Signal enhancement of laser-induced breakdown spectroscopy by applying synchronized buffer gas pulses

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We have demonstrated a method that enables the instant analysis of the results of laser-induced breakdown spectroscopy (LIBS) using high-density jet-type gas pulses synchronized with laser pulses. It was easily measurable without an auxiliary chamber and showed the performance of an ordinary buffer gas. Several parameters were identified to obtain an effective signal enhancement, and LIBS signals according to the height of a laser-induced plasma were investigated. The spatial distribution of the injected gas jet was surveyed by LIBS and the optimal observation position was verified. It was applied to several substances and the remarkable result of increasing the limit of detection was established especially for soft materials. © 2018 The Japan Society of Applied Physics

Laser-induced breakdown spectroscopy (LIBS) is one of the optical emission spectroscopic techniques. In LIBS analysis, a laser beam is focused on a target sample to ablate constituent atoms and to ignite a plasma that eventually cools down by emitting light. During this process, optical emission spectra can be recorded to obtain quantitative information about the elemental composition of the sample material. LIBS has the following advantages over traditional elemental analysis techniques. LIBS analysis can be performed in open air without any sample chamber or vacuum equipment. It can analyze distant samples in a remote manner. Also, most of the chemical elements can be measured irrespective of the physical state of the sample. Hence, it has been employed for the exploration of deep sea, Mars mission, and the investigation of nuclear fusion reactors, which do not allow humans to approach the material to be analyzed. Moreover, a LIBS plasma is produced by the laser ablation of materials around a few tens of nanograms. This minimally destructive analysis capability enables us to use LIBS to investigate the composition of old relics.

However, there are a few limitations of the analytical performance of LIBS. One of them is the limit-of-detection (LOD) performance that falls in the range from a few to several hundred parts per million for metallic elements with relatively high performance LIBS setups. For nonmetallic elements, the LOD value typically increased to several hundred parts per million to a few percent. This makes the analysis difficult for trace elements in a sample. So far, several methods have been developed to improve this. Dual-pulse LIBS using two laser sources is one of the ways to improve LOD performance, and a variety of geometry configurations have been devised. To ameliorate the analytical performance, increasing the number of electrons that participate in the transitional radiation process can be one of the solutions. Previously, we suggested another way to increase the LIBS signal intensity and consequently to decrease the LOD value. This method is based on the usage of buffer gases that provide richer electrons with LIBS plasmas than air does. Collisions between electrons and atoms or ions in a laser-induced plasma (LIP) play a key role in the optical emission process. Thus, the higher electron density in the LIP results in the higher intensity and longer lifetime of atomic or ionic emission lines. This process may contribute to the signal enhancement effect. However, even in this case, a closed chamber for buffer gases is necessary and the target sample should be analyzed only within the chamber. Thus, the advantage of the nonpreparation of LIBS in real-time field analysis is lost. Furthermore, owing to the low gas density, the signal amplification process is limited. Accordingly, in order to make the gas have a high density, jet-type pulses are injected at a high pressure momentarily. When the pulse is synchronized with the laser pulse, the high-density gas can play a prominent role in signal amplification as well as improve the LOD performance of LIBS analysis.

Herein, we investigated the LIBS signal depending on the temporal and spatial changes of the buffer gas jet to identify the proper conditions for signal enhancement. Using the LIBS signal, the distribution profile of the gas jets ejected from the nozzle was presented. Moreover, spectrally dispersed plasma plumes were observed along the height direction to examine the spatial characteristics of ionic and atomic emissions by the gas pulse jet. It was applied to several substances and showed that LOD performance was improved especially for low-density materials.

The experimental setup is schematically illustrated in Fig. 1. The basic concept is to focus the pulse laser to generate a plasma on the target material, and the optical emission is recorded by a spectrometer. All experiments were conducted in an open chamber at room temperature. A frequency-doubled Q-switched Nd:YAG laser (Quantel Brilliant b, 10 Hz, ~8 ns, 532 nm) was used as an ablation source. The laser beam was guided by a mirror to be vertically incident on the surface of the aluminum target mounted on a three-axis motorized stage through a plano-convex focusing lens (f = 70 mm) to generate a plasma. The light emitted from the plasma was collected through f = 70 mm plano-convex lenses in the top-view and side-view directions, and it was sent to a 50 cm Czerny–Turner monochromator (Acton Research SpectraPro-500) with an intensified charge-coupled device (ICCD; Oriel Instaspec V, 1024 × 512 pixels). A solenoid-
driven nozzle capable of high-speed switching was employed to make the gas jet pulses. Ar gas (0.5 MPa) in the form of pulses was synchronized with the laser pulses. All the temporal arrangements of operations, such as nozzle switching for gas jet pulses, the delay time of laser pulses, and the gate open time of the ICCD detector, are managed by a delay pulse generator (Stanford Research System DG535). All data about emission lines were referenced from the NIST database.\(^\text{13}\) Spectral intensity values were estimated as the areas under the Lorentzian functions with fitted parameters. For an appropriately selected wavelength region, the continuum background emission was assumed as the linear line and subtracted from the observed spectrum.

Figure 2(a) shows the intensity variations of Al characteristic lines at energies of 5, 20, 50, and 100 mJ/pulse supplied with a laser. The top two filled-shaped graphs are for the Al I 396.152, 309.271 nm line emission with Ar gas pulses, while the third and fourth unfilled graphs below show the same line emission without Ar gas pulses. The fifth and sixth plots show the case of using Ar gas pulses at a 281.619 nm ionic line and the case of not using it, respectively. Generally, the intensity of the emission line is low for the ionic transition and high for the atomic transition. Also, Ar gas pulses show that the use of Ar gas improves the spectral signal intensity. However, the trend of such an intensity decreases in the case of the 100 mJ/pulse signal affected by Ar gas and even the

SER is less than 1. Figure 2(b) shows the SER obtained with Ar gas pulses for each energy supplied. As the laser energy increases, the SER decreases. At an inflection point of 20 mJ/pulse, the amplification of the signal increases sharply at an energy below that. This is caused by the plasma shielding effect owing to the increased number of electrons, which is consistent with the tendency of a common buffer gas.\(^\text{14,15}\)

In the ionic transition line where the signal is weak, the lower the supplied energy, the higher the enhancement ratio. Therefore, in this study, the experiment will be conducted by supplying a laser energy below 10 mJ/pulse to exclude the plasma shielding effect. This can increase the signal amplification ratio and minimize damage to the target sample.

The time evolution of Al line emission by Ar gas jet pulses is presented in Fig. 3. It was measured by changing the delay time between the opening of a gas nozzle and the laser pulse incidence. After the gas is injected, the Al emission signal intensity sharply reaches a peak at 0.2 ms and rapidly decreases after. When the nozzle is opened, the pressure difference between the gas reservoir and the experimental room instantaneously increases, so that the gas is rapidly ejected at a high density. From 0.25 to 3 ms, a stable gas jet flow rate is observed without a change in Al emission signal intensity. After 3.0 ms, it decreases and disappears. Accordingly, it is recognized that the effect of Ar gas pulses is valid for about 3 ms after releasing them. With the laser-gas delay time set to 0, Ar is not detected. This means that the Ar gas injected repeatedly every 100 ms (10 Hz) dissipates in air within 100 ms. As a result of the experiment using Al, it takes 0.1 ms for Ar gas to occupy the ambient atmosphere and to create the same effect as the gas chamber filled with Ar gas, which lasts up to 3 ms. Besides, it is possible to obtain the maximum amplification ratio of the spectral signal from a target at about 0.2 ms. However, a stable signal enhancement can be achieved by using the time between 0.25 and 2.5 ms.

Figure 4 shows the spatial intensity distribution of the Ar gas jet injected from the nozzle by detecting Ar signals using LIBS. It was obtained by moving the nozzle at intervals of 1.27 and 0.635 mm (0.05 and 0.025 in., respectively) in the X- and Y-directions in the gas injection range from the position of 0.5 mm away from the nozzle. The laser pulse energy was 23 mJ/pulse and the ICCD gate was opened for 1 µs. The intensity of the Ar emission line was high in the range of 4.5 mm from the inlet of the nozzle [Fig. 4(a)]. The intensity of the Ar emission line observed 10 mm far from the nozzle is 50% that observed near the nozzle inlet. However, Fig. 4(c), in which measurement point is slightly off the center of the injection axis of the nozzle, shows an intensity of 30%. Figure 4(b) shows almost no Ar line emission at the outer
edge of the gas jet. From these results, the gas jet profile was found to spread with a spray angle of 0.2 rad. The emission lines of argon and nitrogen were detected simultaneously in the region where Ar gas was injected, and it can be seen that the two gases exist in a mixed form. By comparing the nitrogen signal of region (b) in which Ar is not detected, it can be inferred that nitrogen also has a signal enhancement effect owing to argon in regions (a) and (c) because argon is denser in the pulsed jetting area and has a higher ionization energy than nitrogen. As described above, the intensity of the Ar gas signal is proportional to the signal increase rate of the target material when Ar gas is applied as buffer gas. Therefore, to obtain the effective signal enhancement effect of the target material, it is preferable to observe the signal at a distance of about 1 to 4.5 mm from the nozzle injection direction.

Figure 5 shows the temporal change of the spectral intensity from the Al plasma to compare the effects of Ar gas pulses. At the time interval between 0.5 and 2.6 µs, the average RSD is estimated to be ~11% under Ar gas pulses and ~13% under normal conditions. The gate open time of the ICCD was set to 0.2 µs and the delay time between a laser pulse and ICCD gate open was varied. Ar gas was injected and the laser was incident with a time delay of 2.5 ms because the SER obtained by Ar gas jet is relatively stable in this time period. The spectrum signal begins to appear after 0.7 µs, and the rapid signal increase can be seen as the plasma ignition caused by the laser. It continues for 0.7–0.9 µs, which shows a high intensity increase of 3–5 times with Ar gas pulses. On the other hand, it maintains an almost constant intensity without Ar gas. The emission signal of the target material rapidly decreases after 0.9 µs, but still remains strong when using Ar gas pulses and lasts for 2.5 µs. It can be interpreted that the transitional radiation is most activated at 0.6–0.8 µs, and the maximum peak appears at around 0.7 µs. The graph of 281.619 nm has a sharp drop after 0.8 µs, while the curve of 396.152 nm has a gentler slope. In both cases, the Al I emission line at 396.152 nm is stronger than the Al II emission line at 281.619 nm and exhibits a longer-time-lapse emission spectrum, since the lifetime of the ion peak is shorter than that of the atom peak. After igniting the plasma by the laser, spectral radiation is observed. The gate open time of the ICCD can be reduced between 0.7 and 2.5 µs, so that the background noise can be minimized and an efficient signal-to-noise ratio can be obtained. LIBS signals without Ar gas pulses approximately last for 0.6 µs, which has a shorter effective observation time. Thus, Ar gas pulses affect the plasma lifetime and it increases up to 2 µs. It allows the emission of a high flux by 3–5 times and induces a high signal enhancement effect.

Figures 6(a) and 6(b) show the vertical scanning of the spatially dispersed plasma spectrum generated by a focused laser pulse of 10 mJ on aluminum. The spectral intensity of Al measured without Ar gas is low as shown in Fig. 6(a). When Ar gas pulses are applied, as shown in Fig. 6(b), the transition line emission becomes stronger and the spectral bandwidth broadens. The linewidth broadening, known as Stark broadening [Δλ_{Stark} (nm) = 2wn, \((\text{cm}^{-3})/10^6\)], where \(w\) is the electron impact parameter, is proportional to the electron density, indicating that Ar gas pulses contributed to the electron density increase of the plasma. The changes in linewidth are clearly visible around the characteristic wavelength at high ratios in Fig. 6(c). Also, there are differences between the rates of increases in the intensities of atomic and ionic transitions along with the height. The ratio of the two intensities between ionic and atomic transitions is proportional to the plasma temperature and a hot core appears at a height of 1.5 mm. This means that the plasma temperature near the hot core is higher and that the electron density also increases. The increase in electron density at this ratio implies that most of the electrons newly supplied by Ar gas injected from the surface of the Al sample plate moved upwards unevenly in the plasma. In this way, a large number of electrons introduced into the vicinity of the core have higher collision probabilities, resulting in spectral broadening due to bremsstrahlung radiation. Thus, the radiation generated in the sparse wavelength band of the transition radiation makes the SER at the plasma interface around the dotted ellipsoid higher. Eventually, the electrons supplied by Ar gas pulses increase the intensity of the line emission and broaden the spectral bandwidth. Most of the atoms that make up the plasma are supplied from Al and Ar at the lower side of the LIP. However, many electrons move to the upper area of the LIP during the initial plasma expansion, where the electrons collide closely with each other, equilibrating the energy and maintaining the LTE state. The kinetic energy resulting from the ionization of Al and Ar transports energy spatially through the electron collisional process. Hence, because electrons and stable atoms at a
position away from the energy exchange engine already lost their kinetic energy, it is difficult to generate ionic transitions, which have a lower intensity than atomic transitions. In Fig. 6(a), the Al II 281.619 nm line emission of the plasma plume is 20% weaker than the Al I 396.152 nm line emission. After Ar gas pulses are applied, the Al I line emission increases 6 times, whereas the Al II line emission increases more than 12 times. The number of electrons increased by Ar gas reduces the relative population of Al II species. However, Ar gas, which has a high ionization energy, increases the plasma temperature by increasing the upper-level ionic transitional radiation with a high ionization potential. Consequently, the injection of Ar gas pulse causes a higher signal enhancement effect in ionic emission. Figures 6(a) and 6(b) show that the hot core of the plasma plume is located at a height of 1.5 mm from the surface of the Al target plate such that the maximum emissivity can be obtained therefrom.

Figure 7 shows the comparison of LIBS signals from several substances. Glass has a relatively high density of hard material compared with the other two materials, resulting in a high intensity. This indicates that glass contains iron, lead, and silicon through spectral signals observed near 280 nm, and the characteristic peaks of such components are Fe II 279.720, Pb I 280.200, and Si I 288.158 nm, respectively. We used a typical transparent glass that contains about 55 wt % Si, 0.5 wt % Pb, and 0.5 wt % Fe. In the case of paper, a Ca II ionic peak was observed at 393.366 and 396.847 nm, indicating the presence of calcium. We used qualitative filter papers that are known to include about 140 ppm calcium. A Cl I characteristic peak was also observed at 776.916 nm, indicating that chlorine remained in the wood flake. Glass and paper show similar SERs of 4–6 times when Ar gas was used. The overall spectral signal of the paper and wood flake is weak owing to the low density of the soft material. The SER close to 20 times is seen in the wood flake, implying that it can be achieved by supplying electrons through Ar, although the laser power is too small to observe the characteristic radiation. As can be seen here, it is advantageous to increase the spectral signal through the electron supply rather than the ablation of the target element, so that the sample is less damaged. From these results, we have confirmed that the buffer gas jet pulse that we designed has a remarkable effect on signal enhancement and can be applied to various materials. In particular, it has been affirmed that it is a useful method for a material having a low-density distribution to amplify a signal effectively. For the excessive input of the CCD or ICCD, it is necessary to perform the measurement cumulatively several times with a weak signal. Our method is suitable for enhancing relatively weak signals produced by a small laser pulse energy. Aside from Ar, other inert gases such as Kr were applied by using the synchronized gas pulse system. It identified a better signal enhancement property than Ar. The increased number of electrons not only led to the increase in characteristic radiation, but also led to the increase in unwanted continuum background signal intensity due to bremsstrahlung radiation. Accordingly, further research related to appropriate conditions and application fields has to be continued.

In conclusion, we have taken advantage of buffer gas properties to improve the analytical performance of LIBS without a sample chamber equipped with a vacuum pump. The time interval between a gas and a laser was adjusted to optimize the observation time. To find the optimal observation time and position, the signal characteristics of a plasma and the distribution of the injected gas were examined. There is a significant signal enhancement effect in a trace elemental analysis with a low density, which can be a good alternative to overcome the LOD.

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