Effect of Sample Temperature on Radiation Characteristics of Nanosecond Laser-Induced Soil Plasma

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An Nd:YAG single pulse nanosecond laser of 532 nm wavelength with an 8 ns pulse width was projected on the soil samples collected from the campus of Bengbu College under 1 standard atmospheric pressure. Laser-induced breakdown spectroscopy at different sample temperatures was achieved. The intensity and signal-to-noise ratio (SNR) changes of different characteristic spectral lines could be analyzed when the sample temperature changes. The evolution of plasma electron temperature and electron density with the sample temperature was analyzed through Boltzmann oblique line method and Stark broadening method. The cause of the radiation enhancement of laser-induced metal plasma was discussed. Experimental results demonstrated that the spectral intensity, SNR, the electron temperature and electron density of plasma are positively related to the sample temperature, and reach saturation at 100 °C.

Key words: Sample temperature, Spectral intensity, Signal-to-noise ratio, Soil, Electron temperature, Electron density, Laser-induced breakdown spectroscopy

I. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is a widely used analytical atomic spectrometry technique and is valued for its remarkable analytical and technical characteristics. This rapid, versatile, and noncontact technique is capable of providing qualitative and quantitative analytical information for any sample in a virtually nondestructive manner without substantial sample preparation. The simple, robust, and compact instrumentation enables remote analysis. Although LIBS technology is widely used in biomedicine [1, 2], food detection [3–5], environmental monitoring [6–8], and material analysis [9–11], it can increase the detection limit of low-content elements. Further improving the sensitivity of LIBS to trace elements has attracted considerable attention from researchers. Researchers commonly change experimental conditions to improve sensitivity and accuracy of LIBS detection. For example, Zhang et al. [8] used single pulse LIBS technique to analyze the soil of Huaiyuan farm in Anhui Province. The distribution of trace element Mn in field soil samples was determined using traditional calibration and internal standard methods. The experimental results showed that accuracy of the measurement was improved to some extent using internal standard method. Wang et al. [11] used peak-stripping to deduct the sawtooth background noise in a spectral signal and correct the absolute intensity of spectral line using standard spectral data of the radiation calibration light source.

Increasing the sample temperature properly can enhance the sensitivity of LIBS to trace elements [12–14]. However, few studies are available on the effect of sample temperature on plasma characteristic parameters. In this work, the effect of sample temperature on the spectral intensity and signal-to-noise ratio (SNR) of laser-induced plasma in soil (soil from Bengbu College campus) was studied. The effect of sample temperature on plasma temperature of Fe element was calculated and analyzed using Boltzmann slant method under local thermal equilibrium condition. The effect of sample temperature on electron number densities was estimated from the Stark broadened profile of Al(I) (394.4 nm). The electron number density of plasma at different sample temperatures presents theoretical and experimental references for the effect of sample temperature on plasma spectral signal.

II. EXPERIMENTS

A. Sample preparation

The soil samples to be tested in the experiment were collected from the campus of Bengbu University. The collected samples were placed outside and naturally air-dried, then the impurities were removed. After being dried, milled and sieved, the samples were rolled into a cylinder by a table-type oil press.
B. Characterization

The device mainly includes a laser (Spectra-Physics, LAB170-10, 10 Hz, 8 ns, 532 nm, 0 to 150 mJ), spectrometer (corresponding wavelength range of 200 nm to 900 nm, grating constant 1200 lines/mm, focal length 195 mm, resolution 0.023 nm), and intensified charge-coupled device (ICCD). The sample can be heated on the platform of JF-956A type constant temperature heating plate, and the temperature can be adjusted as needed. The temperature of the sample can be monitored using infrared temperature collector at the same time. In the experiment, pulsed laser is at an incident vertical to the target through a flat convex lens with focal length of 25 cm, and plasma emission was obtained using a concave mirror with focal length of 15 cm at an angle of 45° to the surface of the sample. The fiber introduced light into the spectrometer for light splitting. An ICCD detector (Princeton Instruments, ICCD, PIMAX 1024) was fitted to the spectrograph that measured time-resolved atomic emission from plasma. Spectral acquisition was triggered using a synchronization signal from the laser. Finally, the received data are processed using a spectrum software.

III. RESULTS AND DISCUSSION

FIG. 1 shows the obtained LIBS spectra of soil (100 °C) in the range of 270 nm to 430 nm with pulse energy of 60 mJ, ICCD gate delay of 1200 ns, and ICCD gate width of 500 ns.

A. Spectral line intensity and signal-to-noise ratio of plasma at different sample temperatures

Integrated intensity of emission spectral line and SNR, which are important parameters that measure the sensitivity of LIBS technology, can directly obtain the detection ability of LIBS technology. FIG. 2 shows the emission spectral data recorded from laser-induced soil plasmas at different sample temperatures (18, 30, 50, 80, 100, 120, 140, 160, and 180 °C). The effects of sample temperature on spectral line intensity and SNR of the seven lines (Fe 288.20 nm, Cr 334.9 nm, Ca 396.84 nm, Mg 280.27 nm, Cu 396.24 nm, Al 396.84 nm, Mn 279.83 nm) have been calculated quantitatively, as shown in FIG. 3.

The experimental results demonstrated that plasma spectral line intensity and SNR of different elements increase based on pulse energy of 60 mJ, 500 ns ICCD gate width, and 1200 ns gate delay with the increase of sample temperature, and amplitude of increase was different and reached saturation at 100 °C. The results showed that spectral intensities for Fe, Cr, Ca, Mg, Cu, Al, and Mn at 100 °C increased by 1.93, 1.67, 2.15, 1.67, 1.65, 1.97, and 2.5 times compared with those obtained at 18 °C.

FIG. 1 LIBS spectrum of soil in the range of 270–430 nm.

FIG. 2 Emission spectral data of soil plasma at different sample temperatures.

FIG. 3 (a) Intensity ratio and (b) SNR ratio of the seven spectral lines as a function of temperature, which are compared to the values at 18 °C.
at 18 °C. SNR values of these elements also increased by 1.82, 1.4, 1.94, 1.6, 1.86, 1.93, and 2.07 times under the same conditions. The quantitative changes of spectral line intensity and SNR shown in FIG. 3 are consistent with the qualitative analysis results shown in FIG. 2. It is obvious that the intensity of all characteristic lines increases with the increase of sample temperature. The reason is that the increase of the sample temperature will increase the mass ablation rate of the sample [12, 13], and there will be more samples excited than that in the lower temperature state, which will increase the signal intensity of the spectral line. Sample temperature is a crucial factor that affects spectral quality. Properly increasing the sample temperature can enhance detection ability of trace elements using LIBS technique.

**B. Electron temperature of plasma at different sample temperatures**

In this study, a part of divalent ion lines of Fe elements exist with some in the multiplet. Therefore, Saha-Boltzmann multigraph method cannot be used to calculate electron temperature. In this study, electron temperature of plasma is measured using Boltzmann slant method [15]. The formula is presented as follows:

\[
\ln \left( \frac{I_m \lambda_m}{g_m A_m} \right) = -\frac{E_m}{k_B T_m} + C
\]

where \(I_m, E_m, \lambda_m, g_m, T_m, A_m,\) and \(k_B\) are the relative spectral line intensity, upper level energy, wavelength, statistical weight of the upper level, electron temperature, transition probability, and Boltzmann constant, respectively. As electron temperature in this study is calculated using univalent ions or atoms, \(C\) in the above mentioned formula is a constant. If \(E_m\) is considered as the transverse coordinate and \(\ln(I_m \lambda_m/g_m A_m)\) as the ordinate, linear fitting can obtain \(k_BT_m\), and electronic temperature can finally be calculated.

Electron temperature of plasma under different sample temperatures was calculated through Boltzmann plots using the measured spectral line intensities of the five Fe(I) lines at 279.55, 318.02, 396.24, 404.58, and 422.74 nm. Table I lists the relevant line transition parameters needed to calculate electron temperature. The variation trend of plasma electron temperature enhancement with the sample temperature is shown in FIG. 4. Electron temperature of plasma increases linearly when the sample temperature rises from 18 °C to 100 °C. Electron temperature increases from 7326 K to 8506 K. The analysis demonstrates that reaction mainly results from the widespread laser ablation [12, 13] and the increased plasma internal energy during the early rise of sample temperature. Additionally, these contribute to the increased electron temperatures in the formed plasma, increased numbers of atomic and ionic excited states, improved spectral lines, and increased electron density values. These changes increase the collision probability of electrons and atoms, and excite more atoms. The temperature reaches an equilibrium point after increasing to a certain extent, thus causing dynamic equilibrium to spectral intensity.

**C. Electron density of plasma at different sample temperatures**

Griem recommends the formula for calculating the density of electrons [17]:

\[
\Delta \lambda_{1/2} = 2\omega \left( \frac{N_e}{10^{16}} \right) + 3.54 \left( \frac{N_e}{10^{16}} \right)^{1/4} \times \\
\left( 1 - \frac{3}{4}N_D^{1/2} \right) \omega \left( \frac{N_e}{10^{16}} \right)
\]

Where \(\Delta \lambda_{1/2}, \omega, N_e,\) and \(N_D\) are the full width half maximum (FWHM), electron impact width parameter, electron density, and number of particles in the Debye hemisphere, respectively. Under the experimental conditions, quasi-static ion broadening exhibits decreased influence on total spectral line width. The proportion is less than 2%, thereby indicating that perturbations caused by ions negligible compared with electrons. \(N_e\) is obtained by measuring the full width half maximum.
FIG. 5 Electron density ratio of Al(I) at 394.4 nm as a function of temperature, which is compared to the value at 18 °C.

(FWHM) $\Delta \lambda_{1/2}$ of the broadened atomic line using the following equation:

$$\Delta \lambda_{1/2} = 2\omega \left( \frac{N_e}{10^{16}} \right)$$

where $\omega$ is the electron impact width parameter.

Electron density $N_e$ is a crucial parameter of plasma that influences the ionization equilibrium for each element in the system. Eq.(3) presents that the electron density of plasma under different sample temperatures, which was also calculated using Stark broadening method and the measured spectral line intensities of Al(I) (394.4 nm). FIG. 5 shows that the variation trend of plasma electron density enhancement of Al(I) at 394.4 nm with the sample temperature. The electron density of Al(I) (394.4 nm) plasma increased by 4.0$\times$10$^{16}$ cm$^{-3}$ at 100 °C compared with that obtained under 18 °C. This finding is consistent with the variation trend of electron temperature. Properly increasing the temperature of the sample increases the density of electrons, which increases the probability of collisions between electrons and atoms and excites more atoms. Increasing the temperature of the sample can enhance the intensity of spectral lines.

IV. LOCAL THERMODYNAMIC EQUILIBRIUM

When electron temperature and electron number density of plasma are calculated using relative strength of emission spectral line and full width of half maximum, local thermodynamic equilibrium (LTE) condition is required in the evolution of plasma. Based on McWhirter standards [18], the minimum electron density required for local thermal equilibrium is presented as follows:

$$N_e \geq 1.6 \times 10^{12} \Delta E^3 T_e^{1/2}$$

where $N_e$, $T_e$, and $\Delta E$ refer to the electron number density, electron temperature, and energy difference between upper and lower energy states, respectively. In laser-induced soil plasma, the minimum electron density calculated using Stark broadening is 10$^{16}$ cm$^{-3}$, which is considerably higher than the minimum electron density of 10$^{15}$ cm$^{-3}$ using the McWhirter standard. Therefore, the experimental condition satisfies the LTE condition.

V. CONCLUSION

In this work, laser ablation of soil samples using a 532 nm Nd:YAG pulse laser was performed at different temperatures. The effects of increasing sample temperature on plasma line intensity, SNR, electron temperature, and electron density were analyzed and calculated. The experimental results showed that the increase of sample temperature contributed to the increasing trends of plasma spectral line intensity and SNR for different elements. With the increase of the sample temperature, electron temperature and density increased and then reached a saturation point. The analysis demonstrated that the reaction mainly resulted from widespread laser ablation and increased plasma internal energy during the early increase of sample temperature. In turn, these helped to increase electron temperatures in the formed plasma, increase numbers of atomic and ionic excited states, improve spectral lines, and increase electron density values. These changes increased the collision probability of electrons and atoms, and excited more atoms. The temperature reached an equilibrium point after increasing to a certain extent, thereby causing a dynamic equilibrium to spectral intensity. On the basis of these experimental results, increasing the sample temperature appropriately can improve the resulting spectral quality. This technique can promote the use of LIBS technology in the detection of faint spectral signals of trace elements and enhance its limit of detection.

VI. ACKNOWLEDGEMENTS

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