Chapter 4

LIBS system: Performance evaluation and optimization of conditions for quantitative analysis

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ABSTRACT

The LIBS set up assembled in our laboratory (Chapter III) with a high-resolution broad-range echelle spectrograph and Intensified Charge Coupled Device (ICCD) was used to investigate the effects of various experimental parameters on the plasma spectra. The dynamics and resultant spectral behavior of atoms and ions in laser plasmas as a function of laser spot size, laser irradiance, gate width, gate delay, multi channel plate gain of ICCD, distance and angle of signal collector from sample surface, surrounding atmosphere etc. were studied for pure elements, alloys, and complex samples, so that optimal experimental procedures could be standardized for a variety of samples. Apart from this, spatial and temporal variations in laser produced plasma were also investigated. The results are presented and discussed in this chapter.
4.1. INTRODUCTION

Many analytical techniques, used for both qualitative and quantitative analysis used at present, have many limitations considering their practical application. These involve sample collection, transportation, sample preparation/pre-processing and actual laboratory analysis which are labor intensive, costly and require a considerable amount of time for the results to be available. Thus it is desirable to develop an analytical technique which is quick, sensitive, and is also capable of analyzing the material in situ, especially in situations involving hazardous materials. LIBS as mentioned in the previous chapters, which can be easily adapted from laboratories to field applications, have many advantages (1-12). It requires no special sample preparation, any type of material (solid, liquid, gas etc) may be analyzed in situ and it is capable of detecting and analyzing several elements at a time (13).

In LIBS the sample is first ablated by a high-power laser pulse to form the plasma. Intensities of spectral lines of atoms and ions from this radiant plasma are used for qualitative and quantitative analysis of the sample (10, 11, 13-24).

In this chapter, we discuss the optimization of our LIBS system consisting of high resolution broad-band echelle spectrograph; ICCD sensitive in the 200-900nm range; delay and gate generator for selection of optimum-signal/noise ratio window; optical system adapted for efficient collection of plasma emission; and data processing techniques for improved results in detection and quantification of trace elements. Various important experimental conditions of this system were studied and optimized to increase the signal strength and detection efficiency for plasma spectroscopy, using copper and brass samples. To get best signal/noise ratio for the quantitative analysis of minor and trace elements, LIBS signals were recorded by changing the various experimental parameters namely laser spot size, laser irradiance, gate width, gate delay, multi channel plate (MCP) gain of ICCD, distance and angle of signal collector from sample surface, surrounding atmosphere etc (13, 25). The results were analyzed using data processing techniques like blank subtraction, signal addition, and correlation function calculation.
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4.2 PARAMETER OPTIMIZATION

4.2.1 System reproducibility

In continuation of the studies mentioned in the previous chapter, we have further optimized the echelle spectrograph-ICCD system to achieve good signal with better signal-to-noise ratio. In quantitative trace analysis, like source stability, spectrum reproducibility is also very crucial. Hence we have monitored the detector reproducibility by recording several spectra (15 trials) using Hg-Ar lamp (HG-1, Ocean Optics, USA) which provides a stable source. The lamp has SMA connector and hence coupled to the echelle spectrograph using an optical fiber. Exposure time of the detector was set to 3 sec and lamp power was measured to be 2mW. The variation in relative intensity of the two Mercury lines i.e. 546.07nm and 435.8nm is shown in Figure 4.1. The standard deviation (RSD) in these values was found to be negligible (i.e. 0.11%).

![Graph showing relative intensity vs trials](image)

**Fig 4.1** Reproducibility check of the LIBS system using Hg-Ar lamp

We have also checked the reproducibility of the LIBS (laser irradiance 4.46 x 10^8 W/cm^2, gate delay 700ns, gate width 1000ns and the collector probe was kept 20cm away from the target at an angle 45°) spectra of copper using relative intensities of 521.82nm line with respect to other copper emission lines as shown in Table 4.
Table 4 Spectrum reproducibility check for laser induced copper plasma

<table>
<thead>
<tr>
<th>Intensity ratio of Cu lines</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I_{521.82}/I_{330.795}</td>
<td>5</td>
</tr>
<tr>
<td>I_{521.82}/I_{465.112}</td>
<td>19</td>
</tr>
<tr>
<td>I_{521.82}/I_{515.324}</td>
<td>8</td>
</tr>
<tr>
<td>I_{521.82}/I_{529.252}</td>
<td>12</td>
</tr>
<tr>
<td>I_{521.82}/I_{578.213}</td>
<td>18</td>
</tr>
</tbody>
</table>

It is observed that the RSD of relative intensities varies as 5%, 19%, 8%, 12% and 18% for 521.82/330.795, 521.82/465.112, 521.82/515.324, 521.82/529.252 and 521.82/578.213 respectively as shown in Figure 4.2. Variations of these magnitudes are acceptable for trace analysis. By examining the actual intensities of these lines, it was inferred that the variations in the ratios arise mostly from variations in the lines corresponding to the denominator. The results can thus also be used to choose the best spectral lines for analysis.

4.2.2 Effect of laser irradiance on LIBS signal

Influence of laser intensities (irradiance) on the plasma generation was studied using copper foil as target at different incident laser energies. This is achieved by the use of neutral density filters kept before the focusing lens. Gate delay and gate width were kept constant at 1000ns and the signal was accumulated for 120 laser pulses. The results are shown in Figure 4.3.
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Fig 4.3 LIBS signal variation of copper plasma for different laser powers

As expected, the signals keep increasing linearly in direct proportion with increase in the laser irradiance. This is very crucial since it is essential that small day-to-day or operator variations in laser power should not lead to any errors in the results. In Figure 4.3, the intensities of 521.82nm and 515.32 nm lines is the average of three experiments under same conditions. An interesting result from the above studies is the observation that the slope of the intensity variation with power is different for the two lines. This can give information on the dynamics of the plasma, since the levels corresponding to these two lines may be getting populated through different channels.

In order to investigate the plasma plume response for varying incident laser energies in LIBS, we have also recorded plasma images at different laser energies using copper and zinc as target materials using a Charge Coupled Device (CCD) procured from Holmarc, Kochi. The images and their corresponding surface plot are shown in Figure 4.4. In surface plotting, the luminance of an image is interpreted as height in X-Y-Z directions of the plot. For this purpose, we have used ImageJ software (1.44p, Wayne Rusband National Institute of Health, USA).
4.2.3 Measurement of laser spot size on the target material and its influence on LIBS signal

Laser spot size measurement is very critical in order to manipulate the laser power (irradiance) for LIBS experiments. Also for many applications, (eg. archaeological materials, corrosion studies, IC-s) it may be necessary to analyze selected areas in the object, with minimum contamination from the rest of the sample. Using lenses with different focal lengths we can vary the laser spot size and hence the irradiance. This spot size variation on a copper target after laser ablation is recorded using a microscope (Nikon, Eclipse, DiU, Japan). The spot size and the microscopic images are shown in Figure 4.5. The experimental parameters were: average power of the laser 325mW with 6ns pulse width and 10 Hz repetition rate. Hence we can calculate energy per pulse and peak power per pulse as follows:
Fig 4.5 Interaction of laser having different spot sizes on a copper surface

Energy per pulse = 325mW / 10 Hz = 32.5mJ

Peak power per pulse (P) = 32.5mJ/6ns = 5.42 x 10^6 Watt

We have used biconvex lenses of different focal lengths namely 5cm, 10 cm and 20 cm. The spot size is calculated theoretically using standard formula $1.22 \frac{f \lambda}{D}$, where $f$ is the focal length of the lens used, $\lambda$ is the wavelength of the laser line (355nm here) and $D$ is the diameter of the laser beam (8mm here). Experimental spot sizes have been measured from the microscopic images using ImageJ software (ImageJ 1.44p, Wayne Rusband National Institute of Health, USA). Peak power density (irradiance) calculation (experimental) using different lenses are as given below.

Focal Length 5cm

Laser Spot size (Experimental) $\sim 54.4 \ \mu m = 2r_1$

Area ($\pi r_1^2$) $= 0.2323 \times 10^{-4} \ \text{cm}^2$

Peak power density ($D_{Exp}$) $\sim \frac{P}{\pi r_1^2} = 2.33 \times 10^{11} \ \text{Watt/cm}^2$
Focal Length 10cm

Laser Spot size (Experimental) ~ 120.87 µm = 2r₂

Area ($\pi r₂^2$) = $1.1469 \times 10^{-4}$ cm²

Peak power density ($D_{Exp}$) ~ $P / (\pi r₂^2)$ = $4.73 \times 10^{10}$ Watt/cm²

Focal Length 20cm

Laser Spot size (Experimental) ~ 161.76 µm = 2r₃

Area ($\pi r₃^2$) = $2.0541 \times 10^{-4}$ cm²

Peak power density ($D_{Exp}$) ~ $P / (\pi r₃^2)$ = $26.6 \times 10^9$ Watt/cm²

It is clear from the above calculations that as spot size increase the irradiance decreases. So it is easy to set breakdown threshold irradiance for any material by adjusting the laser spot size rather than using a neutral density filter to reduce the incident laser beam energy. For all studies discussed in this thesis, plasma has been initiated in air (unless and otherwise stated) and mostly using copper as target material. The breakdown threshold irradiance of copper was reported to be ~ (5-10) x $10^8$ Watt/cm² (14, 26). In order to achieve this, the laser spot size has been varied (10 µm, 1mm, 1.5mm, 2mm etc) on the copper sample and studied the plasma dynamics for different power densities (irradiance). This has been done as depicted in Figure 4.6.

![Laser spot size measurement (Theoretical)](image)

**Fig 4.6 Laser spot size measurement (Theoretical)**
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Using a 200mm focal length lens, a 10 µm spot size (theoretically) on the sample surface was made. Using trigonometric calculations as shown in Figure 4.6, we measured the distances to be moved towards the lens side from the focal spot in order to get 1mm, 2mm etc spot sizes (which in turn gives the necessary breakdown threshold irradiance) on the sample surface and then recorded the LIBS spectra. Table 5 gives the details of these results for 230mW average power of laser.

Table 5 Distances to be moved towards focusing lens (FL20cm here) in order to get different laser spot sizes

<table>
<thead>
<tr>
<th>Laser power (mW)</th>
<th>Peak laser power (W)</th>
<th>Required laser spot (micron)</th>
<th>Distance to be moved (microns)</th>
<th>Spot area (cm²)</th>
<th>Laser pulse intensity (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>3830000</td>
<td>100</td>
<td>2491.280518</td>
<td>0.0000785</td>
<td>4.88E+10</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>200</td>
<td>4982.561036</td>
<td>0.000314</td>
<td>1.22E+10</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>300</td>
<td>7473.841555</td>
<td>0.0007065</td>
<td>5.42E+09</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>400</td>
<td>9965.122073</td>
<td>0.001256</td>
<td>3.05E+09</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>500</td>
<td>12456.40259</td>
<td>0.0019625</td>
<td>1.95E+09</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>600</td>
<td>14947.68311</td>
<td>0.002826</td>
<td>1.36E+09</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>700</td>
<td>17438.96363</td>
<td>0.0038465</td>
<td>9.96E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>800</td>
<td>19930.24415</td>
<td>0.005024</td>
<td>7.62E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>900</td>
<td>22421.52466</td>
<td>0.0063585</td>
<td>6.02E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1000</td>
<td>24912.80518</td>
<td>0.00785</td>
<td>4.88E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1100</td>
<td>27404.0857</td>
<td>0.0094985</td>
<td>4.03E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1200</td>
<td>29895.36622</td>
<td>0.011304</td>
<td>3.39E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1300</td>
<td>32386.64674</td>
<td>0.0132665</td>
<td>2.89E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1400</td>
<td>34877.92725</td>
<td>0.015386</td>
<td>2.49E+08</td>
</tr>
<tr>
<td>230</td>
<td>3830000</td>
<td>1500</td>
<td>37369.20777</td>
<td>0.0176625</td>
<td>2.17E+08</td>
</tr>
</tbody>
</table>

We have recorded LIBS spectra of copper sample by changing the laser spot size (or irradiance) as shown in Figure 4.7. As expected there is a linear relation between the LIBS signal strength and laser irradiance as shown in the inset of Figure 4.7.
In order to validate this methodology to set breakdown threshold irradiance for LIBS studies of different materials, further studies have been carried out to measure the spot size experimentally. A laser paper, which is normally used to measure laser spot size, was utilized for this purpose for different distances from the target for a 20cm focal length lens. We have calculated the theoretical spot size at certain distance from the target and compared the results with the experimentally measured value using a laser paper at these distances. Excellent correlation with unit slope was observed and is shown in the Figure 4.8. Hence this method was adopted for all future LIBS studies.

Very good correlation between the theoretical and observed spot sizes indicates that the large differences (15-20 times) in theoretical and microscope image sizes may arise from interaction of the initial plasma with the material surface. This is supported by the images in Fig.4.5, where, for higher powers, a central spot is surrounded by rings giving appearance of larger spot size.
Fig 4.8 Correlation between the theoretical and experimental spot size measurements

4.2.4 Effect of incident laser radiation on the surface of the sample

If we focus a pulsed laser beam continuously at the same spot on the target material, the LIBS intensity was found to be decreasing with time as shown in Figure 4.9 for a laser induced copper plasma (Laser intensity $4.82 \times 10^8$W/cm², gate delay 1000ns and gate width 1000ns). This decrease may be due to the formation of an oxide layer or more likely a crater at the sample surface (13).

Fig 4.9 Effect of continued ablation from same spot on the surface of the copper target
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Crater size changes as we expose the laser beam continuously at the same spot. Hence in order to obtain good reproducible LIBS signal, we need to focus the laser beam on to a fresh surface for each measurement. This can be achieved with the help of a motorized translation motion (X-Y Motorized translation stage with microcontroller, Holmarc, Kochi) of the sample.

4.2.5 Effect of angle and distance of the signal collector probe from the target

The collector probe (which is used to collect the radiation from the plasma efficiently and feed to echelle spectrograph with proper F-matching) distance from sample and its angle with respect to incident laser beam have been optimized. For this study, plasma was generated on a copper target with laser power \(4.46 \times 10^8\) W/cm\(^2\), gate delay 1000ns and gate width 1000ns. Average intensity values of three trials for 521.82nm line of copper are plotted against distance and angle as shown in Figure 4.10.

It can be seen from the Figure 4.10 (a) that there is an exponential decrease in intensity (as expected) as we move the probe away from the sample. However to satisfy the F-matching conditions of our present probe we are keeping the probe 20cm away from the sample. For better signal collection, we have studied the signal level changes with respect to probe orientation. To conduct this study, the optic axis of the signal collector probe was kept at different angles with respect to the incident laser beam. All other experimental parameters were kept constant and the LIBS signal variation was investigated by taking 521.82nm atomic line of copper as reference for different collector probe angles. The intensity of 521.82nm was found to be fairly good for probe angles 20-60° as shown in Figure 4.10 (b). But further increase in angle reduces the line intensity drastically. Hence we kept the collector probe at 45° for all our experiments. This corresponds to the maxima point and thus keeps any variation in signal due to small angle changes. It should be noted that the conditions given here applies to the present experimental set up and for any changes in probe, optics etc optimization has to be done with that set up.
4.2.6 Optimizing the time window of the detection system (Gate delay, gate width and gain)

The goal of the LIBS technique is to create optically thin plasma which is in thermodynamic equilibrium (conditions which are amenable to theoretical treatment), and whose elemental composition is the same as that of the sample. When those conditions are fulfilled, the observed spectral line intensities can be related with concentrations of elements in that sample (14). Typically these conditions are only met approximately and are discussed in detail in coming chapters.

As discussed in the Chapter II, a strong continuum is always expected with spectral line in LIBS emission signal. The continuum background, normally dominates immediately after plasma formation (say few 100s of nanoseconds) but decays rapidly compared to atomic emission. Hence a time resolved technique can be employed to extract fruitful information from laser induced plasma by discriminating the line emission and continuum radiation. To achieve this we need to optimize the gate parameters like gate delay, gate width, ICCD gain etc to create optically thin plasma.
Temporal distribution of plasma is studied as it helps to discriminate the regions where a signal of our interest is predominant. Hence we have recorded time resolved laser induced copper spectra (Figure 4.11) for laser power of $4.46 \times 10^8$ W/cm$^2$ and studied its characteristics for varying delay times by keeping gate width constant at 1000ns and signal collection probe 20 cm away from the target at 45°.

![Gated copper spectra of LIBS plasma as a function of time after plasma initiation](image)

**Fig 4.11** Gated copper spectra of LIBS plasma as a function of time after plasma initiation

Even a cursory look at the above spectra shows that there are noticeable differences in spectral characteristics with time. In the very early stages- for the first few hundred nanoseconds- the spectrum exhibits strong band systems, characteristic of molecular species which almost completely masks the emission lines of atoms and ions. These bands get gradually weaker and the spectral lines of atoms and ions become prominent, exhibiting their own time evolution characteristics. To understand the dynamics of the plasma, therefore, one has to look at the spectral changes that happen in the emission of ions, atoms and molecular species.

Figure 4.12 shows the spectra from copper plasma, recorded with the LIBS system, for the entire range 200-900nm. It can be seen from Figure 4.11 and 4.12 that spectra underwent changes as plasma evolves temporally. Initial delays are dominated by continuum and ionic spectra, but as the plasma decays the continuum also vanishes and we could see good quality LIBS spectrum which can be used for qualitative analysis of sample composition. Quantitative measurement of this information is also
possible by identifying suitable characteristic lines and employing proper calibration methods which will be discussed in the coming chapters in detail.

**Fig 4.12** Temporal evolution of copper spectra in air

Time resolved spectroscopy study has been repeated using a brass sample also with laser power $4.5 \times 10^8$ W/cm² and is plotted in Figure 4.13 for varying gate delays by keeping the gate width fixed for 1000ns and signal collection probe kept 20 cm away from the target at 45°.

**Fig 4.13** Temporal evolution of brass spectrum in LIBS
It is seen that the time evolutions are similar for some lines, while they are different for some other lines.

In view of the above, it is clear that all parameters, namely delay, gate width, CCD gain and accumulation (number of laser pulses) have to be optimized for analysis. Figure 4.14 illustrates how the LIBS signal changes with these parameters using copper plasma generated by inducing laser power of $4.46 \times 10^8$ W/cm$^2$ at 1000ns delay and signal collection probe 20 cm away from the target at 45°. Each point represents average of three trail runs.

![Figure 4.14](image)

**Fig 4.14** Detector parameters optimization study for copper: Variation in LIBS signal with (a) Gate width (b) Number of laser pulses incident on the target and (c) CCD gain.

There are several important conclusions to be drawn from these plots. First of all, the lines show an increase in intensity with increasing gate width up to at least 2000ns. Till this time the 3 lines shown (and most probably other lines also) show different rates of increase (slopes) indicating that the upper levels in each case are getting populated through different pathways, the 515 and 521 similar to each other, while the 578nm, different from the other two. It is also clear from the results that the
signal does not increase after a certain value of gate width. Presumably the plasma has cooled down and there are no further emissions. The cooling time seems to be about 3000ns. Further increase in gate width can increase only noise without addition of signal. It should be noted that unlike in Figure 4.9, where the intensities decrease with increase in number of laser pulses due to ablation of material from the same spot, here the intensities keep on increasing with number of laser pulses, since each pulse ablates material from a different spot and thus conditions are unchanged from pulse to pulse. Finally, a minimum gain of the ICCD, about 150-200, (see the extrapolation of the high-rise portion) is advisable to get good signals.

From Figure 4.14 it is seen that, depending on the LIBS experiments planned, one needs to set a suitable gate width, gate delay and gain to get the best signal. Accumulation of ICCD is the process by which data that have been acquired from a number of similar scans and added together to get resultant averaged spectra. Since a laser with 10Hz repetition rate (10 laser pulses per second) was used for all the studies, accumulation time can be interpreted as number of laser pulses falling on the sample during the signal acquisition. After deciding the best detector window for any particular measurement by adjusting gate delay and width, one can use appropriate gain values for analysis; for example analysis of major components in a sample the gain can be kept low with reduction in noise, and thus improving accuracy, while for trace analysis high gain values can be used in order to increase signal and thereby getting higher sensitivity, at the cost of lower accuracy. So the gate delay, width and gain settings of ICCD are very crucial parameters in any LIBS experimental set-up.

4.2.7 Spatial distribution of laser induced plasma

Usually, collecting radiation from the whole plasma may be better for increasing intensity and improving sensitivity. However, there are situations in which it may be necessary to select suitable regions of the plasma. This is especially necessary in remote LIBS (for example planetary surfaces, industrial waste processing units), where we have no control over the atmosphere. Also, when we use only single line intensity (see later) identifying the region of plasma where this line will be most intense will help in recording a suitable spectrum. We have studied the spatial
distribution of copper plasma for getting this information. Here we have formed a 1:1 image of the copper plasma plume (~4mm) using appropriate lens (5 cm focal length lens kept at 10 cm away from the copper plasma). A variable position slit having width of 350µm was used to scan the plasma image. By moving this lens we could image the required plasma regions on to the slit. We have kept our signal collector probe 20 cm away from this slit to satisfy f-matching conditions. For same delay and width (i.e. 1000 ns) we have recorded spectra (average of three trials) for different positions of the slit and correlated these positions with plasma regions as shown in Figure 4.15. We have also calculated and plotted (Figure 4.15) the plasma temperature at different plasma zones using Boltzman’s relation and Saha equations as described in Chapter II.

From Figure 4.15 it can be seen that the 3 lines, which are very close to each other, show somewhat different behavior with respect to plasma regions. The upper level of the 510nm transition (Table 6 below) is the lower level of the 521nm transition. This could be one reason for the relatively constant intensity in the 510nm transition, which follows the decay from the 521 upper levels.

![Fig 4.15 Spatial distribution of laser ablated copper plasma](image)

On the other hand the upper levels of both 521 and 515 nm transitions are very close to each other, and both show high intensities in the plasma region with very high
temperature. The observation that these two transitions show noticeably increased intensities in regions showing high temperatures indicate that these high energy levels are in thermodynamic equilibrium and have a higher population corresponding to the Boltzmann distribution for the high temperature.

### Table 6 Energy levels of copper lines of interest (27)

<table>
<thead>
<tr>
<th>Line (nm)</th>
<th>Energy Levels (cm⁻¹)</th>
<th>Configuration</th>
<th>Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>510.55</td>
<td>11202.6</td>
<td>3d⁹4s²</td>
<td>²D₅/₂</td>
</tr>
<tr>
<td></td>
<td>30783.7</td>
<td>3d¹⁰4p</td>
<td>²P₃/₂</td>
</tr>
<tr>
<td>515.3</td>
<td>30535.3</td>
<td>3d¹⁰4p</td>
<td>²P₁/₂</td>
</tr>
<tr>
<td></td>
<td>49935.2</td>
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<td>²D₃/₂</td>
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<td>521.8</td>
<td>30783.7</td>
<td>3d¹⁰4p</td>
<td>²P₃/₂</td>
</tr>
<tr>
<td></td>
<td>49942.1</td>
<td>3d¹⁰4d</td>
<td>²D₅/₂</td>
</tr>
</tbody>
</table>

### 4.2.8 Effect of magnetic field on laser induced plasma

The large density of charged particles in the plasma provides a medium which can interact strongly with a magnetic field. Under appropriate conditions this can confine the plasma in space, providing an enhanced brightness and consequent increased optical emission (28-31). Many groups have studied the interaction of plasma with magnetic field. X. K. Shen et al studied and reported the enhancement of optical emission in LIBS due to the magnetic confinement of laser ablated plasmas (32). V. N. Rai et al has done work on the optical properties of laser-induced plasma generated from solid (Al alloy) and liquid (Mn, Cr, Mg, or Ti solutions) samples expanded across an external, steady magnetic field by LIBS (33). Since atoms and ions have a specific magnetic moment, they orient themselves in an external magnetic field and prefer a special direction for radiation. This enhances the collected LIBS intensity.

In view of this, the effects of magnetic field on the LIBS signal using Cu, Zn, Fe, Ni, Cr and Mo targets have been studied. The experimental arrangement for this
study is depicted in Figure 4.16 which is described in detail in Chapter III but with some minor modifications. The laser line is focused with suitable optics to a diffraction limited spot size on the sample surface creating the plasma. The sample is mounted on a motorized translation stage placed inside a variable current electromagnet. A Gauss meter is used to measure the applied magnetic field.

Main aim of this study was to investigate how magnetic field affects laser-induced plasma of different materials. For this purpose, we have used 99.99% pure copper, zinc, iron, brass (70%Cu 30%Zn) samples (Alfa Aesar, USA) and Cr-Ni-Mo alloys (Cr 16.67% Ni 66.67% Mo 16.67%). The laser power was \(4.85 \times 10^8\) W/cm\(^2\) with suitable values of gate delay and gate width according to the sample in use. The chosen line wavelengths of each element for this study are the following: 521.82nm (copper), 481.05nm (zinc), 396.22nm (iron), 520.84nm (chromium), 352.45nm (nickel) and 423.3nm (molybdenum).

![Figure 4.16](image)

**Fig 4.16** Schematic of the system used for the study of magnetic field effect on LIBS

The experiment was conducted for different magnetic fields and typical results are shown in Figure 4.17.
The results clearly show that there is an enhancement in the LIBS signal intensity with the application of magnetic field. Even there was a marked increase in the line intensities of individual elements in alloys. Encouraged by the results obtained from preliminary observations, the work was focused more on copper samples.

Figure 4.18 shows the changes in LIBS spectral intensities of a copper line (521.82nm) with different applied magnetic fields (0-3500 Gauss). The maximum signal count was obtained for maximum applied magnetic field i.e. 3500 Gauss.

Results suggest that there is a clear enhancement in collected LIBS signal intensity in the presence of magnetic field. The increase in the emission intensity of elements can be attributed to an increase in density of the plasma as a result of magnetic confinement during plasma cooling. Also enhanced emission in the plasma can be due to an increase in the rate of radiative recombination. However, results like the rapid increase in intensity from 3000 to 3500 Gauss, are not understood at present.
and further studies need to be done to properly understand the dynamics of plasma in external magnetic fields.

After optimizing all the experimental conditions, LIBS spectra of copper, zinc and brass samples have been recorded by fixing suitable time window and wavelength region of interest for a particular sample under investigation. Temporal history of copper, zinc and brass sample also helps us to monitor the plasma characteristics. Figure 4.19 shows LIBS spectra recorded for certain wavelength region of interest from these samples at gate delay of 1000ns, number of accumulation 15, gain 175 and gate width of 1000ns having laser intensity of $4.88 \times 10^8$ W/cm$^2$.

The full wavelength range LIBS spectra of different materials (copper, zinc, iron, brass, alloys, glass etc) after optimizing different parameters as mentioned above are shown in the Figure 4.20 (a) and (b). These graphs show that the LIBS technique produces extremely complex spectra and quantitative analysis of trace elements in presence of major components can be extremely difficult.
However, with appropriate experimental system with high-resolution echelle spectrograph, the presence of even elements having weak signal intensity in the highly complex spectra can be quantified. This is shown in Figure 4.21 in the case of copper, where the regions of strong lines of copper are plotted on expended scale. It is seen that there are practically no interferences for a chosen line from other lines of this element. The same was observed in complex samples with multi elements. This shows that the developed system can be used for simultaneous analysis of major, minor, and trace elements in any type of sample.
Fig 4.20 LIBS spectra of 99.99% pure (a) single elements- copper, zinc and iron (clock wise) and (b) multi elements- brass, NiCrMo alloy and Mn doped glass (clockwise)
4.3 CONCLUSION

LIBS is a rapid multi-elemental analysis technique with high spatial and temporal resolution. Parameter optimization is an important part of any LIBS system because all of the spectral features and reproducibility of the recorded spectrum depends up on the different experimental parameters and instrumental components used. Hence experimental parameters like laser energy, laser spot size, signal collector probe distance/angle with respect to target, surrounding atmosphere, and detector (ICCD) parameters (gate width, gate delay, accumulation and MCP Gain) have to be studied and optimized. In the present work, different types of samples (Pure materials like copper and iron, alloys (brass, Cr-Ni-Mo), and doped materials were utilized for these studies. The results show that our optimized setup- echelle spectrograph coupled with an ICCD- is highly suitable for LIBS based elemental analysis as spectral lines of elements of interest can be easily selected in any part of the spectrum.

![LIBS Spectrum of Copper](image)

**Fig 4.21** A LIBS spectrum of copper demonstrating the broad range and high resolution of the developed system
Extensive studies done on copper, brass etc using echelle system shows that this system can be successfully used to perform LIBS for ultra-trace elemental analysis in the laboratory, and in situ/remote conditions (see later Chapters). It can also be used as an extremely handy and flexible tool for varied spectroscopy research investigations like plasma dynamics etc.

4.4 REFERENCES

17. G. Kim, J. Kwak, J. Choi and K. Park, "Detection of nutrient elements and contamination by pesticide in spinach and rice samples by using the Laser Induced Breakdown Spectroscopy (LIBS)," Journal of Agricultural and Food Chemistry 60(3), 718–724 (2011)