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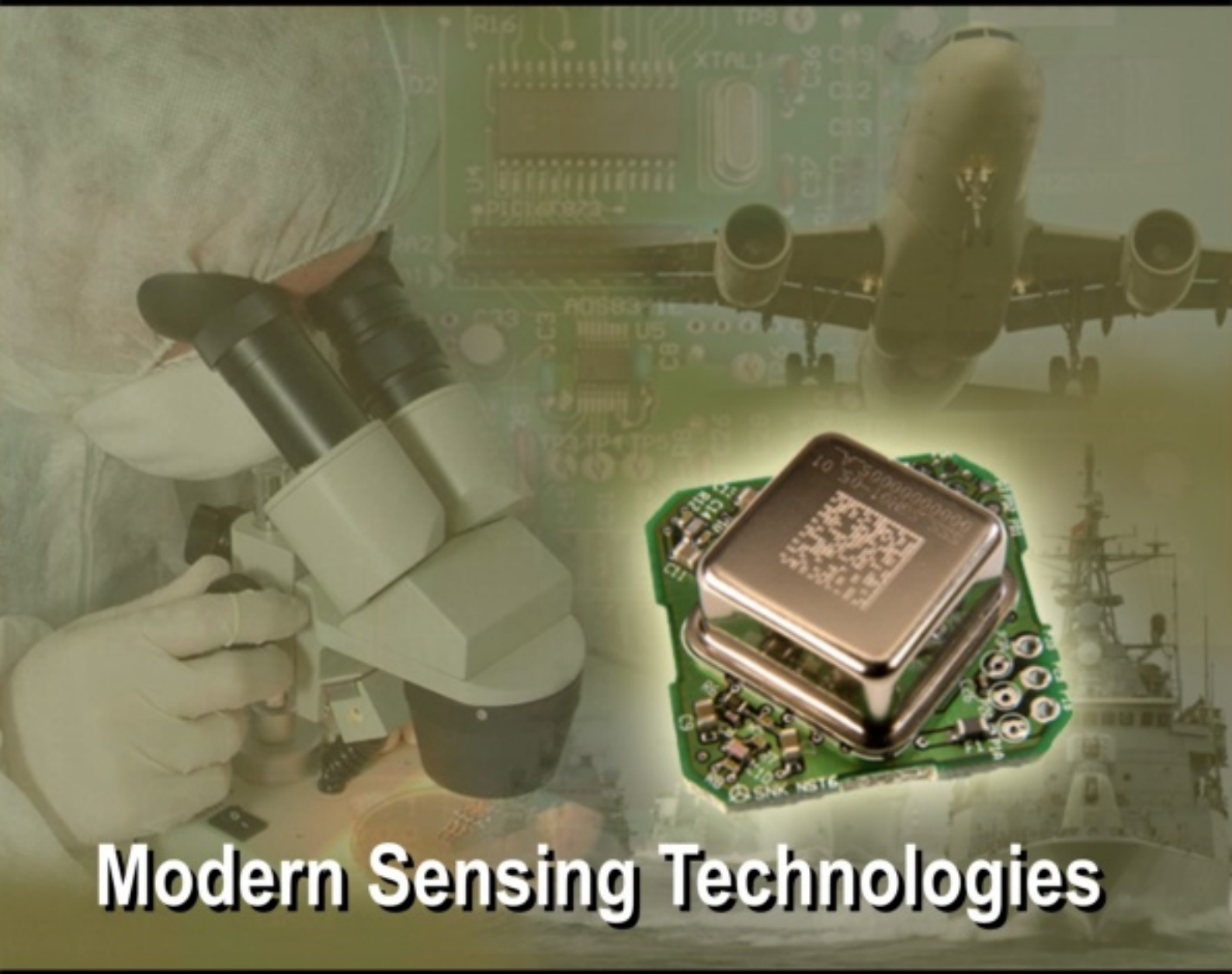

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Sensing Technique Using Laser-induced Breakdown Spectroscopy Integrated with Micro-droplet Ejection System

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Abstract: In this paper, laser-induced breakdown spectroscopy (LIBS) using micro-droplet NaCl solution is described. Since the 1980s, many liquid micronizing techniques for LIBS measurements have been reported. In this study, micro-droplet ejection systems for sampling are designed and presented for two volumes. These micro-droplet ejection systems enable a constant volume of the sample liquid to be obtained and they take advantage of the liquid physical state; the density of the solution can be controlled accurately. The methods presented here generate small droplets (diameter 30 or 50 μm) by confining the entire volume of the sample material in the laser beam spot area (minimum beam spot diameter: 53.2 μm) and separating it from its surroundings. Using these liquid micronizing methods, improved sensitivities are obtained for drawing calibration curves for quantitative LIBS measurements.

Keywords: LIBS, quantitative measurement, Laser, Micro-droplet

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of various materials regardless of their physical state (solid, liquid, or gas) and without any preprocessing; it is a type of atomic emission spectroscopy (AES). In the LIBS technique, a high-energy laser pulse is focused on a sample to create plasma. Emissions from atoms and ions in the plasma are collected using lenses, guided toward a spectrograph, a streak camera, or some other gated detector, and analyzed by a computer. Some of the well-known AES methods for vaporization and excitation involve electrode arcs and sparks, inductively coupled plasma (ICP), direct-coupled plasma (DCP), and microwave-induced plasma (MIP). These methods typically require laboratory analytical facilities for

specific use. AES-based methods for elemental analysis have an advantage: the capability to detect all kinds of elements or multielements simultaneously. In addition, since it requires only optical access to the sample, LIBS has many advantages: it facilitates real-time analysis and *in situ* analysis. LIBS has been investigated extensively to establish a method for the proper chemical analysis of specimens [1]–[3]. Although qualitative analysis results can be performed for a spectrum only by using a wavelength calibration reference, quantitative analysis can be carried out on the basis of several fundamental approaches using conventional methods that require many calibration processes [4] [5].

In this study, the measurements are based on fundamental approaches for quantitative analysis (microsecond time-gated spectroscopy) and on the repetitive single spark for averaging the spectra from many shots. Optimizing the key experimental parameters—proper spark alignment, time-gate delay, and intensity gate width—allows the experimental determination of the detection limit. The intensities can be compared using standard atomic line references, and this method is called optical emission spectroscopy (OES) analysis. Another method is chemometric analysis and it based on the comparison of samples with known composition. This study is based on OES analysis that uses calibration curves obtained from the intensity calibration method.

Figs. 1 and 2 show the evolution of the atomic spectrum of a Na powder sample. The spectrum evolves as the plasma cools. In Fig. 1, the earliest time of the plasma emission is dominated by a continuum that cannot be distinguished from the atomic spectrum. This overlapping is caused by "Bremsstrahlung radiation" and recombination radiation from the plasma as free electrons and ions recombine in the plasma cooling process. The plasma expands with time and the excited species relax further. Fig. 2 shows the spectrum after around 1 μs from the time discrete spectral lines originating from various ionic species start to become visible. After the creation of plasma, both the signal and background emissions evolve and decay at their own rates. The background emission decays at a considerably faster rate as compared to the NaCl atomic emission. To obtain a good signal-to-background ratio, a proper time-gate setting is important.

Our group has been developing the LIBS technique for quantitative analysis so that the LIBS system can be applied to various fields. A large amount of calibration reference data on the intensity, particle size, and air pressure has been obtained [6]–[8]. In addition to this reference data, in order to establish a practical calibration method for quantitative analysis in various environmental conditions, a LIBS solution concentration calibration technique has been developed by using a micro-droplet ejection system with the aim of performing absolute calibration. By using LIBS measurements, the sensitivity of this new method using an inkjet system is compared to that of the conventional technique employing a bulk liquid cell.

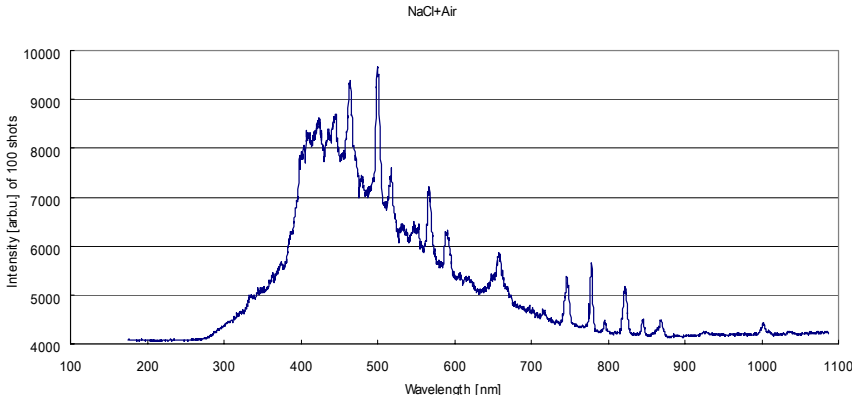

Fig. 1. Breakdown spectrum of NaCl crystal powder from t = 0 to t = 100 ns.

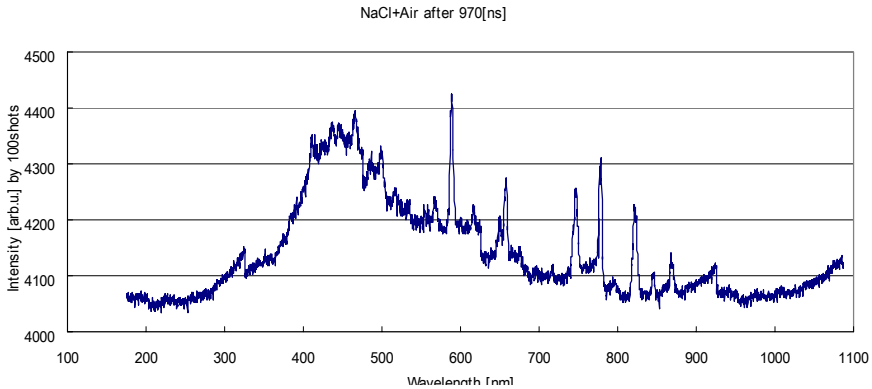

Fig. 2. Breakdown spectrum of NaCl crystal powder from t = 970 to t = 1070 ns.

2. Experimental Setup

2.1. Bulk Liquid Cell LIBS System

This system is represented schematically in Fig. 3. The Nd:YAG laser (Big Sky Laser; model: Ultra) was controlled with the delay pulse generator (Stanford Research System, Inc., Model DG-535).

The laser was operated at 1064 nm to generate a 50-mJ pulse with a width of 8 ns (FWHM). When used for ablation, the laser pulse was focused with a lens that had a focal length of 50 mm, thereby yielding a power density of 10^{12} W/cm^2. Emissions from the laser-produced plasma were collected using additional lenses and they were then guided to a spectrograph (Chromex 250IS). Subsequently, the emitted light was dispersed using a diffraction grating with 1200 lines/mm and the electrical signal was recorded using a streak camera (Hamamatsu Photonics) with a time resolution of 10 ps or greater. Finally, the signal was processed and stored in a computer.

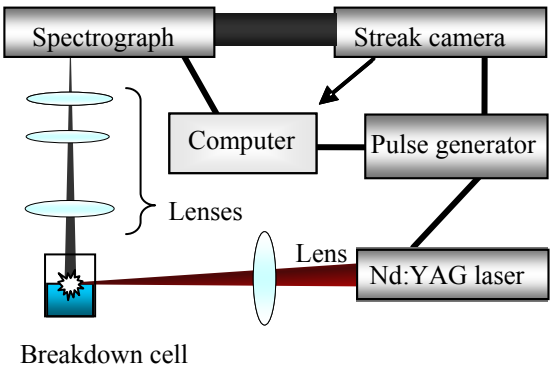

Fig. 3. Schematic representation of LIBS experiment using a bulk liquid cell.

A comparison of the emissions focused (a) into the NaCl solution and (b) on the solution surface is shown in Fig. 4. The LIBS data obtained from the measurements were compared.

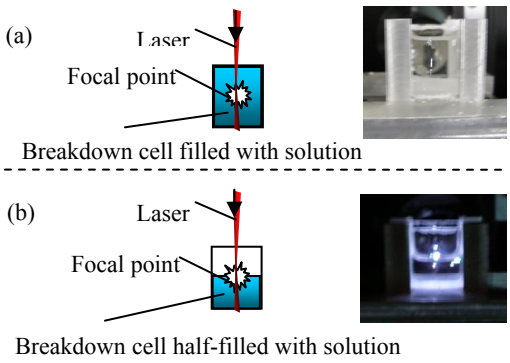

Fig. 4. Comparison of breakdown emission (a) in solution and (b) at the solution surface.

The surface emission had a greater intensity as compared to the internal emission. The lifetime of plasma in a bulk liquid was shorter than that of plasma generated at the liquid surface as most of the energy produced by the laser was utilized for heating the sample. Further, the laser beam was affected by refraction while passing through the sample liquid, causing the plasma region to become narrow.

As a bulk liquid measurement, type (b) in Fig. 4 was used and the emission was focused on the sample surface. The emission intensity of Na atomic species in the spectral region near 589 nm was repeatedly recorded.

2.2. LIBS Experiment Using 50-µm Micro-droplet Ejection System

A schematic representation of this system is shown in Fig. 5. The micro-droplet was released using the piezo head. The sample solution was injected into the piezo head. An electric signal with a specific shape was generated using a wave synthesizer and transmitted through a piezo drive unit. The piezo head was covered with a quartz beaker. The system was designed for wind breaking, liquid recovery, and additional beam condensing functions.

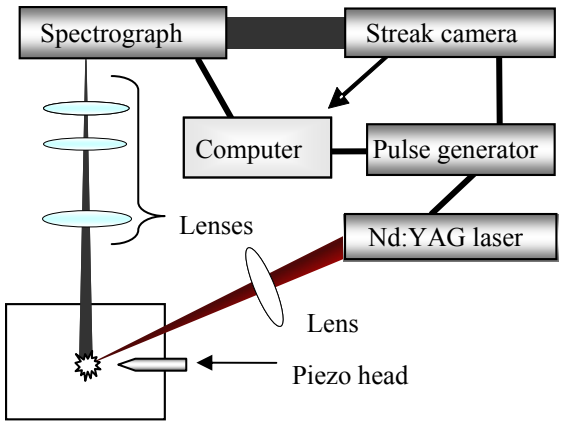

Fig. 5. Schematic representation of LIBS experiment using a 50-µm micro-droplet ejection system.

The "shear-mode-type" piezo head [9] used in this experiment is shown in Fig. 6. The channels and actuators were formed from a piezoelectric element on a lead zirconate titanate (PZT) substrate. The wires for the voltage input were fixed to the actuator. The actuator was attached to the upper surface of the channel using the coverplate and was maintained in a fixed position. The nozzle plate was glued to the front of the channel.

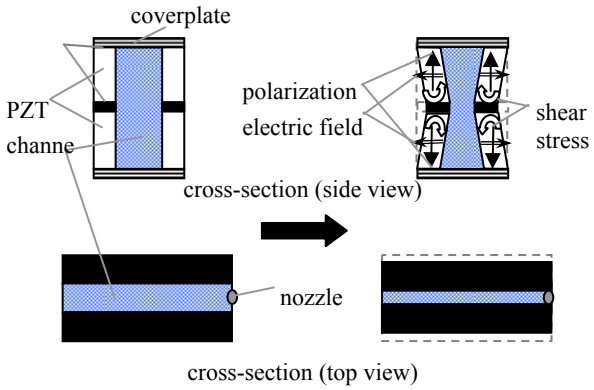

Fig. 6. Structure of shear-mode-type piezo head.

Providing an electric field in a direction orthogonal to the polarization direction of the piezoelectric element leads to actuator winding transformation and the pressurization of the solution in the channel. Pressure was generated in the channel and it spread until the pressure wave was reflected between the nozzle and the solution supply area, and damped oscillations were generated when the pressure wave resonated. This mechanism caused the ejection of micro-droplets by receiving the pressure resonance over a period of time.

2.3. LIBS Experiment Using 30-µm Micro-droplet Ejection System

A schematic representation of the LIBS system using a 30-µm NaCl solution droplet is shown in Fig. 7. The Nd:YAG laser was controlled with the delay pulse generator. The micro-droplet was released by using the dispenser head. Fig. 8 shows the scheme of the micro-droplet subsystem. The sample solution was injected into the piezo head. The micro-droplet generating electric signal was synchronized with the LED strobe output. The region with a continuous stream of micro-droplets was covered during wind breaking for protection from the fluctuation of the droplet position. Emissions from the laser-produced plasma were collected using additional lenses and were then guided to a spectrograph. The emissions were dispersed by the spectrograph and the resulting electrical signal was recorded using a streak camera. The signal was processed and stored in a computer.

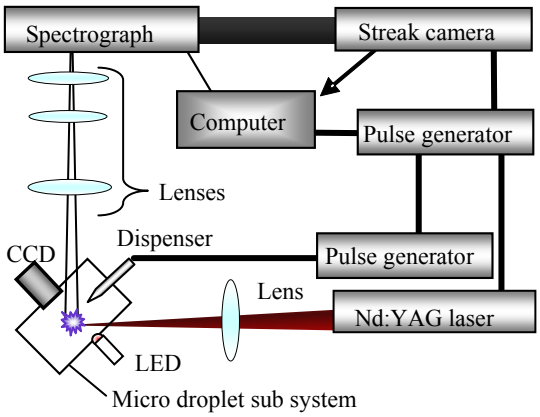

Fig. 7. Schematic representation of LIBS experiment using a 30-µm droplet ejection system.

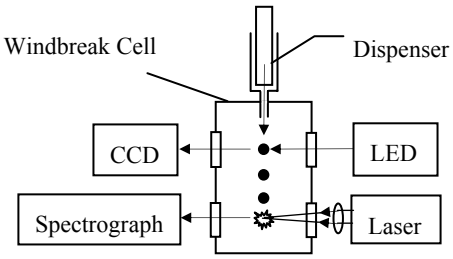

Fig. 8. Schematic representation of micro-droplet sub system.

Fig. 9 shows the microphotograph of a micro-droplet ejection process. The micro-droplet nozzle ejected uniform droplets under stroboscopic illumination by an LED. The piezoelectric dispenser was capable of delivering up to 2000 droplets per second. The nozzle diameter was 30 μm. The droplet size could be varied in a narrow range by adjusting the voltage and voltage pulse duration. The velocity of the droplets increased with the voltage. Larger pulse duration led to larger droplets. In order to obtain the best stability and uniformity for the droplets, the optimum voltage parameters were set for every experiment. The piezoelectric nozzle was a droplet-on-demand device that provided single, isolated droplets with a diameter of 30 μm and an initial velocity of 2 m/s. For the purpose of synchronizing the laser pulses with individual droplets, laser plasma was generated in a gaseous environment.

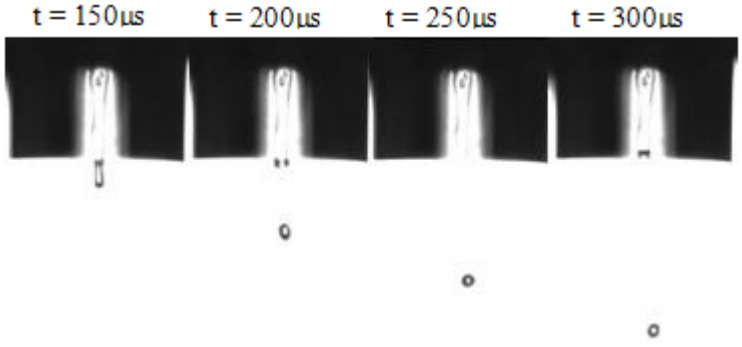

Fig. 9. Photograph of micro-droplet ejection from a nozzle with a diameter of 30 μm. The photograph was taken under stroboscopic illumination at intervals of 50 μs from 150 μs to 300 μs after trigger.

3. Results and Discussion

The breakdown emission intensities were obtained for 0.1 M to 1.0 M NaCl solutions by using a bulk liquid cell. Fig. 10 shows the error ranges of the Na D_2 emission peak intensity. An analysis based on data obtained from 100 laser pulse shots indicated that the central gate point was 18.1 μs from trigger-in and the gate width was 3.9 μs. The analytical gate settings were optimized with 0.1 M NaCl solution. Generally, the intensity increased with the solution density up to 0.3 M. However, for higher concentrations this increase was not proportional, as expected. This indicated that the calibration curves were likely to have an optimum window for data collection. Some problems associated with the splashing of the sample solution were experienced when measurements were performed at the solution surface. With regard to the calibration, fluctuations in the droplet size distribution at the time of the laser spark caused problems.

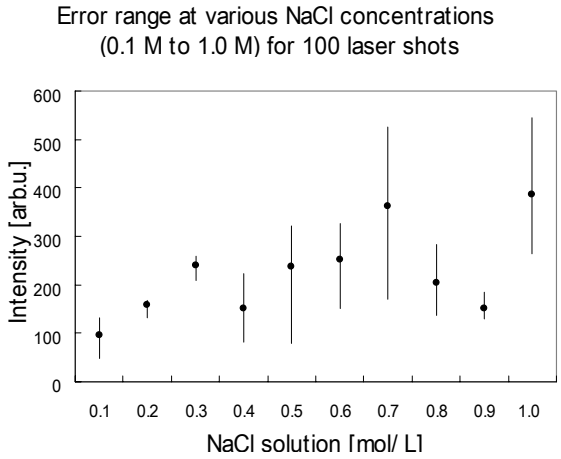

Fig. 10. Error range at various NaCl concentrations (0.1 M to 1.0 M) for 100 laser shots.

Figs. 11 and 12 show the LIBS experimental spectral data for the 0.1 M and 0.7 M NaCl solution samples. These data are presented as an example of data from comparison experiments for bulk-liquid and micro-droplet sampling techniques. The two different concentration samples were taken for the analysis using the 50-μm micro-droplet ejection system for comparison with the old bulk liquid method. The 0.1 M NaCl solution optimized the gate setting for obtaining the best signal-to-noise ratio. The 0.7 M NaCl solution showed the maximum error range for the old technique of bulk liquid measurement. An analysis based on data obtained from 100 laser pulse shots indicated that the gate setting was the same for micro-droplet ejection and the bulk liquid method. The micro-droplet ejection system was used for producing an improved calibration curve. LIBS with the micro-droplet ejection system produced intensities that were larger than conventional methods. A comparison of experimental data between the micro-droplet ejection system and the bulk liquid system is presented below. In Fig. 11, the data for the 0.1 M NaCl solution show that slightly difference between the two measurements. However, a significant difference occurred between the two measurements for the 0.7 M solution, as shown in Fig. 12. This clearly demonstrates that in the quantitative analysis of LIBS, a calibration curve determined using the micro-droplet technique cannot be used for the bulk liquid quantitation method.

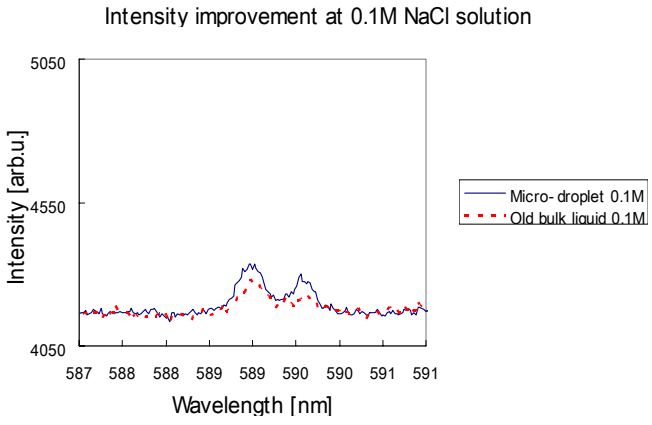

Fig. 11. Intensity difference for 0.1 M NaCl solution between old technique of bulk liquid measurement and 50-μm micro-droplet measurement obtained from 100 laser pulse shots.

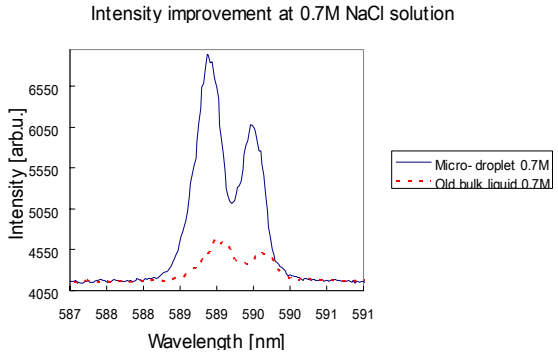

Fig. 12. Intensity difference for 0.7 M NaCl solution between old technique of bulk liquid measurement and 50-µm micro-droplet measurement obtained from 100 laser pulse shots.

Figs. 13 to 15 show the experimental data for 0.1 M to 0.3 M NaCl solution samples; these were obtained from a comparison between the LIBS spectral emission intensities obtained from the old bulk liquid method and those obtained from the 30-µm droplet ejection system. The gate settings were the same in the bulk liquid method and 50-µm droplet ejection system. In Fig. 13, the comparison of data for the 0.1 M NaCl solution between the 30-µm droplet ejection system and the bulk liquid method shows that the micro-droplet ejection system is more effective than the bulk liquid technique. Compared to Fig. 11, intensity difference for micro-droplet volume between 30-µm and 50-µm droplet was unclear. However, from a comparison between the micro-droplet technique and the bulk liquid technique, it was observed that both data showed the advantage of using the new LIBS solution measuring technique. Figs. 14 and 15 show a comparison between the data for the 0.2 M NaCl solution and those for the 0.3 M NaCl solution. From these data, the atomic spectral intensity is observed to increase with the density of the solution. Similar to the case of the 0.1 M NaCl solution, the micro-droplet intensity is higher than the bulk liquid technique. By using the comparison data for 0.1 M to 0.3 M NaCl Solution samples for this 30-µm micro-droplet ejection system, Na calibration curves are shown in Fig. 16. The calibration curves for Na were plotted by using the average intensity of five measurements, each with 100 laser shots. It appears that the plasma conditions were different among these setups. In the case of the plasma in the bulk liquid system, the plasma created by the laser dissipated its energy to its surroundings or constituents. In the laser-created plasma plume, the distribution of atoms was such that the inner core of the plume, which mostly contained excited species, was surrounded by the unexcited species of the outer layer.

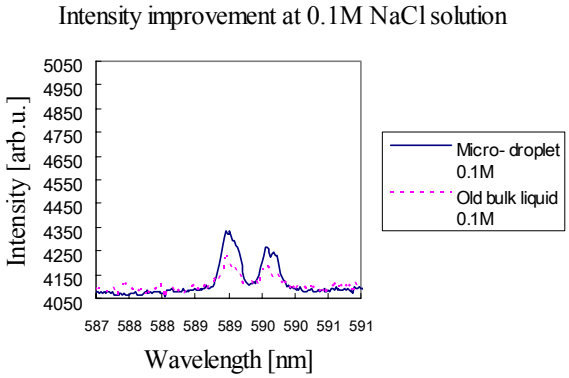

Fig. 13. Intensity difference for 0.1 M NaCl solution between bulk liquid measurement performed using the old technique and 30-µm micro-droplet measurement obtained from 100 laser pulse shots.

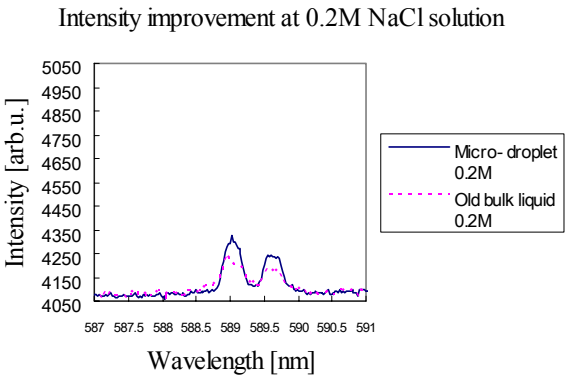

Fig. 14. Intensity difference for 0.2 M NaCl solution between bulk liquid measurement performed using the old technique and 30-µm micro-droplet measurement obtained from 100 laser pulse shots.

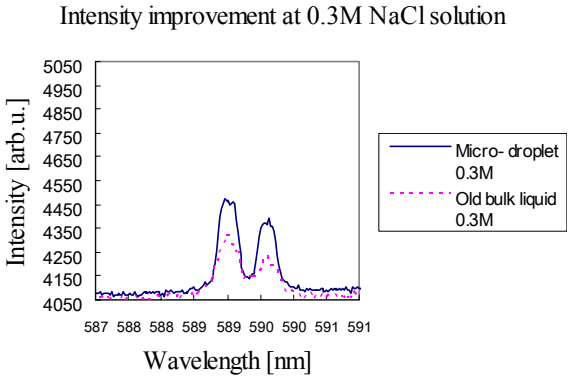

Fig. 15. Intensity difference for 0.3 M NaCl solution between bulk liquid measurement performed using the old technique and 30-µm micro-droplet measurement obtained from 100 laser pulse shots.

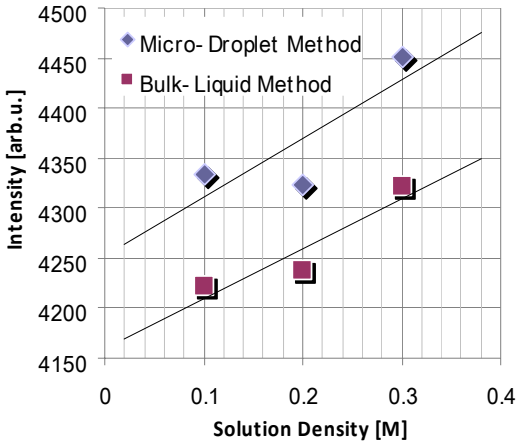

Fig. 16. Intensity improvement for NaCl solution measurements between old technique of bulk liquid method and 30-µm micro-droplet method obtained from 100 laser pulse shots.

4. Conclusions

The new micro-droplet technique described here overcomes many of the disadvantages experienced with LIBS solution measurement. For previous methods, breakdowns on water surfaces produced strong

emissions; however, the splashing of the sample at the water surface and chemical denaturation were practical and marked problems. For breakdowns passing through water, there was no splashing of the sample, but the emissions were very weak. In contrast, the new micro-droplet method described here, by micronizing the sample, made it possible for the entire volume of the liquid sample to be confined to the laser beam spot area and to be separated from the surrounding conditions. The advantages of this method were strong emissions, absence of splashing of the sample, solution density controllability, and absence of chemical denaturation. One disadvantage was that advanced timing control techniques were required. In the bulk liquid, most of the laser energy was used for vaporizing the sample. In contrast, the use of the micro-droplet ejection system allowed most of the laser energy to be consumed by ionizing the sample. Therefore, different data were obtained from each LIBS technique and different calibration curves were required even for the same solution. For the micro-droplet technique, the difference of emission could be caused by the balance between increased emission and absorption within the solution of delocalized and uniformly distributed NaCl particles. These results, to our knowledge, are important indications that micro-droplet output system which could generate same volume of sample has been employed in LIBS experiments. The technique needs to be developed further, but has the potential to overcome many of the problems associated with standard bulk-liquid-based techniques.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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