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Spectroscopy of laser-produced plasmas: Setting up of high-performance laser-induced breakdown spectroscopy system

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Abstract. It is a well-known fact that laser-induced breakdown spectroscopy (LIBS) has emerged as one of the best analytical techniques for multi-elemental compositional analysis of samples. We report assembling and optimization of LIBS set up using high resolution and broad-range echelle spectrograph coupled to an intensified charge coupled device (ICCD) to detect and quantify trace elements in environmental and clinical samples. Effects of variations of experimental parameters on spectroscopy signals of copper and brass are reported. Preliminary results of some plasma diagnostic calculations using recorded time-resolved optical emission signals are also reported for brass samples.

Keywords. Spectroscopy; laser-induced plasma; plasma temperature.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy (LIPS), is basically an emission spectroscopy technique which uses intense, short pulses of laser radiation to ablate the sample surface [1–3]. Ablation of sample results in plasma generation. Spectral lines of atoms and ions of this radiant plasma are used to develop quantitative and qualitative analytical information about the sample. Recent applications of LIBS technique for multi-elemental analysis include environmental samples, biological samples, radioactive waste materials etc. [4–6]. The versatility of LIBS technique for multi-element analysis and its applicability to different types of samples (solid, liquid and gas) make it attractive in detecting and quantifying hazardous pollutants using *in-situ* remote excitation.

In this paper, we report the assembling and standardization of an LIBS system using high-resolution broadband echelle spectrograph coupled with a sensitive ICCD

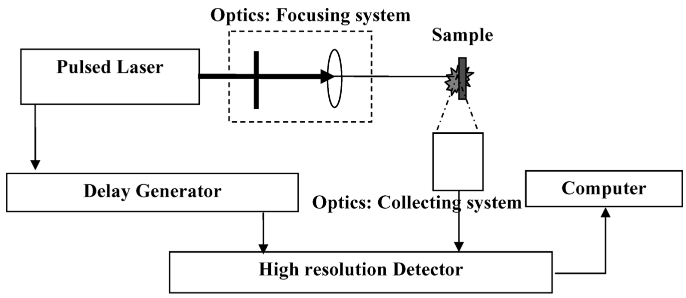

Figure 1. LIBS experimental set-up for multi-elemental analysis.

to detect and quantify trace elements in environmental, clinical and radioactive waste samples. Various important experimental conditions of this system were studied and optimized to increase the signal strength and detection efficiency of this LIBS set-up for plasma spectroscopy of copper and brass samples. Time-resolved plasma temperature for the brass plasma is also studied for finding out the local thermodynamic equilibrium (LTE) conditions required for LIBS elemental analysis.

2. Experimental methods

The schematic diagram of the LIBS set-up used for this study is shown in figure 1. The third harmonic of Nd:YAG laser (Spectra Physics PRO 230-10) with a pulse duration of 6 ns, pulse repetition frequency of 10 Hz and pulse energy of 400 mJ was used for ablation of samples to form the plasma. This laser was focussed onto the sample using a bi-convex lens of focal length 20 cm to achieve appropriate breakdown threshold irradiance for different samples. A collecting/collimating lens/mirror system was used for collecting the emission light from the generated plasma for the best performance of the broadband echelle spectrograph (Andor Mechelle ME5000-DH734-18U-03PS150) of the LIBS system. It was optimized to ensure that all the wavelengths in the range 200–975 nm were collected using fibre-optic cable to the entrance slit of the spectrograph. The detector was kept in proper synchronization with the laser using delay generator to get time-resolved information of plasma evolution.

3. Results and discussion

Wavelength and intensity calibration of echelle spectrograph–ICCD system was done using NIST certified lamps (mercury–argon, deuterium–quartz–tungsten–halogen) as shown in figure 2.

Figure 2b shows that after the intensity calibration, the intensity of 253.7 nm mercury line (which is the strongest line of all) is highest compared to all other lines in the spectrum.

A comparison of the spectral resolution of the present LIBS set-up with Czerny-turner-based system was done by recording the mercury (Hg) spectrum and the

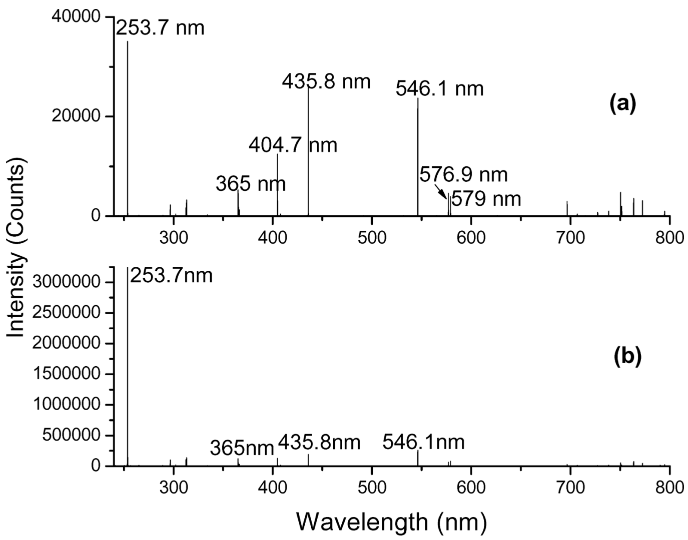

Figure 2. (**a**) Wavelength and (**b**) intensity calibration of the LIBS system using NIST lamps.

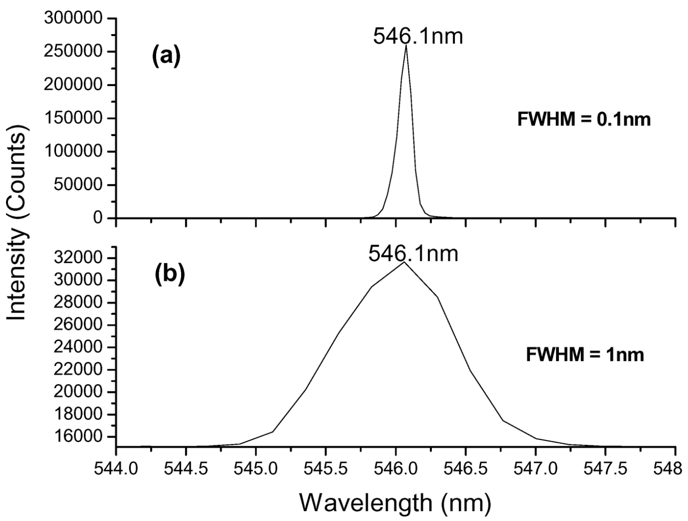

Figure 3. Spectral resolution of (**a**) echelle spectrograph and (**b**) Czerny-turner spectrograph.

results are shown in figure 3. The estimated full-width at half-maximum (FWHM) of the 546.1 nm Hg line in the spectra recorded by both systems is found to be 0.1 and 1 nm respectively. It is evident from figure 3 that the spectral resolution of echelle spectrograph is 10 times higher than that of Czerny-turner spectrograph. LIBS spectrum of a complex sample containing several elements can have overlapping spectral lines of different elements. The echelle system has very high resolution

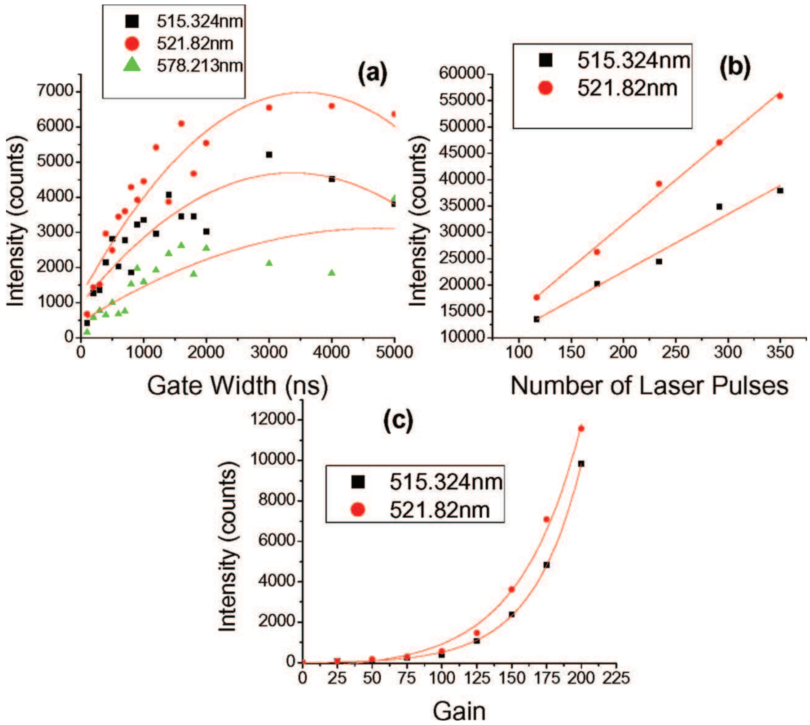

Figure 4. Variation in LIBS signal with (**a**) gate width, (**b**) number of laser pulses and (**c**) gain.

as shown in figure 3a and so it can very well separate out individual lines from different elements.

We have also optimized different parameters of the LIBS system like laser irradiance, collector probe distance and angle from the sample, detector parameters, etc. to achieve good signal with better signal-to-noise ratio. Some of the results are discussed here.

Detector parameters, namely, gate width, gain and accumulation (number of laser pulses) are optimized using copper plasma signals generated by irradiating the sample with a laser intensity of 4.46×10^8 W/cm^2 at a gate delay of 1000 ns. Figure 4 describes how the LIBS signal changes with these parameters. Each point represents an average of three measurements. Well-defined dependence of LIBS signal on gate width, number of laser pulses and gain is clearly seen from the figure. Hence, we have set an optimum possible value of these parameters to achieve good-quality LIBS signal.

After optimizing the experimental conditions, we have carried out time-resolved LIBS study of copper, zinc and brass samples to locate suitable time window of interest for a particular sample under investigation. Temporal history of copper, zinc and brass samples also helps us to monitor the plasma characteristics. Figure 5 shows LIBS spectra recorded from these samples at a gate delay of 1000 ns and a gate width of 1000 ns using a laser intensity of 4.88×10^8 W/cm^2.

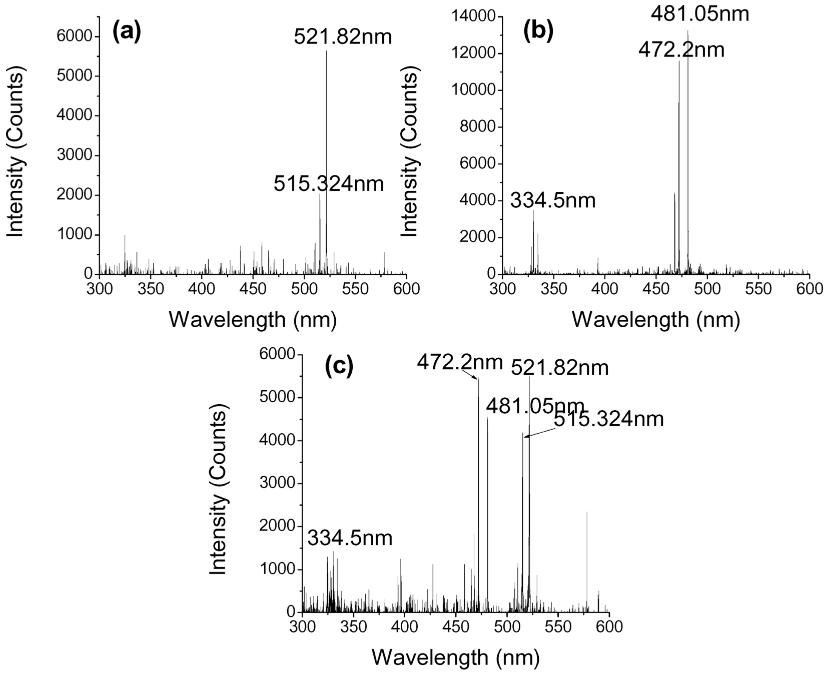

Figure 5. LIBS spectra of (**a**) copper, (**b**) zinc and (**c**) brass samples.

Table 1. Brass plasma temperature measurements.

Gate delay (ns)	Plasma temperature (eV)
300	0.788
500	0.843
700	0.806
1000	0.775
2000	0.774

From figure 5c, one can see that the LIBS spectrum of brass contains all the major lines of copper and zinc. Hence we have recorded brass plasma at different delays and calculated the plasma temperature using the Boltzmann plot. Five Cu I lines from brass plasma (465.112 nm, 510.554 nm, 515.324 nm, 521.82 nm and 578.213 nm) were used for these calculations at 300 ns, 500 ns, 700 ns, 1000 ns and 2000 ns delays. The estimated plasma temperatures are given in table 1. It is observed that after 500 ns the plasma cools down exponentially. Quantitative measurement of this information is also possible by identifying suitable characteristic lines and employing proper calibration methods.

4. Conclusions

A high-performance laser-induced breakdown spectroscopy system has been set up and optimized for studying spectroscopy of laser-produced plasmas of different materials. Broad spectral coverage with high resolution of echelle system provides great advantage to carry out useful, precise, qualitative and quantitative elemental analysis. We have also done time-resolved LIBS study of copper, zinc and brass samples and estimated the brass plasma temperature using this present set-up at different gate delays.

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