Enhancement of Laser-induced Breakdown Spectroscopy Detection Limit for Analyzing Aqueous Solution

Yunu Lee, Sungyeol Choi*
Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
**Corresponding author: sungyeolchoi@kaist.ac.kr*

1. Introduction

While monitoring the radioactive materials in the industrial field is essential, the slurry or aqueous solution including numerous radioisotope make difficult to detect radioactivity for each radioisotope [1-4]. Besides, the environment of a chemical plant which treats highly toxic materials is normally hard to access.

To monitor the radioactive materials in the harsh environment, laser-induced breakdown spectroscopy (LIBS) has been considered. This is because the LIBS can detect analytes remotely and rapidly. For in-situ multi-element analysis, LIBS is the most promising technique as a fast-developing technique. Besides, this technique does not need sample preparation, thereby preventing waste generation. However, there are some technical difficulties for measuring liquid samples. For example, the sample could be splashed to the surroundings by the shock wave arising from plasma breakdown. These can make contamination of optical parts that can distort the laser light or spectra.

In this study, we proposed a single-shot LIBS analysis and a new system configuration which can treat light distortion problems. The proposed methods are a single-shot LIBS analysis which can minimize the contamination of optics and a new system configuration that can erase the splashed samples from the lens. To evaluate the validity of the proposed method, relative standard deviation (RSD) and the limit of detection (LOD) were investigated.

2. Experimental and results

2.1. Experimental setup

A Q-switched Nd:YAG laser (Quantel, Q-smart 450) with 2nd harmonic module which can make frequency-doubled so that the wavelength of 532 nm was used to excite targets. It has a 5.5 ns of pulse width with 1 Hz. 1Hz can reduce the amount of splashed sample. 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-μm^2 pixel-size) was employed for acquiring the LIBS spectra.

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.

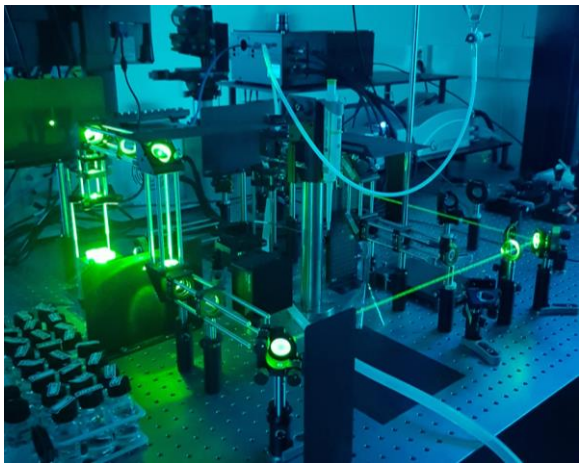

Figure 1. Experimental setup for analyzing aqueous solution.

Figure 2 describes two proposed methods that can treat contamination problems. Normally, the LIBS signals are accumulated about few decades to hundreds of shots to enhance the sensitivity. In this process, the splashed samples are accumulated to optical parts. Therefore, we investigated the ability of LIBS sensitivity when it used single-shot analysis. The single-shot analysis can reduce the contamination a lot. Second, we suggest a gas protective layer that can block the splashed samples.

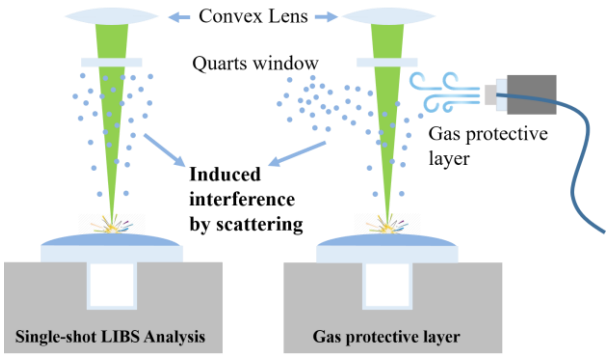

Figure 2. Schematic view of proposed methods. Left: Single-shot LIBS analysis, Right: Gas protective layer.

2.2. Optimization

Figure 3 and 4 describe the amount of contamination by splashed samples after laser irradiation. Figure 3 shows the optical window without a gas protective layer. While there is no significant contamination under 800 shot irradiation, the considerable splashed samples are deposited on the optical window when irradiating laser pulse more than 1200 shots as shown in Figure 3.

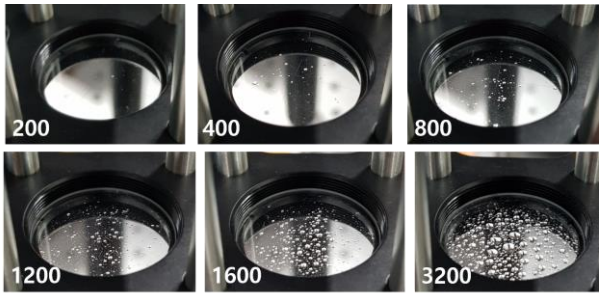

Figure 3. The amount of splashed sample onto an optical window without gas protective layer. From top to bottom, the contamination when 200 times shot to 3200 times shot irradiation.

Figure 4 shows the optical window with a gas protective layer. The considerable amount of splashed samples are blocked by a gas protective layer. Since the splashed samples for each laser irradiation have a tiny mass, gases which have low flow rate are enough to protect the optical parts from the contamination. As shown in Figure 4, the optical window is clean so that it cannot affect to LIBS analysis.

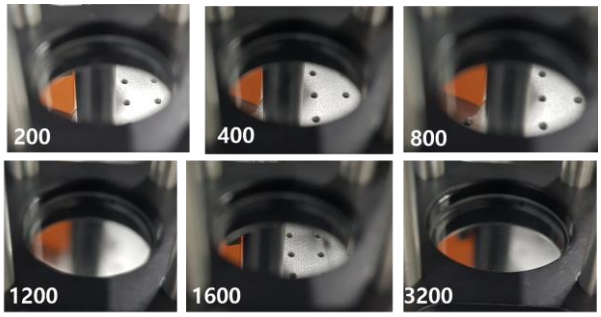

Figure 4. The amount of splashed sample onto an optical window with gas protective layer. From top to bottom, the contamination when 200 times shot to 3200 times shot irradiation.

To compare single-shot LIBS analysis and normal LIBS analysis with gas protective layer appropriately, optimization processes are conducted. The optimization process in the LIBS technique is finding a point of the highest signal-to-noise ratio (SNR). This is because the SNR is defined as the average overtime of the peak signal divided by the root mean square noise of the peak signal over the same time. Therefore, the RSD could be reduced as much as possible for each proposed experimental trials.

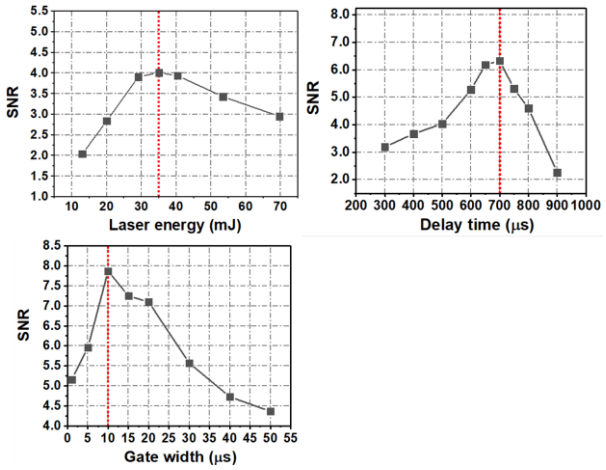

Figure 5. Optimization of LIBS parameters.

LIBS is a type of atomic spectroscopy. The laser pulse is used as an excitation source to make plasma plume at an interesting point. Since the atoms and ions can be excited by absorbing laser energy, the atomic spectrum is emitted through the returning to the ground state. The emitted spectrum is transmitted to a spectrograph and recorded to intensified-CCD. Therefore, three parameters are needed to investigate SNR.

Since laser energy is used to make plasma formation, it should be investigated. Delay time is defined the time after laser pulse left from the main laser body. The suitable delay time is needed because the atomic spectrum does not emit immediately. Gate width is defined as the time from when the shutter is opened in the intensified-CCD to accumulate the light to when the shutter is closed. Therefore, immoderate gate width does not suitable for analyzing the LIBS signal due to the large background noise.

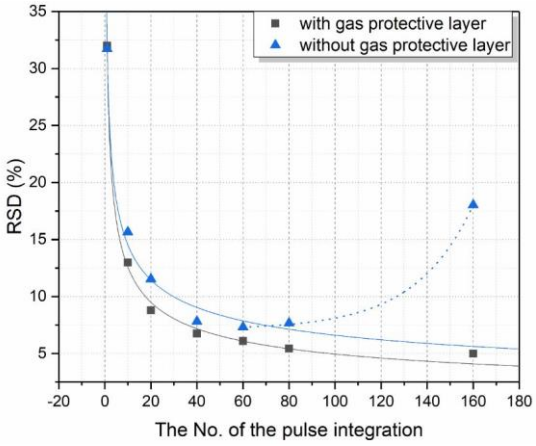

Figure 6. Relative standard deviation with the number of the pulse integration for comparing with/without gas protective layer.

Figure 6 describes the differences of RSD whether the gas protective layer exists or not. For each experimental result, 20 shots were averaged. The effectiveness of RSD enhancement due to the pulse integration without gas protective layer was saturated at 40 ~ 80 times of the pulse integration. More than 60 times of the pulse integration, RSD has been worsened. These correspond exactly with the contamination of optical window shown in Figure 3. Although the optical window was quite clean until 800 times irradiation, we cannot use this any correction when considering the repetition of experiments and various samples with different concentration to make the calibration curve. Therefore, we only conducted the single-shot LIBS analysis for proper uses.

However, the optical window in the experimental setup with a gas protective layer is clean even though 3200 shots irradiation. Accordingly, the RSD has been become smaller by how much it accumulated. The enhancement of RSD when using gas protective layer is getting saturated after the 80 pulse integration. Therefore, we calculate the LOD when using gas protective layer by accumulating 80 signals.

2.3. Results

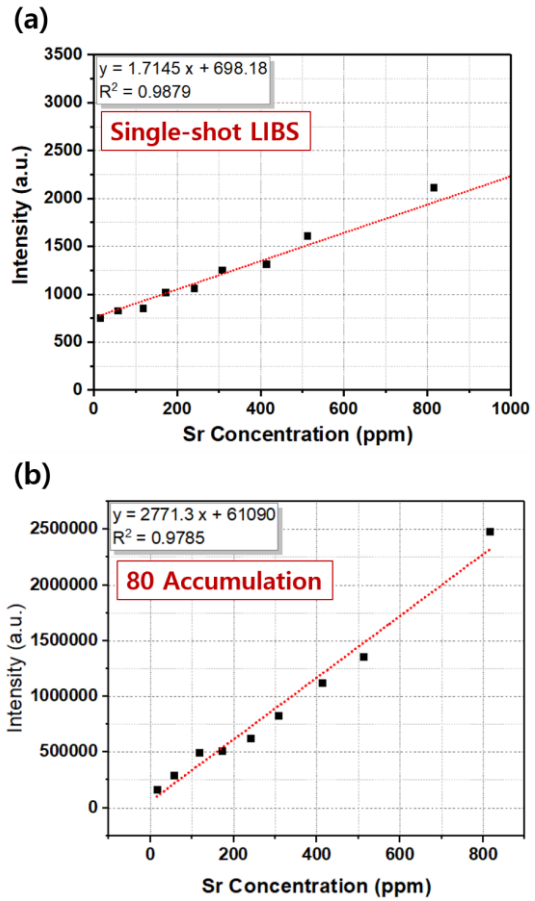

Figure 7. Calibration curve of single-shot LIBS (a) and 80 accumulation results with gas protective layer (b).

Table 1. Limit of detection for two proposed method.

	Single-shot LIBS	***Accumulation with gas protective layer***
LOD (ppm)	**245.7529**	**14.99243**

Figure 7 describes the calibration curves of two proposed method and Table 1 listed the LOD for each method. In Figure 7, the slope of the calibration curve for single-shot analysis is about 1600 times smaller than accumulation data with a gas protective layer. Accordingly, the calculated LOD is also 16 times larger than the accumulation case.

3. Conclusion

This preliminary result shows the gas protective layer can be a useful way to overcome the technical difficulties for analyzing LIBS signal in the aqueous or slurry solution. The LOD of single-shot LIBS is about 245 ppm, while accumulation result with the gas protective layer is about 15 ppm. The gas protective layer was demonstrated that it can block the splashed samples very efficiently and does not affect to LIBS signals. This small technique can treat the complicated problems of liquid LIBS analysis that can be used in a harsh environment such as highly toxic chemical plants or highly radioactive environments.

Acknowledgement

This work was supported by the Nuclear Safety Research Program through the Korea Foundation of Nuclear Safety (KOFONS), granted financial resource from the Nuclear Safety and Security Commission (NSSC), Republic of Korea (Grant No.1703008-0117-SB110).

REFERENCES

[1] I. Gaona, J. Serrano, J. Moros, J.J. Laserna, Evaluation of laser-induced breakdown spectroscopy analysis potential for addressing radiological threats from a distance, Spectrochimica Acta Part B: Atomic Spectroscopy, 96 (2014) 12-20.
[2] A.M. Popov, A.N. Drozdova, S.M. Zaytsev, D.I. Biryukova, N.B. Zorov, T.A. Labutin, Rapid, direct determination of strontium in natural waters by laser-induced breakdown spectroscopy, Journal of Analytical Atomic Spectrometry, 31 (2016) 1123-1130.
[3] M.Z. Martin, S. Allman, D.J. Brice, R.C. Martin, N.O. Andre, Exploring laser-induced breakdown spectroscopy for nuclear materials analysis and in-situ applications, Spectrochimica Acta Part B: Atomic Spectroscopy, 74-75 (2012) 177-183.

[4] A.M. Popov, A.N. Drozdova, S.M. Zaytsev, D.I. Biryukova, N.B. Zorov, T.A. Labutin, Rapid, direct determination of strontium in natural waters by laser-induced breakdown spectroscopy, Journal of Analytical Atomic Spectrometry, 31 (2016) 1123-1130.