in both research and practical applications.

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