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Parametric studies of liquid LIBS for agricultural applications

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is widely used in analytical chemistry, biomedicine, and environmental applications due to its real-time detection of multi-elements. However, the main challenge for LIBS application lies in its low detection sensitivity, especially for liquid sample analysis. When plasma is generated by a nanosecond laser pulse inside the liquid sample, fast quenching of the plasma occurs, and atomic emission intensity becomes weak with a short lifetime. Furthermore, the creation of surface fluctuations during laser ablation reduces the reproducibility of the signal. Researchers started exploring the possibility of improving the plasma signal by investigating different sampling approaches for liquids to increase the signal-to-background ratio of the signal. Liquid LIBS has the potential to become one of the best ultra-sensitive elemental characterization methods by standardizing the technique and making it applicable for potential industrial applications. In this context, this paper investigates two different sampling approaches for liquid LIBS analysis. The experimental configurations, optimization of the experimental parameters, and the limit of detection of the sampling approaches are detailed, followed by its potential application in vertical hydroponic farming.

Keywords: Laser-induced Breakdown Spectroscopy (LIBS), Vertical hydroponic farming, Liquid LIBS, Nutrient monitoring, Sampling approach, Limit of detection

1. INTRODUCTION

Ensuring food security is crucial for the stability of any society and nation. Thus, it is vital for agriculture to be more robust in providing the required products for consumption. Although traditional farming methods remain integral to the current economy and society, they face significant vulnerabilities to climate change and present challenges for countries with limited land resources due to their extensive land requirements [1-3]. Hence, advanced farming techniques, like vertical hydroponic farming, are needed to overcome these obstacles.

Vertical hydroponic farming mainly consists of four main components: plants, lighting, liquid nutrient solutions, and a controlled environment, as depicted in Figure 1. Firstly, the plant selected for cultivation needs to be able to grow in a specialized environment, like hydroponics, effectively and economically. In principle, all plants can be grown hydroponically, but for some, it is not economical to do so due to the added complexity of the system [4]. Secondly, liquid nutrients are used as the medium to transfer nutrients to the plants to ensure proper growth, leading to an increase in production yield. Thirdly, a controlled environment, including temperature, humidity, and air supply, ensures the ideal ambient conditions for optimum plant growth, which would guarantee a controlled environment regardless of the weather conditions, making it less susceptible to environmental factors. Similarly, the lighting needs to be finely controlled to ensure optimal growth conditions for the plants. Furthermore, a key attribute of this method is the multi-layer stacked configuration that would maximize the number of crops grown per unit area, making it ideal for use in land-scarce nations like Singapore [5].

While vertical hydroponic farming is a popular alternative, there is a major issue with precise nutrient monitoring. Most commercial systems employ electrical conductivity (EC) meters and pH meters for this purpose [6]. For an effective monitoring system, an in-situ system needs to be able to monitor the individual elements of the nutrient solution for smart nutrient management and enhance the productivity and quality of the crops. There are many monitoring devices developed for agricultural applications over the years [7-10]. However, most of the techniques are not real-time and they can only indicate the overall change in the complex mixture of the nutrient solution. In this context, we demonstrate laser-induced breakdown spectroscopy (LIBS) as a promising tool for monitoring the hydroponic nutrient solution.

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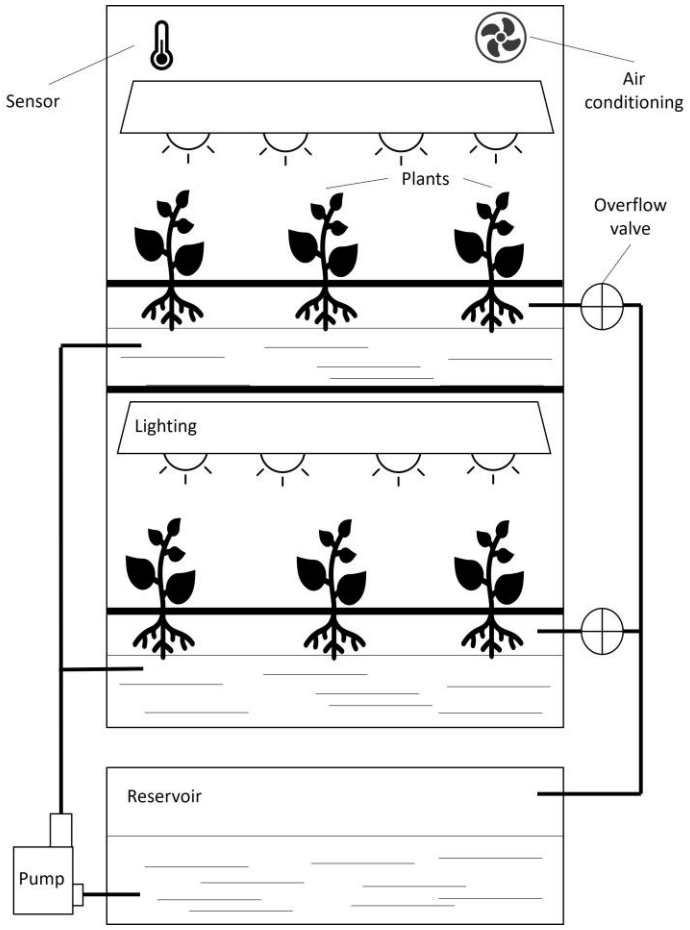

Figure 1: Schematic of a vertical hydroponic farming system.

LIBS is a powerful analytical technique used for elemental analysis. It involves the use of high energy laser pulses to generate plasma on the surface of a sample [11, 12]. This plasma emits a spectrum which contains atomic and ionic emission lines of various elements present in the sample, which is then analysed to determine the elemental composition of the material. LIBS has got a wide variety of applications due to several advantages, including its capability for multi-elemental analysis, remote sensing, in-situ monitoring, and the absence of the need for sample preparation [13-16]. For example, LIBS has been used for precise elemental analysis of soil samples [15].

The working principle of LIBS is depicted in Figure 2 [17, 18]. When a high energy pulsed laser beam is focused onto the sample surface, it leads to the ablation of a small volume of the sample material. This process involves the rapid thermal vaporization and removal of the sample. The high energy of the laser beam creates a highly ionized and excited state of matter known as plasma, containing free electrons, excited atoms, and ions. The initial phase of plasma formation is characterized by high electron density and continuum emission due to ion-electron interactions creating Bremsstrahlung

radiation. As the plasma cools down, the electrons will recombine with the ions, emitting characteristic line emissions. From these line emissions, different elements present in the sample can be identified.

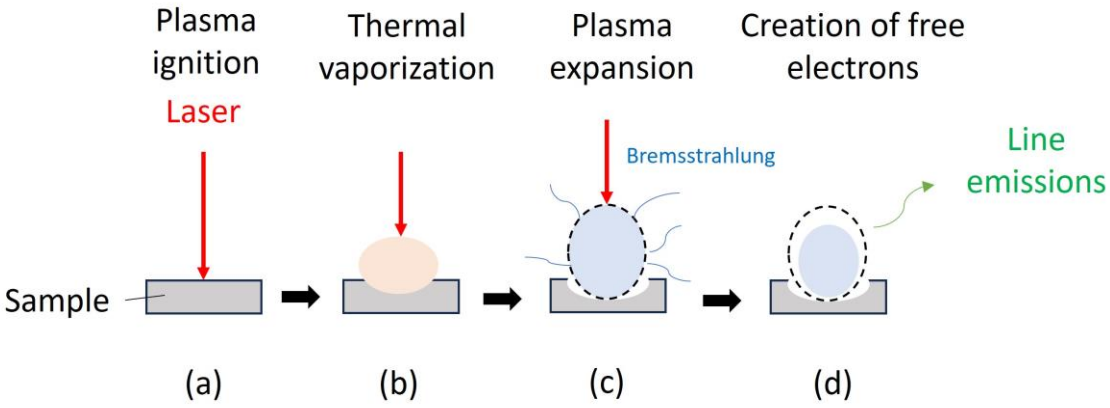

Figure 2: Schematic representation of the LIBS process.

Liquid LIBS poses specific challenges related to the nature of liquid samples and the experimental conditions. Excessive splashing causes the contamination of surrounding optics, which can affect the precision and accuracy of the data taken during experimentation. Additionally, the plasma formed is rapidly quenched by the surrounding medium [19]. These factors will result in low reproducible LIBS signals, which significantly impacts the detection capability of liquid LIBS. In imaging and collection configurations, it is crucial to consider the system design [20, 21]. Similarly, the design, configuration, and optimization of the sampling configurations to improve the liquid LIBS signal collection efficiency are essential for elemental identification and analysis. This paper explores two different sampling approaches for liquid LIBS analysis.

2. METHODOLOGY

The experimental configuration and sampling approaches employed in this investigation are illustrated in Figure 3, incorporating a liquid cell and a liquid jet approach. A Nd:YAG laser emitting high energy pulsed laser pulses at a wavelength of 1064 nm is used to generate plasma in both sampling approaches. The laser pulse energy and the gate delay time was optimized to be 15 mJ and 300 ns, respectively. For the liquid cell approach, a small beaker was filled with 10 ml of the sample solution is used. The laser beam is focused into the liquid using a biconvex lens with a focal length of 50 mm generating a plasma plume in the liquid. The emitted plasma from the sample is then collected using a biconvex lens of focal length of 40 mm and directed to the spectrometer through a fiber conduit (see Figure 3).

For the liquid jet approach, a similar method of plasma generation and signal collection was used, which consists of a reservoir, a pump, and a nozzle. The liquid is circulated through the system using the pump to form a stable jet in ambient conditions. Then, the laser beam was focused onto surface of the liquid jet. Hence, generating plasma on the jet's surface for further analysis.

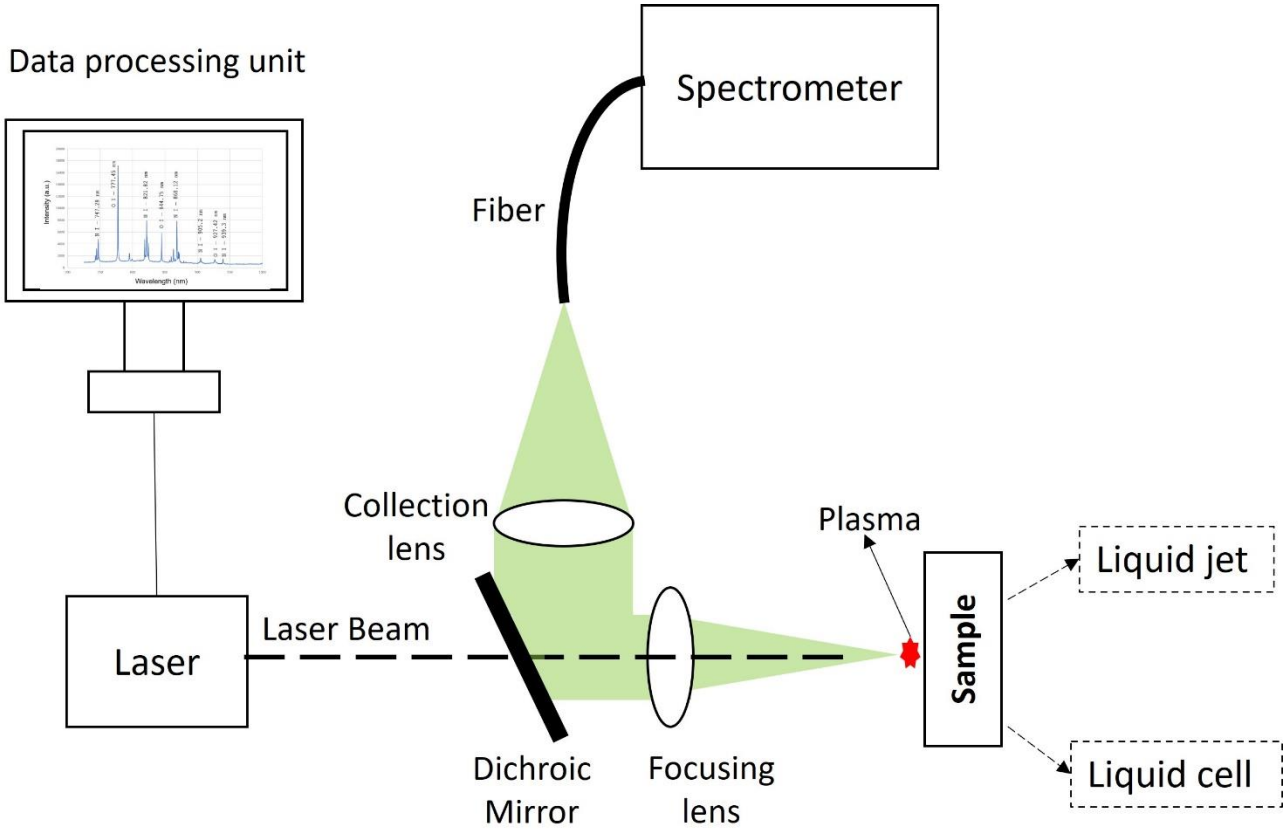

Figure 3: Schematic of the liquid LIBS configuration.

Table 1: Experimental parameters used for the investigation.

Variable	**Attribute**
Solutions used	Aqueous sodium chloride
Laser wavelength	1064 nm
Pulse duration	6 ns
Pulse energy	15 mJ
Repetition rate	10 Hz
Focusing lens's focal length	50 mm
Collection lens's focal length	40 mm

In this experiment, aqueous solutions of sodium (Na) with varying concentrations are prepared, and plasma is generated using the parameters and specifications as outlined in Table 1. From the plasma, the spectra were captured for data analysis. For this investigation, the signal to background ratio (SBR) and limit of detection (LOD) are used as indicators for the sensitivity of the sampling approaches investigated. Ideally, the SBR needs to be as high as possible and LOD needs to be as low as possible.

To calculate the SBR, the following equation is used:

$$SBR = \frac{I_{Line}}{I_{Background}}, \quad (1)$$

where I_{Line} is the emission line intensity and $I_{Background}$ is the average intensity of the background as shown in Figure 4 [22, 23]. Here, the intensity of sodium (Na I) line at 589.14 nm, along with the background in the range of 570 nm to 575 nm is used for analysis.

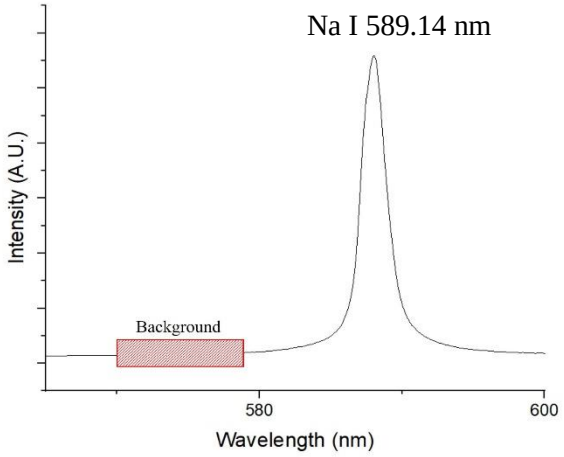

Figure 4: Schematic representation of the definition of signal and background intensities.

The LOD is defined as follows:

$$LOD = \frac{3\sigma}{S}, \quad (2)$$

where σ is the standard deviation of the background intensity and S is the sensitivity, which is the slope of the calibration curve [24]. To generate a calibration plot, different concentrations of the sample are required as different concentrations would yield different SBR. Then, the SBR values obtained from the experiments were plotted against the corresponding concentrations. A linear fit to the data points is generated. The linear fit is based on the equation y = Sx + a and the parameter S is used to calculate the LOD. Here, y and x denote the values of the SBR and concentration, respectively [24].

3. RESULTS AND DISCUSSIONS

In this study, an in-depth analysis was conducted involving two sampling approaches, liquid cell and liquid jet. The investigation was focused on examining the variation in LIBS signal intensity in relation to different concentrations of Na analytes. The representative LIBS spectra of a 600 ppm Na solution using liquid cell and liquid jet configurations are shown in Figure 5(a-b) and Table 2 summarized the SBR of a 600 ppm Na solution and LOD obtained from both liquid cell and liquid jet configuration. As presented in Table 2, the preliminary SBR generated from the liquid cell configuration was 46.2 while the SBR for the liquid jet approach for the same concentration was 27.3. The variation of LIBS signal intensity with respect to different concentrations of Na for the two different sampling configurations was investigated here. The calibration curves given in Figure 5(c-d) was generated by plotting the SBR as a function of the concentration of analyte used. From the calibration curve it is clear that the LIBS intensities decrease with decreasing the analyte particle concentrations.

Table 2: The SBR and LOD values obtained from liquid cell and liquid jet configurations.

Sampling configuration	**SBR**	**LOD**
Liquid Cell	46.2 ± 3.5	5 ppm

Liquid Jet	27.3 ± 4.2	9 ppm

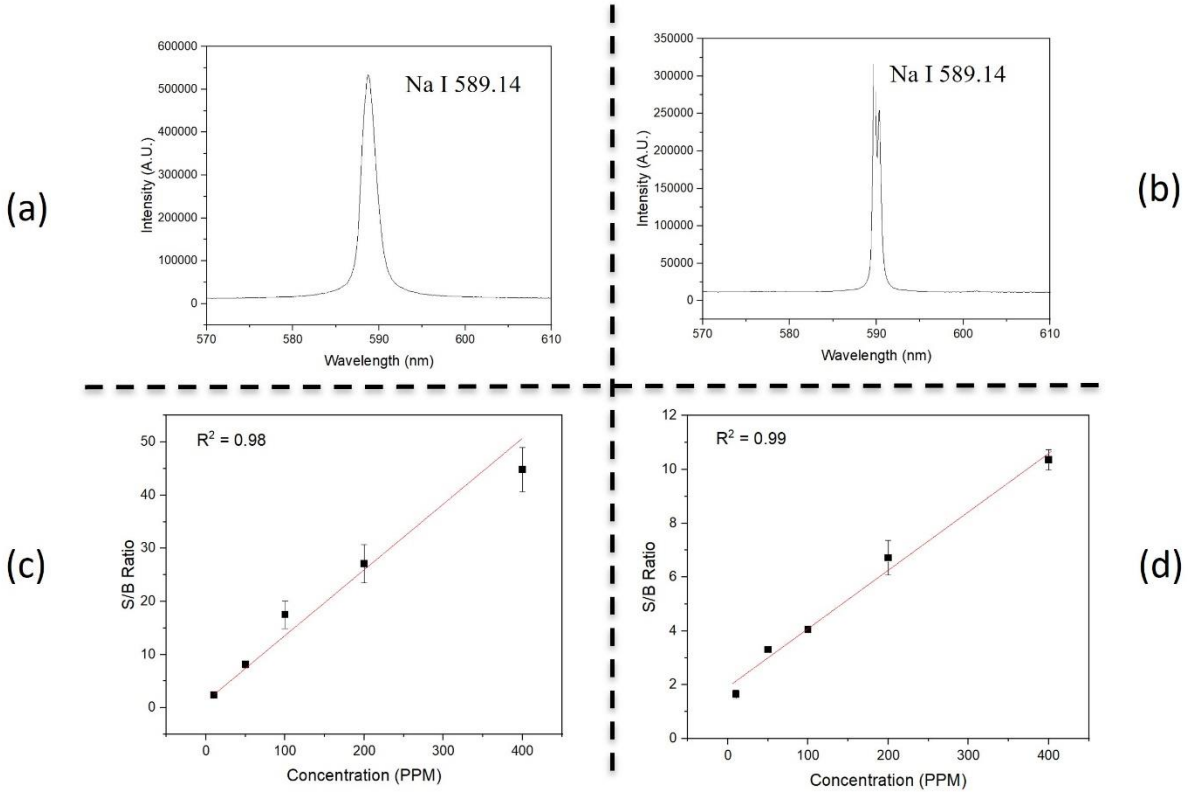

Figure 5: Representative LIBS spectra of Na emission line at 589.14 nm for concentration of 600 ppm obtained from (a) liquid cell configuration and (b) liquid jet configuration. Calibration curve for Na in (c) liquid cell configuration and (d) liquid jet configuration.

It may be noted that for the LOD values generated are 5 ppm and 9 ppm for the liquid cell and liquid jet approach, respectively. However, the liquid cell exhibited greater SBR values. The low SBR exhibited by liquid jet is primarily due to its turbulent and fluctuating flow. Hence, the liquid cell approach is considered to be more suitable for this application due to the higher SBR and lower LOD.

To demonstrate the applicability of the current study to real-world samples, nutrient solution from the hydroponics system were tested with the developed liquid cell sampling configuration. Figure 6 shows a representative LIBS spectrum of the nutrient solution, showing the presence of atomic lines of macronutrient potassium (K) and sodium (Na). Based on the SBR values and the calibration plots, it is possible to calculate the exact concentration of the elements present in the nutrient solution. It is worth mentioning that in a similar way, all components in the nutrient solution can be detected and quantified. The results suggest that the LIBS technique can be successfully used in vertical indoor farming for in-situ nutrient monitoring. Future research will be in this direction, involving detailed experimental investigation leading to the realization of a liquid LIBS based nutrient monitoring system.

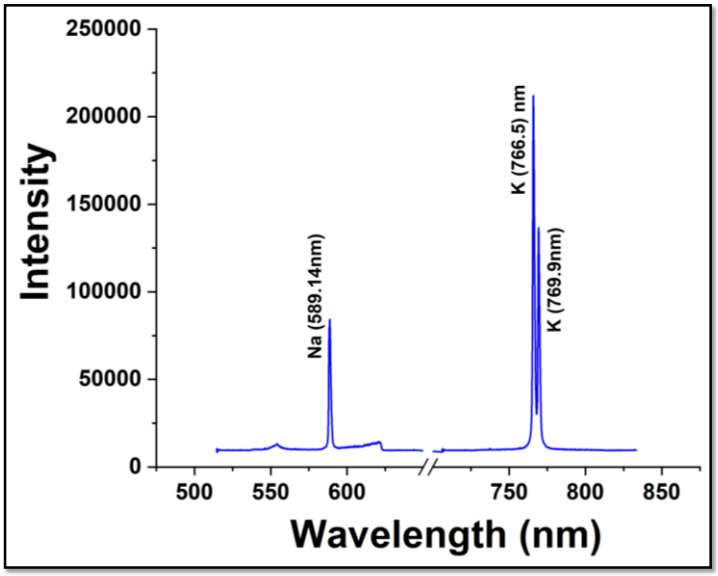

Figure 6: Representative LIBS spectra of liquid nutrient solution captured using the liquid cell approach.

4. CONCLUSION

In the search for a sampling approach for liquid analysis using the LIBS technique, two distinct sampling methods, liquid cell, and liquid jet, were systematically investigated to assess their response to various analytes. From the preliminary results obtained, liquid cell approach is shown to be more effective for hydroponic nutrient monitoring. The proposed approach would require only a minimal sample volume (~ 10 ml). Unlike conventional monitoring system, LIBS based nutrient monitoring system with the proposed sampling approach can provide the exact concentration of the elements in the nutrient solution. This will help to minimize nutrient wastage and reduce the risk of plant diseases, ultimately improving crop production yield in vertical hydroponic farming and enhancing its economic viability.

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