

Study of laser-induced breakdown spectroscopy from micro-droplet of NaCl Solution

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Abstract— The laser-induced breakdown spectroscopy (LIBS) using micro-droplet sodium chloride solution is presented. Micronizing the sample made possible that whole volume of a sample was confined in the laser beam spot area and was separated from its surrounding condition. If the sample's physical state was liquid, the density of solution could be controlled as needed. Originally designed ink-jet system for sampling procedure was presented. According to the new method, improved calibration curves for the LIBS quantitative measurement were obtained.

I. INTRODUCTION

In the laser-induced breakdown spectroscopy (LIBS) technique, a high energy laser pulse is focused on a sample to create plasma. Emission from the atoms and ions in the plasma is collected using lenses, guided to a spectrograph, a streak camera or some other gated detector and analyzed by a computer.

LIBS is investigated extensively to establish proper chemical analysis of specimens. LIBS is a useful method for determining the elemental composition of various materials regardless of their physical state, (solid, liquid and gas) without any preprocessing. While qualitative analysis results can be obtained with such spectrum using a wavelength calibration reference, quantitative analysis can be obtained on the basis of the time integrated amount of intensities from the emission.

In the quantitative analysis, optimizing experimental key parameters of proper spark alignment, time gate delay, and wavelength gate width allowed determining experimentally the limit of detection (LOD). Qualitative results can be obtained with such spectrum using a wavelength calibration reference. There are several methods for LIBS analysis not only to obtain spectral wavelength but also the amount of intensities from the emission. The intensities can be compared with standard atomic line references. It is called optical emission spectroscopy (OES) analysis. Another method is chemometric analysis based on comparing to samples of known composition. Those methods are intensity

calibration references. Calibration curves can be obtained from this intensity calibration method.

We were researching and developing the LIBS technique concerning the quantitative analysis that could be used for each LIBS system for various fields. To establish a practical proper calibration method for quantitative analysis in various states, namely gas, liquid, and solid, we proposed the LIBS technique using a micro-droplet ejection system. The micro-droplet ejection technique of the piezo type ink-jet system was used to delimit the accuracy of solution's sample.

First measurements were performed within a bulk liquid cell. Then liquid was ejected by ink-jet system. In this paper, an originally designed LIBS set-up and experimental data of the sodium chloride solution ejected by an ink-jet head presented here contributes to improvement of calibration curves quality.

II. EXPERIMENTAL SET UP

A. LIBS system using a bulk liquid cell

The LIBS system using a bulk liquid cell is shown schematically in Fig. 1. Nd:YAG laser (Big Sky Laser model ultra) was controlled by a delay pulse generator (Stanford Research System, Inc., Model DG-535).

This laser operated at the 1064nm fundamental wavelength used to generate 50mJ/pulse of 8ns width (FWHM). When used for the ablation, the laser pulse was focused with a 50mm focal length lens, yielding a power density of a 10^{12} W/cm². Emission from the laser-produced plasma was collected using lenses and guided to a spectrograph (CHROMEX 250is). Then the emitted light was dispersed by a 1200-lines/mm diffraction grating and an electrical signal was recorded using a streak camera (Hamamatsu Photonics) with 10-ps time resolution or higher. Finally the signal was processed and stored in a computer.

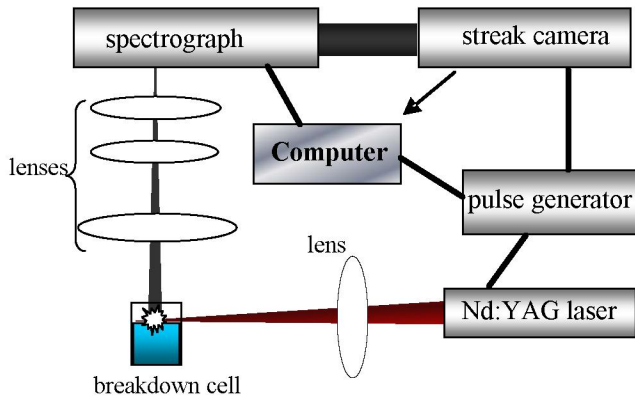


Fig. 1. Schematic diagram of LIBS experiment using bulk liquid cell

In Fig. 2, the comparison of emission focused (a) inside of the sodium chloride solution and (b) on the solution surface is shown. We compared the LIBS data obtained from those measurements.

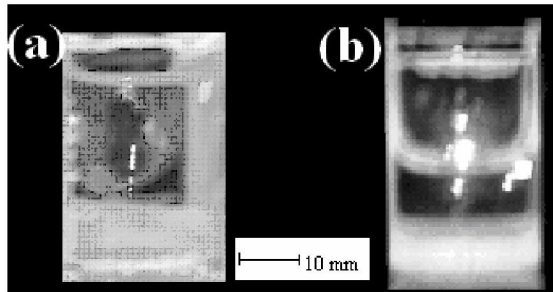


Fig. 2. Comparison of breakdown emission made (a) in the solution and (b) at the solution surface

The surface emission had greater intensity than that of inner emission. The life time of plasma in a bulk liquid was shorter than that generated at the liquid surface because most of the energy produced by laser was utilized to heat the sample. Also, the laser beam was affected by refraction through the sample liquid and then plasma region was narrowed.

We used the method (b): focusing on the sample surface and recorded the emission intensity of sodium atomic species at the spectral region near 589nm repeatedly.

B. LIBS system using a micro-droplet ejection system

The LIBS system using a micro-droplet ejection system is shown in Fig. 3. The micro-droplet was released using originally designed set up with ink-jet head. The sample solution was injected into the piezo head from the syringe through the filter. Electric signal of certain shape was generated by a wavy synthesizer (NF Corporation, model WF1945B), and it was transmitted through the piezo drive unit. The ink-jet head was covered with the quartz beaker. Function of the wind breaking, the liquid recovering, and the additional beam condensing had been provided.

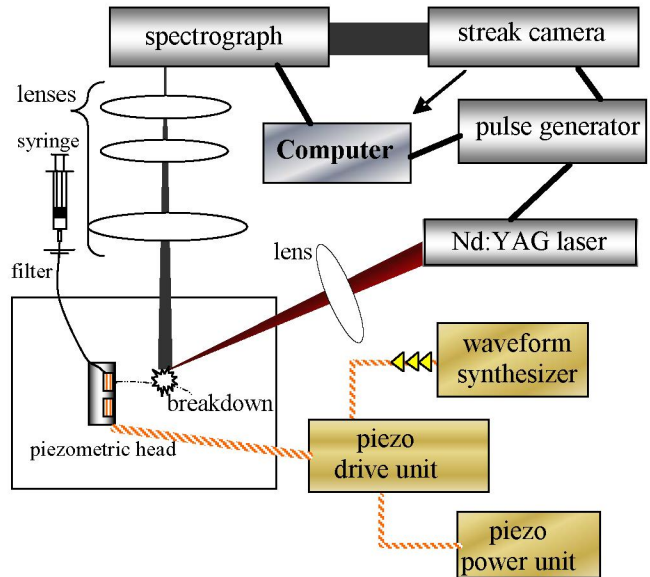


Fig. 3. Schematic diagram of LIBS experiment using micro-droplet ejection system

In Fig. 4, a piezo head that called “shear mode type” used in this experiment is shown. Some channels and actuators were formed of piezoelectric zirconate titanate (PZT) substrate of a piezo-electric element. Wiring that added the voltage was bonded to the actuator respectively. The actuator was bonded to the upper surface of the channel with the cover plate and fixed. The nozzle plate was bonded in front of the channel.

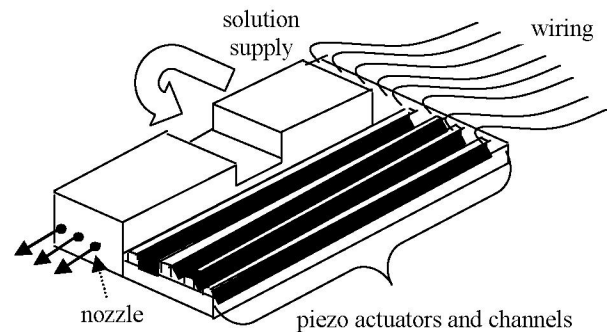


Fig. 4. Structure of shear mode piezometric head

Fig. 5 shows the micro-photograph of the nozzle plate surface. The nozzle diameter and the channel pitch were $52.4\mu\text{m}$ and 0.46mm , respectively. Adding the electric field in an orthogonal direction where the piezoelectric element was polarized led to the actuator winding transformation, and to pressurizing of solution in the channel. The pressure generated in the channel spread, the pressure wave reflected between the nozzle and the solution supply room, and the damped oscillation was generated while resonating. That was a mechanism to eject micro-droplet by receiving the pressure of resonance with time.

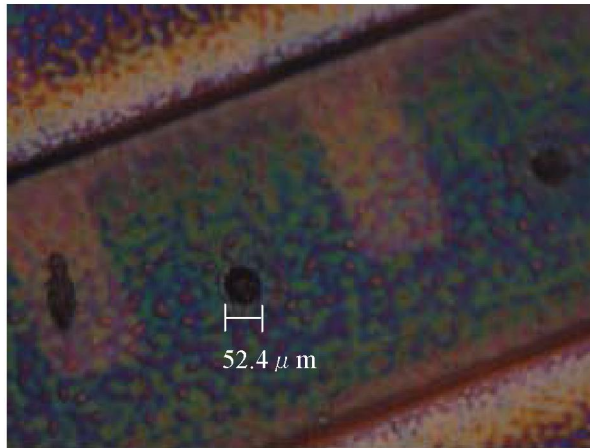


Fig. 5. Photo of a nozzle plate: Nozzle diameter $52.4\mu\text{m}$

At first, the channel room capacity was shrunk by the first pulse created by a piezo-electric element voltage with rising edge and the solution was pushed out. Next, the channel room capacity returned with falling edge of the pulse, and the meniscus on the surface of the solution at the nozzle was drawn in.

In the pull-push drive, meniscus was ejected from the nozzle when the velocity of the droplet became the maximum, and decelerated monotonously until the ejection of the liquid reversed. Therefore, the ejection velocity of droplet at the front edge was faster than the rear end, then ejected in the shape of spindle. The micro-droplet volume was calculated using the equation (1).

$$V_d = \frac{\pi r^2 v}{2f} \quad (1)$$

V_d – volume of micro-droplet,

r – nozzle radius,

v – micro-droplet ejection velocity,

f – resonance frequency,

III. RESULTS AND DISCUSSION

We obtained the results about the breakdown emission intensities from 0.1M to 1.0M density of sodium chloride solution with a bulk liquid cell. Fig. 6 shows the error ranges of this result. Analysis based on data taken from 100 shots laser pulse, the central gate point was $18.1\mu\text{s}$ from trigger-in and the gate width was $3.9\mu\text{s}$. This analytical condition was optimized at the sample of 0.1M sodium chloride solution. It indicates that when one draws a calibration curve, there are a few data points from the optimum data point. There were some problems associated with sample solution splashing when measurements were made at the solution surface. For calibration purpose, the fluctuation in droplet size distribution at the time of laser spark created problems.

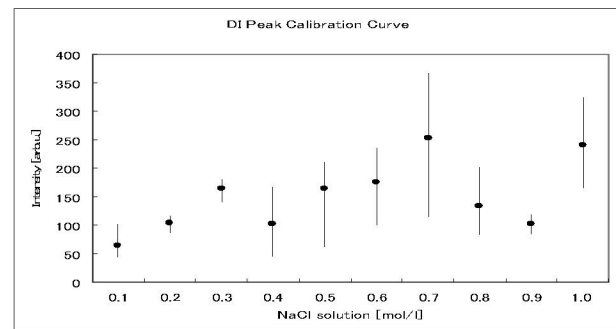


Fig. 6. The error ranges of each concentration from 0.1M to 1.0M at 100 laser shots

On the other hand, in the case of LIBS using a micro-droplet ejection system, we obtained different data. The comparison between the experimental data of micro-droplet ejection system and the one of previous bulk-liquid type is shown as follows.

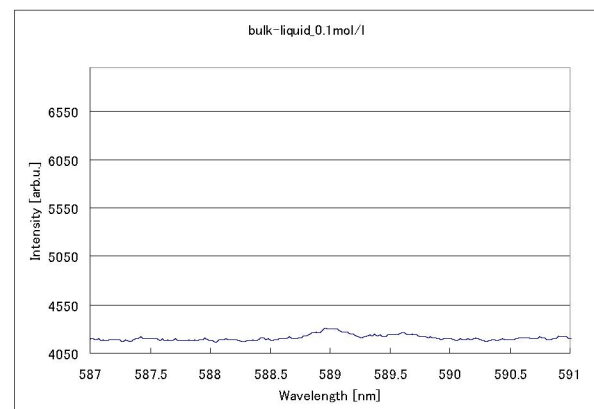


Fig. 7. Intensity of Na 589 nm emission lines, bulk-liquid type, 0.1M density of solution

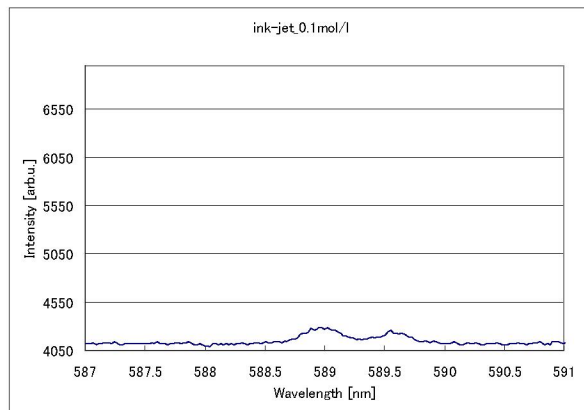


Fig. 8. Intensity of Na 589 nm emission lines, micro-droplet type, 0.1M density of solution

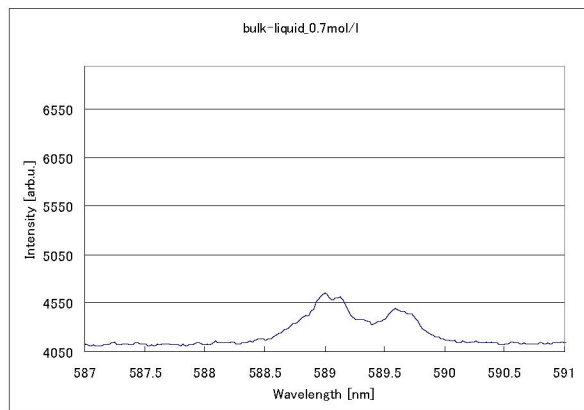


Fig. 9. Intensity of Na 589 nm emission lines, bulk-liquid type, 0.7M density of solution

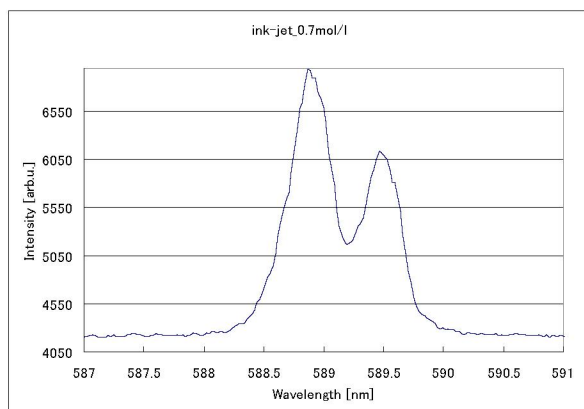


Fig. 10. Intensity of Na 589 nm emission lines, micro-droplet type, 0.7M density of solution

The experimental data for 0.1M and 0.7M density sample as an example of comparing the experiments on bulk-liquid type and micro-droplet type are shown in Figs. 7 ~ 10. In Fig. 7 and Fig. 8, data show that ink-jet micro-droplet's intensity was a little higher than in the case of bulk-liquid type. On the other hand, it was clearly shown that huge difference of intensity exists between the solution of 0.7M density in Fig. 9 and Fig. 10. It was proved that in fixed quantity measurement of LIBS, calibration curve calculated with micro-droplet type cannot be used with the bulk-liquid quantizing method.

IV. CONCLUSIONS

0.7 M density solution showed low intensity in the case of sample form of bulk-liquid type. It turned out that a different data were obtained and different calibration curves would be obtained even with the same solution, if different types of LIBS experimental set up were used. It could be caused by the increased emission within the solution of decentralized and uniformly distributed NaCl particles. This was the first time, to our knowledge, that micro-droplet ejection system in LIBS experiment was employed.

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