

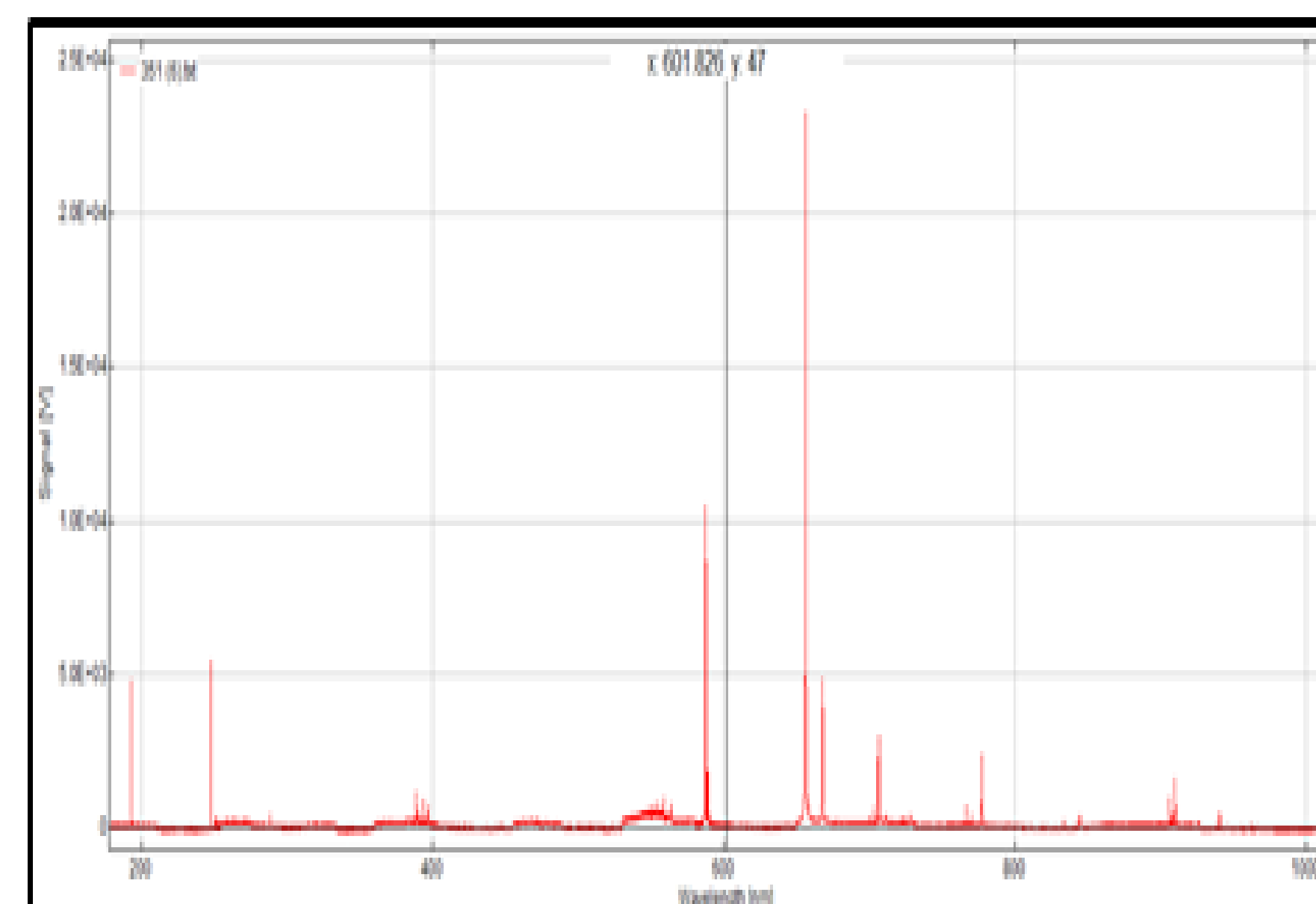
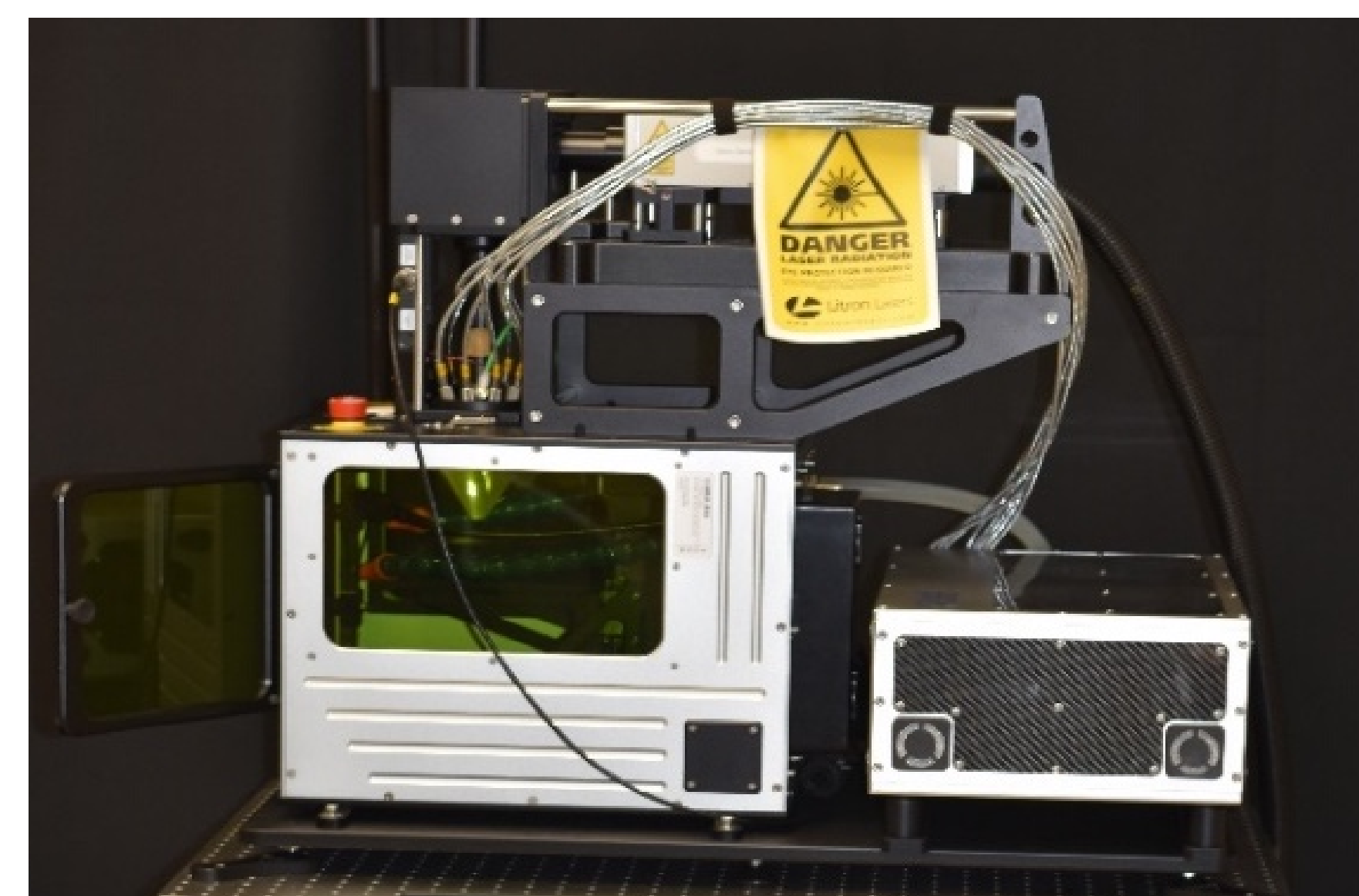
Motivation

The contamination of crops with toxic elements is a major concern for food safety around the world. There are numerous methods for testing crops to ensure their safety, but few of these methods are capable of in-situ testing. Possessing the technology to perform the testing of crops on-site could save money, time, and crop production. An instance where this technology could be particularly useful is the analysis of rice plants that have been contaminated with heavy metals, such as Arsenic. Many countries are dependent on rice as their main food source, so the contamination of rice plants threatens sustainable food production for these populations. The common method of testing these crops is inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) which involve extensive destructive extraction. While these methods are effective for determining the levels of heavy metal contamination, in particular, the ICP-MS is a highly sensitive method, it is less efficient than *in-situ* non-destructive testing. An alternative method explored through this project is the use of Laser-Induced Breakdown Spectroscopy (LIBS) for *in-situ* testing of heavy metals in rice plants.

Background

LIBS is a novel atomic emission spectroscopy technique, which has the advantages of fast analytical speed, little sample preparation, the ability to perform elemental mapping, and in-situ testing capabilities. The basic principle of LIBS is based on exciting matter (solid, liquid or gas) to plasma state through irradiation by high power laser pulses. The plasma formed contains atoms and ions in different excited states, free electrons and radiation. The photons emitted in the plasma are analyzed by spectrometers that output data in the form of a spectrum. The data can then be utilized to determine the elemental composition of the ablated sample by matching the wavelengths detected in the spectrum to the known wavelengths of various elements. This project focused on determining the ideal settings that result in the consistent detection of Arsenic (As) in rice plants.

Figure 1: (a) image of a laser-induced breakdown spectroscopy (LIBS) and (b) an example signal demonstrating the optimal delay time.



Experimental Studies

(a) Filter paper test for optimal delay time

The testing of filter papers soaked in Arsenic solution served as a way to optimize the testing parameters before testing the rice plants. Two solutions of Arsenic salts were used; the As(III) solution was composed of NaAsO_2 >90% and the As(IV) solution was composed of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ >98%. The sample was prepared by dispensing 0.3mL of solution onto the paper via single drops onto the center, letting the paper dry between each drop. After dispensing, the entirety of the filter paper was saturated by the solution. It was determined that the concentration of Arsenic on the filter paper was $0.031 \frac{\mu\text{g}}{\text{cm}^2}$. Following the optimization of the system parameters such as repetition rate, Q-switch delay, integration delay, and the translation-stage setting under a vacuum, an integration delay scan was performed to compare the delays: 0.86, 2.01, 2.51, 3.01, 3.51, 4.01, 4.51, and 5.01 μs . It was determined that an integration delay of 3.51 μs yields the spectra with the best signal-to-noise ratio, **Figure 1b**.

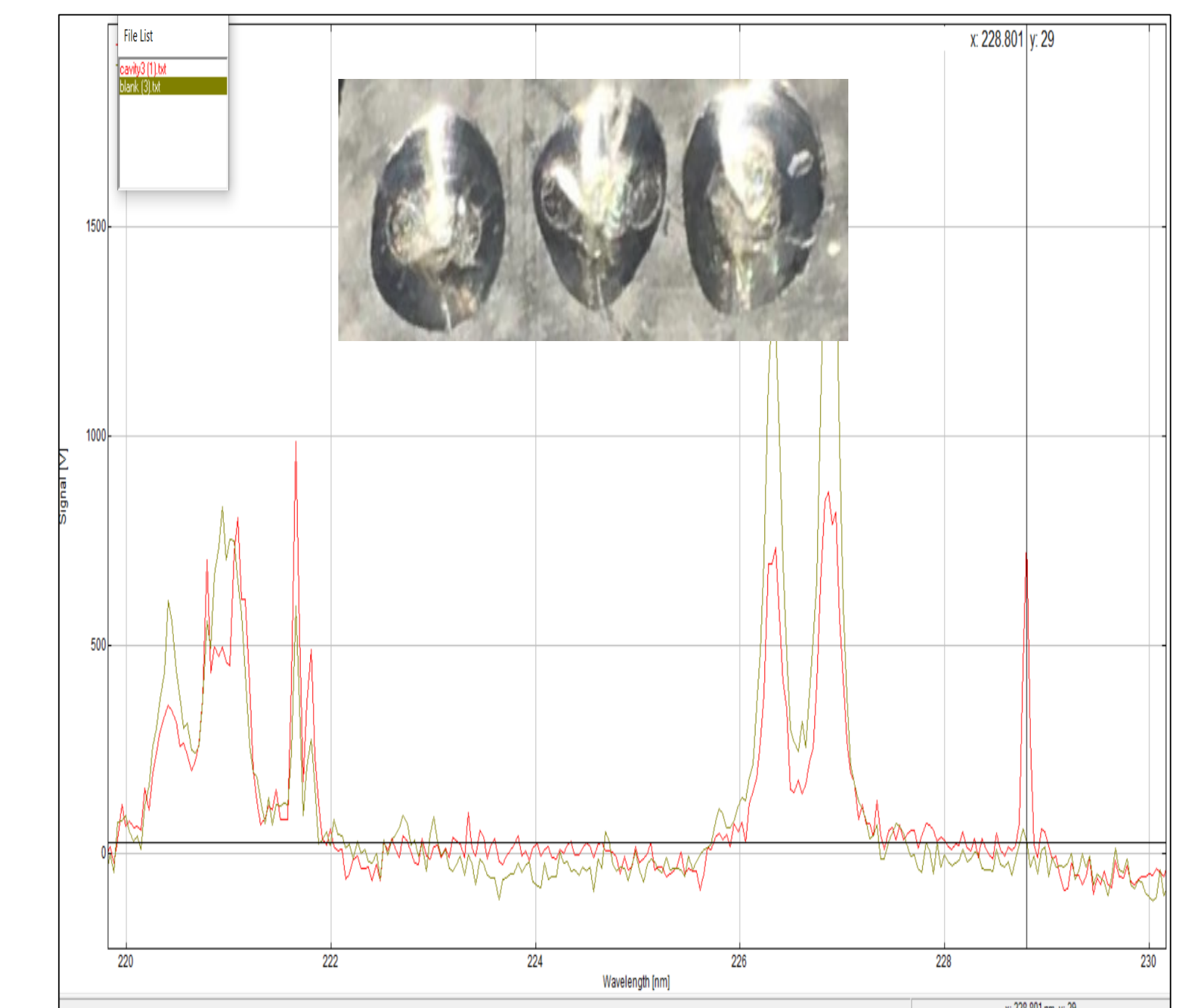


Figure 2: arsenic peaks detected with LIBS

(b) Cavity enhanced LIBS for arsenic detection

Cavity enhanced LIBS testing was performed for arsenic detection. The cavities had a surface area of 0.17cm^2 and were prepared by drilling holes into an aluminum disk. The samples were prepared by dispensing 5 drops of As(V) solution, each drop being 0.01mL, resulting in a As concentration of $0.59 \frac{\mu\text{g}}{\text{cm}^2}$ in each cavity. The testing parameters were a Q-switch delay of 130 μs , a repetition rate of 1Hz, a sample distance of 2mm, an integration delay of 3.51 μs , and an integration gate width of 1.0ms. The results showed strong Arsenic lines at the wavelengths: 228.8 and 234.97nm, **Figure 2**.

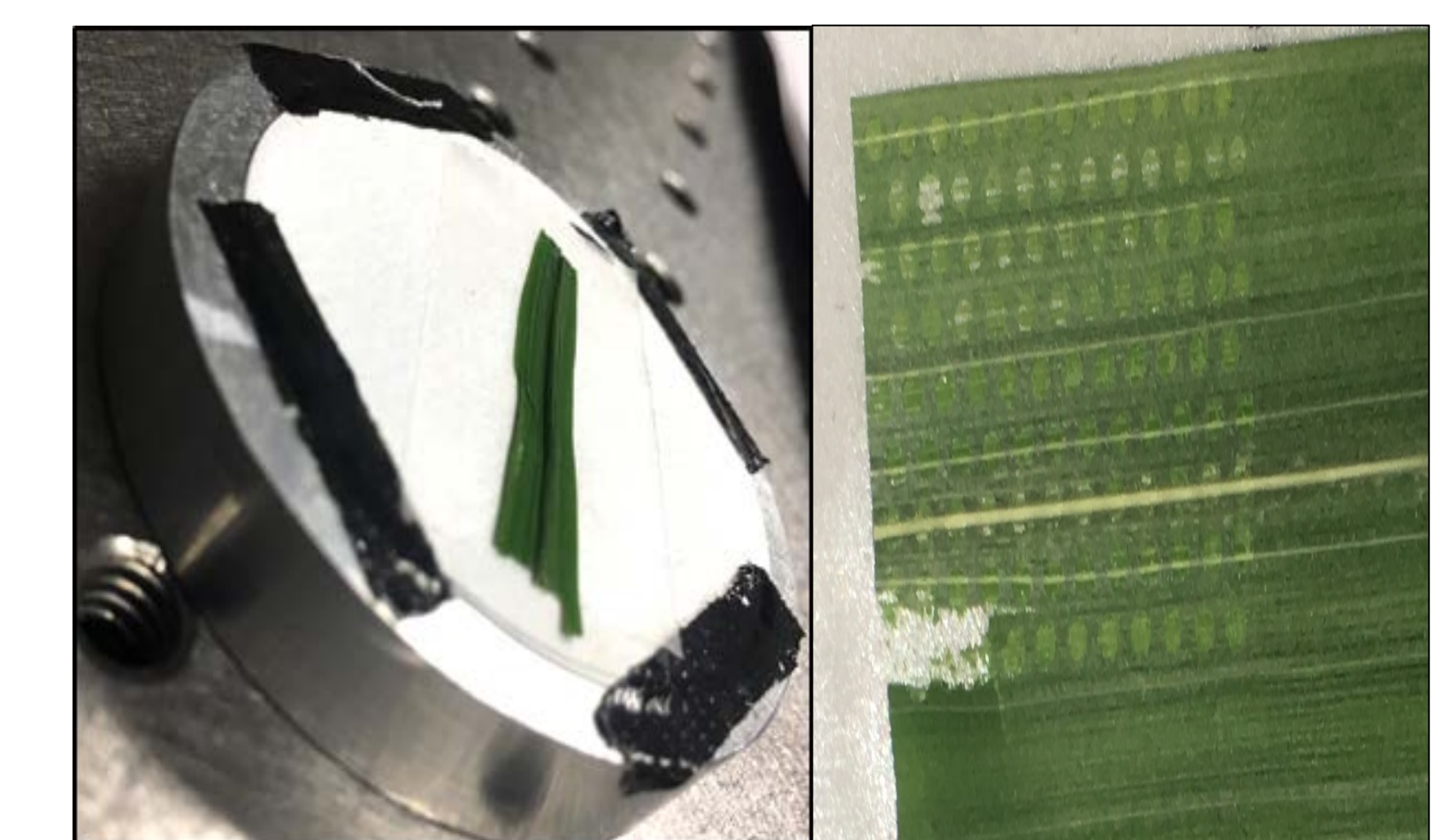


Figure 3: Sample preparation of rice leaves for analysis.

(c) Detection of Arsenic in Rice Leaves

The rice plants used for testing were grown to a mature state, then doped with the previously mentioned As(V) solution. The samples were kept moist in paper towels prior to testing, then a 2cm section of leaf was pressed flat onto a piece of double-sided tape. Beneath the double-sided tape was a filter paper taped to an aluminum block. The first set of testing showed that the ideal parameters were a repetition rate of 1Hz, a sample distance of 2mm, and a step size of 0.75mm. Power scans were then conducted by testing the Q-switch delays: 130, 140, and 150 μs . All testing was performed under a vacuum and Helium gas purge. The other parameters were held constant at the previously optimized settings and an integration delay of 5.01 μs and integration gate width of 1.0ms. It was found that a Q-switch delay of 150 μs achieved the best signal without tearing apart the leaf. The signal was too weak to be detected by LIBS.

Conclusions

LIBS can be an effective in-situ non-destructive method to determine concentrations of heavy metals in plant tissues, however, it is not as sensitive as other destructive methods. It may be used for areas with high background contamination for screening of highly contaminated areas.