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Application of laser-induced breakdown spectroscopy for the determination of Cd and Pb in water: Influence of ambient gas on the detection sensitivity

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) with a combination of UV and visible laser pulses has been utilized for quantitative analysis of trace amounts of heavy metals in water. In collinear beam geometry, the first UV (355 nm) laser pulse generated a pre-ablation spark in air in front of water jet, and the other visible (532 nm) laser pulse reheated the air plasma and formed new plasma on the surface of water jet. Under optimized conditions, a sensitivity enhancement was observed compared to single-pulse LIBS. Furthermore, the surrounding gases, such as helium, nitrogen, argon, and air, influenced the emission intensity of heavy metal analytes. For instance, the emission intensity of cadmium ionic species in argon was boosted by a factor of 20 compared to other ambient gases. Limits of detection for cadmium and lead were obtained in the range of several hundred ppb concentrations.

1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is one of the atomic analysis techniques. LIBS can provide rapid and multi-elemental analysis with no sample preparation, and therefore this technique is suitable for on-line monitoring of heavy metals in water. In this work the dual-pulse LIBS (DP-LIBS) with a combination of third-harmonic and second-harmonic Nd:YAG laser pulses was applied to analyze cadmium and lead in water. After examining the effects of lens-to-sample distance, interpulse delay and gate delay from the second laser pulse on the signal intensity, the detection limits for cadmium and lead were obtained. In addition, the effect of different buffer gases such as helium, nitrogen, argon, and air on the emission intensities was investigated.

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2. EXPERIMENTAL

The laser-induced plasma was created by third harmonic (355 nm) and second harmonic (532 nm) of the Nd:YAG lasers in a collinear configuration. The laser pulses were focused onto the surface of a water jet using a bi-convex lens with 25.4 mm of diameter, 50.6 mm of curvature radius, and 5.1 mm of thickness. The focal lengths for 355 nm and 532 nm laser wavelengths are 54.0 mm and 55.8 mm in air, respectively, and the difference of focal positions for laser-induced plasmas produced by two lasers is 1.8 mm, as shown in Figure 1. This phenomenon occurred due to a distinct refractive index for different laser wavelengths. The pulse energies for the first (355 nm) and second (532 nm) lasers were kept constant at 30 mJ and 70 mJ, respectively.

A laminar flow was generated by a home-made nozzle by means of a peristaltic pump, and the diameter of water jet was ~ 0.7 mm. For the experiments in different gas environments, the home-made sample cell includes two gas inlets and one gas outlet. The laser beam was focused at ~ 6 mm below the nozzle exit, and the focused position of beam on the liquid surface was adjusted precisely using a micro-translation stage. In order to keep the plasma window from fogging up caused by humid hot condition of the inside of cell, warm-air was supplied toward a window by a dryer.

For multi-element analysis, an echelle spectrometer (LLA, Model ESA3000) was utilized. The plasma emission was collected and focused by a combination of 30 mm and 40 mm fused-silica lens into the entrance of an optical fiber with a 600 μm core diameter.

A total liquid volume of 50 mL was used for each measurement. Liquid samples were prepared with the use of cadmium chloride (Aldrich, ≥99.99% purity) and lead nitrate (Aldrich, ≥99% purity). The concentrations of Cd and Pb in the solutions were measured before the DP-LIBS experiments by inductively coupled plasma atomic emission spectroscopy.

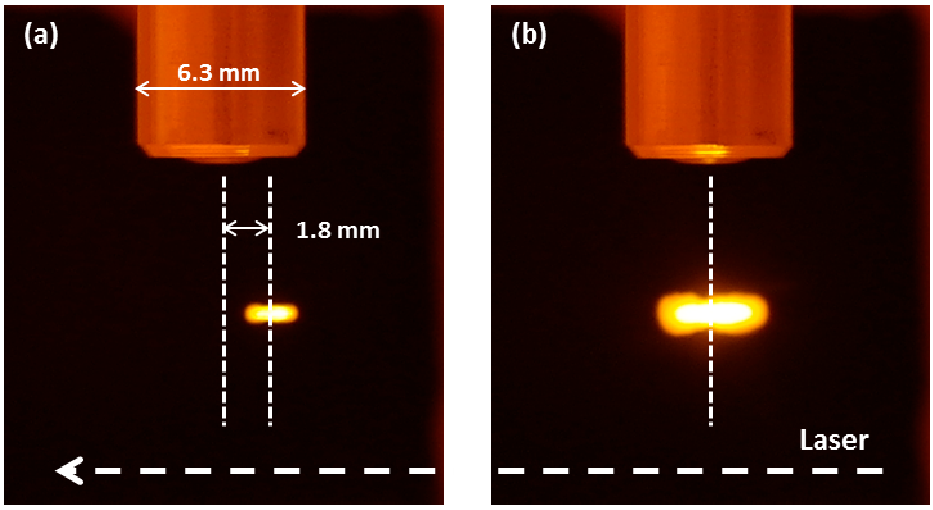

Figure 1. Images of laser-induced plasma produced by (a) 355 nm wavelength of laser and (b) 532 nm wavelength of laser in air. The difference in the focal position for each wavelength of laser is 1.8 mm.

3. RESULTS AND DISCUSSIONS

3.1 Signal Enhancement

The emission intensities of Cd(I) 228.80 nm, Cd(II) 226.50 nm, and Pb(I) 405.78 nm from dual-pulse (DP) mode were compared to the single-pulse (SP) configurations. The interpulse delay and gate delay from the second laser pulse were 1 μs and 4 μs for DP-LIBS, respectively. The intensities for SP-LIBS were obtained by using 532 nm laser pulse and gate delay was 4 μs. Each spectrum was attained by accumulating 300 laser pulses using a solution containing 150 ppm of cadmium and 56 ppm of lead. It was observed a six-fold and eight-fold signal enhancement in Cd(I) and Cd(II) emissions, respectively. For lead, dual pulse excitation provides a four-fold increase of line intensity in comparison with single pulse. In case of the signal-to-noise ratio, seven-fold, eleven-fold, and nine-fold increases were obtained for Cd(I), Cd(II), and Pb(I) emission lines, respectively.

A signal enhancement was naturally estimated in DP-LIBS due to an additional pulse. However, in this experimental configuration, the first laser pulse rarely participated in sample excitation and a significant absorption of second laser pulse by the first generated plasma was also observed. Therefore, additional irradiance is not sufficient to explain the signal enhancement. The signal enhancement of this configuration can be explained by combination of several mechanisms including the coupling of the second laser-induced plasma with the first generated plasma, increasing the exciting efficiency of droplets created by second laser pulse due to sufficient number of free electrons in the first generated plasma, raising temperature of sample and ambient air above sample surface by first laser-induced plasma, and rarifying atmospheric pressure and number density (Stratis 2000, Scaffidi 2006).

3.2 Limit of Detection

After investigating the effects of interpulse delay and gate delay from the second laser pulse, optimal experimental conditions were obtained at interpulse delay of 1 μs and detector gate delay of 1.4 μs and 4 μs for Cd and Pb, respectively. In order to plot the emission intensity vs. the Cd and Pb concentration, the emission intensities were measured for Cd concentration ranging from 12.4 ppm to 160 ppm and from 15.5 ppm to 200 ppm for Pb. Calibration curves showed a simple linear relationship between the emission intensities and sample concentration except for saturation intensity at higher concentrations. The detection limits were calculated by using $3\sigma/S$ definition, where σ is the standard deviation acquired from pure Milli-Q water and S is the slope of a linear calibration curve. The obtained detection limit for Cd and Pb were a few ppm range.

3.3 Effect of Ambient Gas

It is well known that the characteristics of the laser-induced plasma such as plasma temperature, electron density, time evolution, and emission intensity are strongly affected by ambient gas surrounding the sample (Kuzuya 1993, Lui 2003). The emission intensities obtained at atmospheric pressure of helium, nitrogen, argon, and air were compared. Under helium, nitrogen and air, the spectra were obtained by using 300 laser shots. However, 100 pulses were utilized for argon gas due to much stronger emission intensities. The interpulse delay and gate delay from the second laser pulse were kept at 1 μs and 4 μs, respectively.

The emission intensities of neutral and ionic lines for cadmium (100 ppm) were compared in helium, nitrogen, argon, and air. It was observed that the argon atmosphere provided fifteen-fold increase of the Cd(I) emission signal and twenty-fold increase of the Cd(II) emissions signal in comparison with air atmosphere. In the case of helium, the emission intensity showed the lowest values. The difference in emission intensities was caused by the different properties of gases such as ionization energy, density, and thermal conductivity. The thermal conductivity of Ar (42.57×10^{-6} cal s^{-1} deg^{-1} cm^{-1}) is smaller than N_2 (62.70×10^{-6} cal s^{-1} deg^{-1} cm^{-1}), O_2 (63.64×10^{-6} cal s^{-1} deg^{-1} cm^{-1}), and He (360.36×10^{-6} cal s^{-1} deg^{-1} cm^{-1}) (Iida 1990). This difference in the thermal property result not only in a stronger emission, which is related to the higher plasma temperature, but also in a longer emission lifetime which is led by slower cooling process in argon (Iida 1989).

4. CONCLUSION

The dual-pulse laser-induced breakdown spectroscopy has been applied to detect cadmium and lead metal ions in water using a combination of UV-Visible wavelength laser pulse with collinear configuration. The first UV pulse was employed to generate air-plasma above the surface of water jet and some fraction of the sequent visible pulse was absorbed in the plume of the first generated plasma and the remaining second laser pulse created new plasma from the water surface. Under this condition, the limits of detection for cadmium and lead in water were achieved in the range of a few ppm concentrations in air and several hundred ppb concentrations in argon gas.

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