Chapter 7

LIBS- Other applications and future directions
ABSTRACT

In this chapter, a few other applications of LIBS are discussed and the initial results are reported. The quantitative analysis of manganese in manganese-doped glass samples in air at atmospheric pressure has been done using the LIBS system with laser irradiance of $1 \times 10^9$ W/cm$^2$. A calibration curve for Mn is produced from the LIBS spectra of four certified Mn-doped glass samples. Using this linear calibration curve, Mn concentrations in the four certified samples are determined. Preliminary work done on remote LIBS set-up which can be a convenient technique for standoff analyses of materials is also discussed in this chapter. The capability of this system was investigated using single, mult and complex elements and soil samples for realistic conditions by varying the collection distance from 10 cm to 3 meters from the sample surface. It was observed that even at a distance of 3m we could get reasonably good signals without additional optical/mechanical accessories. A LIBS system was designed for liquid samples (mainly for clinical applications) and optimized it for routine studies. Finally methods to increase the LIBS signal collection efficiency using different optics schemes were tried and it was shown that the efficiency can be improved 20 times or more for dedicated applications.
7.1 INTRODUCTION

LIBS has been well recognized as a simple, fast and direct analytical technique for the elemental analysis of complex materials by a number of groups all over the world (1-11). During the last two decades, LIBS has attracted a lot of attention, leading to an ever increasing list of applications like real time analysis of metals, plastics, minerals, aerosols, biological tissues and liquids, both in laboratory and in industry (11-26).

The attractive features of LIBS involve the following: low analysis cost per sample, ability to analyze a large number of samples in a short period of time, measurement precision sufficient for screening many elements of interest, high sensitivity and possibility of in situ analysis of remotely located samples. Portable LIBS systems (27) can be used for in situ field applications such as archaeology, food analysis etc. But for applications in hostile environments such as identification of highly radioactive waste (28) or the monitoring of molten alloys (29), remote LIBS is required. LIBS has been successfully used for the laboratory detection and identification of chemical and biological warfare agents, explosives and other hazards (30-32) and the technique can be easily extended for remote operation, which is often required for these applications. The use of optical fibers to guide the laser beam and collect the emitted light to / from the sample (remote LIBS system) allows investigation of targets where access is difficult or represents a hazard for the analyst (33). By the use of telescopes the collection of the plasma emissions can be done with long distances between sample and measurement device over an open path or a stand-off LIBS system (34). Mainly the use of telescopes to focus the laser beam and to collect emitted light from the plasma allows the measurement at large distances from the sample. Recently the combination of LIBS with other spectroscopic techniques like Raman-spectroscopy have been studied to receive additional information at one measurement (35, 36). In this chapter, as an initial step towards the development of remote LIBS technique, the signal collection ability of the developed LIBS system has been studied at much longer collection distances from the sample than usually used for laboratory analyses.
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It is presumed that the very high temperatures prevalent in laser produced plasmas lead to complete ionization of all the elements in the matrix, which then relax to the various excited ionic and atomic stationary states through collisional interactions, mostly with the high energy electrons in the plasma. Further relaxation by radiation emission gives rise to a large number of atomic and ionic lines which can be used for quantitative analysis. However, it is also possible that in some of the excited states, the atoms (ions) may undergo collisions among themselves, and if their energy states are suitably placed, they may combine to form molecular species in excited states. The laser plasmas are thus, in favorable situations, suitable sources for observation of molecular species in highly excited states. The intensities of the atomic and molecular spectral lines are very much dependent on the dynamics in the plasma. In this chapter, some early results on the dynamics of copper plasmas producing molecular species, by laser ablation of copper is reported.

Few other applications like quantitative analysis of elements in glass matrix with a future goal to do analysis of nuclear waste fixation materials has been done using manganese doped glass samples. Also, the current LIBS system was optimized for elemental analysis of liquid samples (mainly clinical samples like serum etc) and some preliminary results are presented in this chapter. LIBS, as mentioned earlier, has got lot of biomedical applications. LIBS experiments conducted on calcified tissues confirm the potential of this technique for such applications and initial findings are discussed in this chapter. Attempts have been made to improve the LIBS signal collection efficiency and hence the measurement capabilities. Results obtained from these preliminary studies were promising and will help in further improvement of the system to a greater extend for various analytical applications.

7.2 LIBS- OTHER APPLICATIONS

7.2.1 Quantitative analysis of elements in glass

In this study, quantitative LIBS analysis of manganese (Mn) in manganese-doped glass samples (Obtained from Nuclear Recycle Board & Process Development Division, Bhabha Atomic Research Centre, Mumbai) is done in air at atmospheric
pressure. The plasma is generated with an irradiance of $1 \times 10^9 \text{ W/cm}^2$ on the sample surface. The detector gate width of 2 $\mu$s and the detector gate delay of 2 $\mu$s were chosen for recording the plasma emission signals, discriminating the continuum radiation which is intense at initial delay time ($< 300$ ns) and decreases at later times.

LIBS spectra of four certified Mn-doped glass samples were recorded for the quantitative compositional analysis of Mn in the samples. All LIBS spectra were derived from an integration of 120 laser pulses to ensure reproducibility of the spectra. A typical LIBS spectrum of one of the certified Mn-doped glass samples is shown in Figure 7.1. The spectral lines of Mn I and Si I of interest are shown in the figure.

![LIBS Spectrum of Mn-Doped Glass Sample](image)

**Fig 7.1** A typical LIBS spectrum of a Mn-doped glass sample showing Mn and Si atomic lines

A calibration curve for Mn present in the samples was prepared from the LIBS spectra of four certified Mn-doped glass samples, employing the internal standardization method, considering the analyte Mn atomic line (482.35 nm) and the reference Si atomic line (288.16 nm) as shown in Figure 7.2. The logarithm of the relative intensity ratio of the analyte (Mn) element and the reference (Si) element...
lines is plotted against the logarithm of the given relative concentrations of the four Mn-doped glass samples for the preparation of calibration curve of Mn.

![Calibration curve for Mn at 2000 ns detector gate delay with linear regression equation and its coefficient using four Mn-doped glass samples]

**Fig 7.2** Calibration curve for Mn at 2000 ns detector gate delay with linear regression equation and its coefficient using four Mn-doped glass samples

The linear regression equation and the regression coefficient for the calibration curve are also given in the Figure 7.2. As seen from the figure, the calibration curve in this experiment is well characterized by a straight line without any saturation effect. Using the linear calibration curve, the Mn concentration in the four certified samples is determined. The results of these calculations are presented in Table 18.

Calibration plots have also been constructed using only lines of manganese (478.34nm and 482.35nm), without internal standard rationing, for different concentrations of manganese in the glass matrix. The regression coefficients for these calibrations curves were found to be excellent as shown in Figure 7.3. It is seen that in both cases the curves extrapolate to zero intensity for zero concentration.
Table 18 Correlation of the LIBS determined concentration ratio Mn/Si with its certified value and the corresponding uncertainty of four Mn-doped glass samples using the calibration base method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified concentration ratio Mn/Si</th>
<th>LIBS determined concentration ratio Mn/Si</th>
<th>Correlation uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.609</td>
<td>0.625</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.383</td>
<td>0.340</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>0.182</td>
<td>0.204</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>0.035</td>
<td>0.034</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig 7.3 Calibration curves for two emission lines of manganese in a glass matrix using LIBS
7.2.2 LIBS of liquid samples

We have also tested our LIBS system for elemental detection and quantification of liquid samples. For this, the normal experimental setup was slightly modified as shown in Figure 7.4. For the preliminary experiments, samples were prepared by adding known concentrations of copper sulfate (Sigma Aldrich, USA) into HPLC grade distilled water (Sigma Aldrich, USA) and filling the solution in the syringe pump (Holmarc, India) as shown in the figure.

Using this syringe pump we can adjust the flow rate of the liquid sample. The focused laser light was made to fall on the liquid stream and LIBS signal was recorded and analyzed as discussed in earlier chapters. Normally the laser line intensity to create plasma on liquid samples is higher compared to solids and is of the order of $\sim 10^{11}$ W/cm$^2$. Detector gate delay was set at 500ns. A typical LIBS spectrum of HPLC grade water and copper sulphate solution were recorded using this set up and is shown in Figure 7.5.

Calibration curves for copper were prepared from these data. Different methods have been adopted for drawing calibration curve. Initially we have directly noted the intensities of 521.82 nm line of copper and plotted the calibration graph as shown in Figure 7.6.
The measured limit of detection (3σ/slope, where σ is the standard error of the calibration plot) was found to be 0.164ppm for this method of analysis. Further to improve the sensitivity of this technique we have subtracted the water LIBS spectrum (considering it as a background) of solvent water from the spectrum of copper sulphate solution as shown in below Figure 7.7. The calibration curve now extrapolates to zero intensity for zero concentration indicating the validity of background subtraction.
The measured limit of detection (3σ/slope, where σ is the standard deviation of the least concentration) after background subtraction was found to be 0.104 ppm. The results are very encouraging and prove the feasibility of the modified LIBS with liquid samples for detection and quantification of water pollutants, trace elements in body fluids etc.

### 7.3 LIBS- SOME FUTURE DIRECTIONS

#### 7.3.1 Remote LIBS

Schematic diagram of the LIBS set-up used for this study is shown in Figure 7.8 below. The laser line is focused on to the sample surface with a 50cm focal length lens. No attempt was made to increase this distance, since longer distances can be easily obtained with required power on the sample, by using appropriate optics at such distances and increasing the power of the laser.

With an aim to study the LIBS signal collection ability of the system we have varied the distance from the sample to collection optics (signal collector in figure) in

**Fig 7.7** Calibration curve for copper in HPLC grade water with background subtraction
steps of 25cm. In order to optimize the experimental conditions the measurement was done on a copper target first. The results were encouraging, and so the runs were repeated on more complex samples like soil, which is a heterogeneous mixture of many elements. Collection system was moved up to a distance of nearly 3 meters.

Fig 7.8 Schematic diagram of the set-up used for preliminary remote LIBS studies

For an increased distance between the plasma and the signal collecting system the measured intensity of the plasma emission from the point source decreases. The reduction can mainly be described by inverse square law:

\[ I = \frac{P}{4\pi r^2} \]  

(1)

where the intensity \( I \) that can be measured at the distance \( r \) to a point source emitting the power \( P \). Further reduction of intensity is due to scattering and attenuation of light, which may be important for measurements in the open field over long distances under adverse atmospheric conditions (36).

The aim of this work is to investigate the performance of the given LIBS setup for measurements in stand-off LIBS system. The distance between the target and the light collecting system is increased in several steps. At first single-element, then double-element and finally multi-element targets are used for investigation. The measured intensities of emission lines were evaluated and conclusions are drawn on
the performance of the setup at increased target-distances. Also calibration curves for a set of samples of different Ni-Cr-Mo-compositions were investigated at the different distances.

For every target material six measurements were done at every distance step. After changing each position of the collection system it was focused to the target using the alignment laser. From the recorded spectra the intensity of specific emission lines of the target elements were deduced. The lines were selected with the aid of NIST database (37) and they are listed in Table 19.

Table 19 Sample composition and measurement parameters for LIBS investigations

<table>
<thead>
<tr>
<th>Material (% wt)</th>
<th>Number of laser pulses</th>
<th>Gate pulse delay [ns]</th>
<th>Gate pulse width [µs]</th>
<th>Number of trials</th>
<th>Beam intensity [mW]</th>
<th>Focal length of focusing lens [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 99.99</td>
<td>240</td>
<td>700</td>
<td>3</td>
<td>4</td>
<td>372</td>
<td>50</td>
</tr>
<tr>
<td>Zn 99.99</td>
<td>240</td>
<td>700</td>
<td>3</td>
<td>6</td>
<td>385</td>
<td>50</td>
</tr>
<tr>
<td>Fe 99.99</td>
<td>240</td>
<td>500</td>
<td>3</td>
<td>6</td>
<td>375</td>
<td>50</td>
</tr>
<tr>
<td>Brass 99.99</td>
<td>240</td>
<td>700</td>
<td>3</td>
<td>6</td>
<td>395</td>
<td>50</td>
</tr>
<tr>
<td>Steel</td>
<td>240</td>
<td>700</td>
<td>3</td>
<td>6</td>
<td>395</td>
<td>50</td>
</tr>
<tr>
<td>NiCr33</td>
<td>120</td>
<td>500</td>
<td>3</td>
<td>6</td>
<td>375</td>
<td>10</td>
</tr>
<tr>
<td>NiCr25Mo8</td>
<td>120</td>
<td>500</td>
<td>3</td>
<td>6</td>
<td>375</td>
<td>10</td>
</tr>
<tr>
<td>NiCr21Mo12</td>
<td>120</td>
<td>500</td>
<td>3</td>
<td>6</td>
<td>375</td>
<td>10</td>
</tr>
<tr>
<td>NiCr17Mo17</td>
<td>120</td>
<td>500</td>
<td>3</td>
<td>6</td>
<td>375</td>
<td>10</td>
</tr>
</tbody>
</table>

7.3.1.1 Single-element systems

For the initial investigations on distance dependent studies targets of single elements were used, namely copper, zinc and iron. All the target materials were of
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99.99% (Alfa Aesar, USA) purity. The averages LIBS intensities of 6 measurements (at times best 3 of 6) are taken from each sample for plotting as shown in Figures 7.9, 7.10 and 7.11.

The intensity decline over distance $x$ in the plots is described by a nonlinear regression in the form of

$$y = ax^b$$  \hspace{1cm} (2)

as it should follow the inverse square law in eq. (1).

Copper

Copper gives strong LIBS signal up to a measured distance of 240 cm. Even at this distance the spectral lines can be clearly distinguished from the background signal. The regression results of the different spectral lines are displayed in Table 20.

![Fig 7.9 Intensity decline as a function of distance between copper target and signal collecting system](image-url)
Table 20 Results of nonlinear regression of measured intensity as a function of distance for copper target

<table>
<thead>
<tr>
<th></th>
<th>y = ax^b</th>
<th>a</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>515.13 nm</td>
<td>1.91x10^6</td>
<td>-1.295</td>
<td>0.9578</td>
<td></td>
</tr>
<tr>
<td>521.82 nm</td>
<td>5.37x10^6</td>
<td>-1.360</td>
<td>0.9207</td>
<td></td>
</tr>
<tr>
<td>578.21 nm</td>
<td>0.36x10^6</td>
<td>-0.979</td>
<td>0.9312</td>
<td></td>
</tr>
</tbody>
</table>

Zinc

Zinc gives less intense emission signal compared to copper. But still the specific emission lines can be clearly distinguished from the background noise at the largest investigated distance of 240 cm. The regression results are displayed in Table 21.

Fig 7.10 Intensity decline as a function of distance between zinc target and signal collecting system
Table 21 Results of nonlinear regression of measured intensity as a function of distance for zinc

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>a</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>468.01</td>
<td>0.40x10⁶</td>
<td>-1.009</td>
<td>0.9553</td>
</tr>
<tr>
<td>472.22</td>
<td>2.27x10⁶</td>
<td>-1.201</td>
<td>0.9660</td>
</tr>
<tr>
<td>481.05</td>
<td>2.55x10⁶</td>
<td>-1.193</td>
<td>0.9898</td>
</tr>
</tbody>
</table>

Iron

When iron is used as a target material the evaluation of the spectrum was found to be difficult due to the large number of emission lines. The intensities of the iron emission lines are less compared to that of copper and zinc. Therefore the signal-to-noise ratio for iron lines at a distance of 240 cm is not as good as copper and zinc. Still the signal intensity is high enough to distinguish the specific emission lines from the background noise. The regression results are displayed in Table 22.

Fig 7.11 Intensity decline as a function of distance between iron target and signal collecting system
Table 22 Results of nonlinear regression of measured intensity as a function of distance for iron

<table>
<thead>
<tr>
<th>y = ax^b</th>
<th>a</th>
<th>b</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>406.34 nm</td>
<td>7.56x10^5</td>
<td>-1.361</td>
<td>0.8842</td>
</tr>
<tr>
<td>432.58 nm</td>
<td>4.87x10^5</td>
<td>-1.168</td>
<td>0.9004</td>
</tr>
<tr>
<td>495.76 nm</td>
<td>5.30x10^5</td>
<td>-1.180</td>
<td>0.9377</td>
</tr>
</tbody>
</table>

In conclusion the measurement of single-element targets gives good signal strengths up to the distance of 240 cm. All the investigated emission lines were clearly distinguishable from the background signal. The decline of intensity with increasing distance between target and signal collecting system more or less follow the inverse square law.

7.3.1.2 Double-element system

In this study, samples consisting of two elements were used. The averaged intensities and the inverse square regression for each element in the sample are displayed in the Figure 7.12.

Brass

The brass sample is an alloy consisting of about 70 wt% of copper and 30 wt% of zinc. At a distance of 240 cm also the typical spectral lines of copper and zinc were clearly seen without any background interference. The derived exponents from nonlinear regression are similar to those of the pure elements.
7.3.1.3 Multi-element systems

Steel

The precise composition of this sample was not known, but common percentage weight of chromium are in the range of 10 wt% to 20 wt%, nickel are in the range up to 10 wt%, and iron will be having the highest wt%.

The averaged intensities and the inverse square regression for iron, chromium and nickel is depicted in Figure 7.13. Chromium and iron lines showed very high intensity as expected. For nickel only weak intensity values could be measured. Due to this low intensity at higher distances, system was not able to pick the nickel signals.
Nickel-base alloys

Final measurements were done with a set of samples of nickel-base alloys Ni$_2$(Cr, Mo) obtained from Structural Metallurgy Section, Materials Group, Bhabha Atomic Research Centre, Mumbai. All samples consisted of 66.66 wt% Nickel and different amounts of chromium and molybdenum. The compositions are summarized in Table 6 (Chapter V).

The averaged intensities and the inverse square regression for nickel and chromium are displayed in Figure 7.14. At distances higher than 180 cm the nickel signal found to be weak. Chromium emission lines follow better inverse square trend compared to nickel. Hence calibration curves were constructed at different distances for varying chromium concentrations as shown in Figure 7.15. It is clear from the figure that even after collecting LIBS signal from a distance of 240 cm from the sample, a good calibration curve was achieved. This shows the strength of this method and clear promise for stand-off measurements of hazardous materials.
**Fig 7.14** Intensity decline as a function of distance between target and light collecting system for nickel and chromium in nickel-base alloys

**Fig 7.15** Calibration curve for chromium at different distances
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The experiment was repeated on soil pellets, with laser line intensity of 8.26 x10^{11} \text{ W/cm}^2 with a delay of 500 ns and gate width 6\mu s. Here the collector distance was varied from 10 cm to 285 cm. All measurements were done for \sim 500 pulses of the laser. The change in the intensity of iron peak (396.22 nm) is shown in Figure 7.16. It is evident from the figure that LIBS signal can be collected using this system even at a distance of 285 cm away from the sample.

![Image](image.png)

**Fig 7.16** (A) Iron peak intensity variation in soil with collection distance (B) Plot depicts the intensity variation with collection distance

It is thus evident that using the current system, without even any further modification, can be used for routine analysis of major components of inaccessible samples, at reasonable distances up to few meters. The detectivity can be further increased, if required, by improving the collection efficiency of the system (see later).

### 7.3.2 LIBS for biomedical applications

From preliminary experiments carried out on clinical a sample (calcified tissues or teeth) for trace elemental detection, it was found that LIBS is a robust tool for such applications. Elemental analysis of calcified tissue after hard tissue Osteotome (Figure 7.17) has been tried using LIBS. Calcified tissue samples utilized
for this study were obtained from oral surgery department, Manipal college of dental sciences, Manipal.

![Figure 7.17 Hard tissue Osteotome image and the regions chosen for the current study](image)

A typical sample (Fig. 7.17) was divided into 3 regions where the elemental composition of the teeth is expected to vary. Generally in teeth, the calcium and phosphorus concentrations decrease from region 1 to region 3 (i.e. enamel to root) but the magnesium concentration increases (38).

To verify this, each region of the sample was exposed to laser (irradiance $\sim 10^{11}$ W/cm$^2$) and LIBS spectra were recorded for 500ns gate delay, and 3 $\mu$s gate width. A typical spectrum is shown in Figure 7.18.

![Figure 7.18 LIBS spectrum of a calcified tissue or teeth](image)
Further analyses of recorded LIBS spectra of calcified tissues gave rise to interesting results. Excellent correlation between literature and results has been observed. The intensity of calcium emission lines falls as we moved from region 1 to 3. The same trend was observed in 6 different emission lines of calcium which confirms the results. Also magnesium emission intensity was increasing from region 1 to 3. Phosphorous spectral behavior was matching with that of calcium. The results are shown in Figure 7.19.

**Fig 7.19** LIBS spectral variations of calcium, magnesium and phosphorus at different regions in calcified tissue sample

Figure 7.20 shows the LIBS intensity changes in calcium and magnesium in a single spectrum as we move from one region to other. The results clearly demonstrate how the elemental concentration varies from one region to other in calcified tissues.
Fig 7.20 LIBS spectral variations of calcium and magnesium at different regions in calcified tissue sample

It is thus seen that the presence and relative concentrations of major elements (calcium, phosphorus and magnesium) in human tissue (tooth) can be easily determined using LIBS technique. The importance of this study comes in anthropology where tooth and bone are main samples from which reliable data can be easily retrieved. Also, trace element identification provides valuable information concerning alimentary habits and community life conditions of groups and individuals (39). Conventional methods utilized for these studies require elaborate sample preparation, with partial destruction of samples. However, further studies need to be done to properly understand the spectral behavior so that quantitative analysis can be done and the results can be correlated to life patterns.

7.3.3 Time evolution and dynamics of laser produced copper plasma

Our studies on time resolved emission from an LIBS plasma of copper, in atmosphere, showed that at short delays, atoms in certain excited states collide with one another producing copper dimers in excited state, which relax to lower states, giving rise to molecular emission bands. The technique can be used to produce diatomic species from non-volatile elements. The molecules are often in highly
excited states and analysis of the spectra can thus give information on inter-stellar molecules which often exist under similar conditions of temperature and pressure.

Often the broad background is attributed to continuum emission from the ionization continuum of the atoms in the plasma. But a closer examination of the spectrum in expanded scale, Figure 7.21, shows that the emission consists of closely spaced bands showing characteristic band structure observed in molecular spectra (40), the structure disappearing after about 500ns, while the atomic lines of copper go on increasing in intensity.

![Figure 7.21 Temporal evolution of copper plasma in the wavelength region 500-525nm](image)

The bands are observed only for a short time after initiation of plasma that is before the plasma has expanded, and hence has a high density of the excited atoms/ions. Collisions between the excited atoms might have lead to the formation of these "Excimer" molecules. It is seen that while the copper lines in the other regions (eg. 325.047nm, 399.330nm, 582.583nm and 780.766nm) remain more or less constant in intensity and show a sudden decrease after about 1000 ns, the 3 lines around 500nm increase in intensity with delay. This leads to the possibility that the molecular bands originate from those excited states which are associated with these lines, the upper states of these being continuously replenished by decay of other higher states. An examination of the energy level diagram of copper (41) shows that all the 3 lines in this region have the same 3.8 eV level either as the upper, or the
lower, state. This indicates that the molecules involved are generated from collisions between atoms in this level with other copper atoms/ions, giving molecules in energy close to 3.8 eV giving the emission in this region.

It is very interesting to note that the spectra observed in the present work cover a very wide spectral range, the entire visible range. Earlier workers, who have produced the Cu dimer by supersonic beams, sputtering etc have been able to get only very few bands in the 450-500nm region. In the present work, extensive spectra are observed because the high-energy laser plasma produces a large density of excited atoms which on collision form molecules in high lying vibrational states of the dimer. These give rise to the long wavelength bands. It is also possible that since the atoms/ions are produced in a large number of excited levels, they might have given rise to molecular formation involving other states also. This is supported by the observation that at longer delays a new band system seems to appear around 325nm (Figure 7.22).

![Temporal evolution of copper plasma in 300-380nm & 420-650nm region](image)

**Fig 7.22** Temporal evolution of copper plasma in 300-380nm & 420-650nm region

The plasma is produced in normal atmospheric conditions. The only atomic species available in the plasma or surrounding atmosphere are thus, Cu, O, and N. But since the molecules are observed at very short interval after initiation of plasma, that is before the plasma has expanded, it is unlikely that any external atmospheric atoms
have entered the plasma and are involved in their formation. Hence we conjecture that the bands observed are from Cu$_2$ molecules. However, further studies need to be done to confirm this observation.

### 7.3.4 Improvement of LIBS signal collection efficiency

Though the results obtained from different materials using the current LIBS system show that it is sufficiently sensitive for trace analysis at ppm levels with less than microgram quantities of sample, further improvement can be of use in many applications, and for better measurement accuracy and precision. In order to achieve this using the current LIBS system, the first thing one need to focus is to improve the collection efficiency of it. Currently the signal collector with a single optical fiber has been utilized for all studies reported in this thesis. It was understood that the signal collector works efficiently and feeds sufficient plasma light to the detector system in order to get a good LIBS spectrum with high S/B ratio.

The signal collector in the present studies was kept at 200 mm away from the sample surface in order to get proper f-matching with the spectrograph. At a distance of 200mm, only a small fraction of the total light from the plasma (since emission is isotropic- in all directions) will be collected by the lens of 30mm diameter of the signal collector, and remaining light is lost. A high sensitivity technique can’t afford this all the time and hence we need to develop an alternative collection schemes using optics to tackle this issue. We have done some preliminary studies in this direction and the results are discussed here.

Figure 7.23 shows the experimental set up proposed and tested for improved LIBS signal collection. Here all other components of the normal LIBS system are retained except the signal collector. A copper sample is used for this study and plasma is generated for optimized settings of experimental parameters.

Instead of the normal signal collector/collimator assembly, different optic schemes have been tried. Lenses used for these experiments are 4cm focal length 1” diameter (F/1.6), 5cm focal length 1” diameter (F/2), 5cm focal length 2” diameter (F/1) and the normal system (200mm focal length 1.2” lens ~ F/7). These lenses were
fixed at distances equal to 2f, from sample surface as shown in the figure in order to get 1:1 plasma image behind the lens at the same distance. A home built optical fiber probe having 6 optical fibers of 200µm core diameter and 0.22 numerical aperture arranged circularly is used for light collection at the image point. This fiber probe is connected to the detector.

**Fig 7.23** Experimental set up for improved LIBS signal collection

For all lenses same methodology was adapted. LIBS signal was collected from the copper plate using different lens scheme by keeping all other experimental settings constant. Three emission lines (515.324nm, 521.82nm and 578.213nm) of copper have been chosen to analyze the results as shown in Figure 7.24.

Tremendous increase in the signal intensity has been observed for all lens schemes employed compared to the normal set up. If 521.82nm line of copper is used for a comparison, 20 times increase in the LIBS recorded signal was inferred using 4cm focal length 1’ lens scheme than the signal recorded using normal set up. This trend is true for other two lines of copper as well. This is due to the fact that 4cm lens is collecting plasma light from a distance of 8cm away from plasma which is the closest compared to all other arrangements. Hence it’s proved that these
methodologies can be successfully used for LIBS laboratory experiments for trace elemental detection. From Figure 7.24, it is seen that by going from an F/7 lens to an F/1.6 lens we have increased the intensity about 20 times, which is theoretically expected. Further improvement in signal collection can be achieved by using better F-matched systems.

![Fig 7.24 Collected LIBS signal for different lens schemes](image)

**Fig 7.24** Collected LIBS signal for different lens schemes

### 7.4 CONCLUSION

The analytical performance of the LIBS system through the correlation of the LIBS determined concentration of Mn with its certified value has been studied. The relative accuracy of the elemental performance using the LIBS method by their relative deviation from the certified values of the samples was evaluated. Good agreement is seen in the results of this work and the certified concentrations.

Results inferred from preliminary studies conducted on remote LIBS set-up show that LIBS is a promising tool for the remote analyzing of complex samples. In these measurements the signal intensity of copper, zinc and iron in single- and double-element targets was detectable up to the maximum distance of 240 cm. The
composition of these specimens could be determined qualitatively. For elements that show high signal intensity in multi-element samples, like chromium in nickel-base alloys, a quantitative composition analysis can be carried out for larger distances by use of calibration curves. Iron in soil was detected at a distance ~3m from the sample. Increasing the collection efficiency by the usage of appropriate optics one can further increase the collection distance. This will make LIBS an efficient tool for the analysis of toxic elements and hazardous materials from a safer distance from the sample.

Observed results on calcified tissue samples by LIBS technique are very encouraging. From the present study, we infer the robustness of LIBS in biomedical, anthropological and paleontological applications.

Time resolved emission from an LIBS plasma of copper in atmosphere show that at very short delays, atoms in certain excited states collide with one another producing copper dimers in excited state, giving rise to molecular emission bands. This gives rise to the possibility of producing and studying exotic molecules by appropriately tailoring the plasma conditions and matrix composition. The technique may be very useful for astrophysical applications, and study of molecules of refractory/non-volatile elements (C, S, Si, etc) and metallic/intermetallic molecules, in highly excited states. The identification and analyses of the molecular spectra, especially of mixed species, can give information on the dynamics of the plasma, since the molecule formation depends on the relaxation processes of the ions and atoms in excited states.

Studies conducted on improving the sensitivity of current LIBS system by efficient collection of plasma emission using different lens systems yielded promising results. 20 times or more increase in the LIBS signal can be achieved using these arrangements which will in turn help to improve the limit of detection of the system for trace elemental identification of complex materials in lab conditions.

7.5 REFERENCES