

## Laser-induced Breakdown Spectroscopy for *in-situ* Analysis of Nuclear Materials: Aqueous Solution

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### 1. Introduction

Since the laser-induced Breakdown Spectroscopy (LIBS) can measure an analyte rapidly and remotely, it is the most promising technique for monitoring and identifying nuclear materials [1-3]. Rapid and remote can reduce the risk of direct personnel exposure. In addition, this technique does not need sample preparation, thereby preventing waste generation.

This study proposes an *in-situ* analysis method for monitoring nuclear materials. The proposed method attempts to determine the presence of strontium in an aqueous form which is common nuclear fission products. To evaluate the feasibility of LIBS for monitoring nuclear materials in aqueous form, the limit of detection (LOD) for strontium was investigated.

### 2. Experimental and results

#### 2.1. Experimental setup

A compact Q-switched Nd:YAG laser (Quantel, Q-smart 450) with 2<sup>nd</sup> harmonic module which can make frequency doubled so that the wavelength of 532 nm was used to excite targets. It has a 5 ns of pulse width with 1 Hz. An Echelle spectrograph (Andor Me5000, f/7, 200-975 nm wavelength range, 195 mm focal length) fitted with an intensified-CCD (Andor iStar DH334T, 13 x 13- $\mu\text{m}^2$  pixel-size) was employed for acquiring the LIBS spectra.

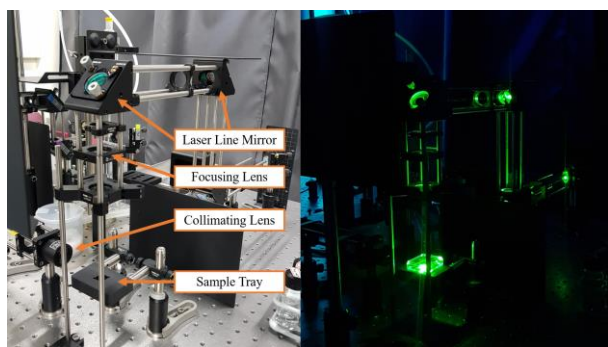


Figure 1. Experimental setup for aqueous samples.

Figure 1 describes the setup of the LIBS detection system for aqueous samples. To irradiate pulse to aqueous sample, the laser must be transmitted from above. For this, three laser line mirrors and a UV fused silica plano-convex lens with a focal length 150 mm

were used to examine the target. For acquiring signals, two plano-convex lenses (75 mm and 100 mm focal lengths, sequentially) were used to focus the plasma emission for delivering to an optical fiber. Finally, the atomic spectra were conveyed to the spectrograph and analyzed.

#### 2.2. Optimization

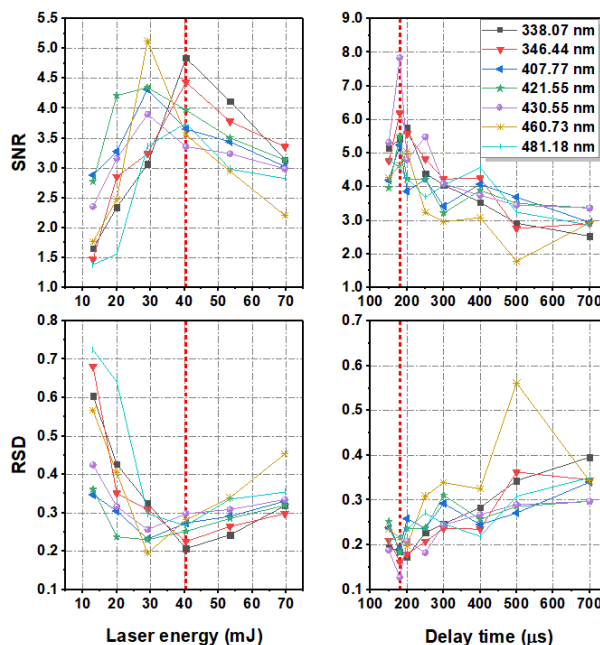


Figure 2. Optimization point of LIBS conditions.

To determine the optimum point of laser energy, gate delay time, and integration time, signal-to-noise ratio (SNR) was investigated with the various condition. The range of 13 to 70 mJ for laser energy and 150 to 700 ns for gate delay time were investigated. Based on the national institute of standards and technology (NIST) atomic spectroscopic database, the spectral emission lines of 338.07, 346.44, 407.77, 421.55, 430.55, 460.73, and 481.18 nm are persistent lines of strontium [4]. Therefore, these spectral lines are selected to determine optimum condition to detect strontium in the aqueous medium.

Since the LOD is calculated using the following equation 1, the SNR and relative standard deviation (RSD) is the most important factor to enhance LOD. As shown in Figure 2, the most significant SNR with the lowest RSD was observed at the laser power of 40.4 mJ

and the delay time of 180 ns. Therefore, these parameters were used to detect strontium in aqueous form.

$$LOD = 3 \cdot S_{bi} \cdot \frac{\Delta C_L}{\Delta I_L} \quad (1)$$

where  $S_{bi}$  is the standard deviation of the blank measures,  $C_L$  is the surface concentration in  $\mu\text{g}/\text{cm}^2$ ,  $I_L$  is the signal intensity.

### 2.3. Samples

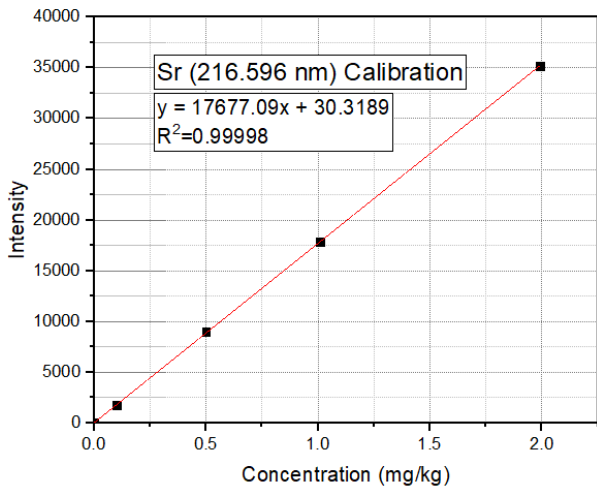


Figure 3. Calibration curve of standard solution for ICP-OES.

To calculate LOD appropriately, 11 samples with various concentration which range is from 15 to 1670 ppm were investigated. The concentrations for all samples were determined by ICP-OES. In Figure 3, the reference calibration curve using ICP standard solution was depicted. After a series of dilution process for our samples, the concentrations of our samples were calculated based on the results of ICP-OES.

For each sample,  $\text{SrCl}_2$  was used due to the highly soluble in water. These 11 samples well determined Sr concentration were investigated by LIBS technique through the single laser shot, thereby reducing the strong splashing for samples which affects the LIBS experiment repeatability and performance analysis. In addition, 30 times of trials using single shot irradiation were conducted and averaged to enhance reliability.

### 2.4. Results

The strontium chloride was detected in eleven different concentration, using a single shot for the LIBS. The elemental spectra of Sr were analyzed at 407.77, 421.55, and 460.73 nm, which are highly detectable in visually. The LODs were calculated to vary considerably in different emission lines.

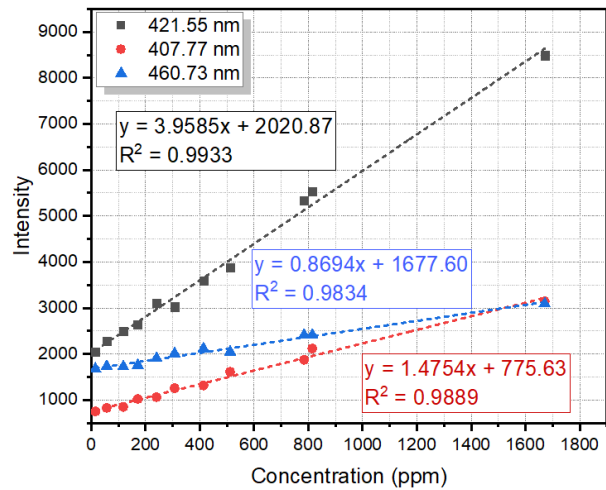


Figure 4. Calibration curve of LIBS investigation for numerous samples.

As shown in Figure 4, the calibration curves of strontium for three persistent emission line were fitted based on the results of LIBS spectra. In the range of 15 ~ 1670 ppm, a good fits with linear regression ( $R^2 = 0.9889$  at 407.77 nm,  $R^2 = 0.9933$  at 421.55 nm, and  $R^2 = 0.9834$  at 460.73 nm) for each three emission were established. The smallest slope of the regression curve was observed at 460.73 nm while the largest slope of the calibration curve was observed at 421.55 nm. Since the LOD was calculated using the slope of the calibration curve, these could affect LOD directly. In addition, clear emission lines of 421.55 nm with different concentration were identified within the LIBS spectra of the aqueous solution as shown in Figure 5. All solid line of Sr corresponds to the concentration shown in Figure 4.

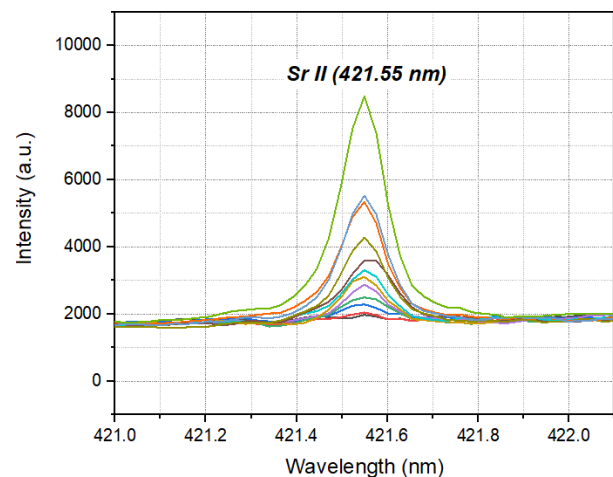


Figure 5. The spectral line of strontium (421.55 nm) with different concentration.

In Table 1, the LODs for each emission line of strontium were listed. The lowest LOD was observed at 407.77 nm even though the largest slope of the calibration curve was founded at 421.55 nm. This is

because of a tiny amount of standard deviation of blank measurements for 407.77 nm. Compared to 421.55 nm, the standard deviation of blank for 407.77 nm is about 3.8 times more stable. However, the large slope of 421.55 nm makes the LOD decrease so that not much difference was founded.

In the case of 460.73 nm, relatively poor detection sensitivity in terms of LOD was caused by the significantly high standard deviation of blank measurements. In addition, the lowest slope under than 1 (0.8694) makes worse to LOD. Based on the experimental data, these results imply that the LOD is highly dependent on the emission line for the aqueous sample.

Table 1. The LOD for each emission lines of strontium.

Wavelength	407.77 nm	421.55 nm	460.73 nm
LOD (ppm)	197.805	285.579	862.108

### 3. Conclusion

These preliminary results show the LIBS can be used for a potential method monitoring nuclear materials in various application. Since the experiment for each trial only required 1 ms, this technique is well suit for on-line monitoring systems such as pyro-processing, liquid waste treatment, and environmental monitoring. However, the LOD should be studied more to enhance the advantage of the LIBS. This can be achieved through accumulating the laser pulse certain times which require about a few seconds. Normally in the LIBS technique, accumulating laser pulse can enhance the signal-to-noise ratio in proportion to the square, thereby enhancing the LOD about thousands of times with certain times of accumulating.

### Acknowledgement

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