Chapter 5

Calibration-based and calibration-free quantitative analysis by LIBS

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ABSTRACT

As discussed in previous chapters, for LIBS analysis the plasma has been produced by focusing 355 nm pulsed Nd:YAG laser having pulse duration of 6 ns, onto solid samples (copper, brass, alloys) in air at atmospheric pressure. The temperature and electron density characterizing the plasma are measured by time-resolved spectroscopy of neutral atom and ion emissions in the time window 300-2000 ns. The temperature is obtained using the Boltzmann plot method and the electron density is determined using the Saha-Boltzmann equation method. Both parameters are studied as a function of delay time with respect to the onset of the laser pulse. The results are discussed in detail in this chapter. The time window where the plasma is optically thin and is also in local thermodynamic equilibrium (LTE), necessary for accurate analysis, is deduced from the temporal evolution of the intensity ratio of two Cu I lines. Quantitative analysis using calibration based and calibration free LIBS methods are also discussed in this chapter. An algorithm relating the experimentally measured spectral intensities with the basic physics of the plasma is developed. Using the algorithm, a method was standardized for the determination of the Zn and Cu concentrations in brass sample with accuracy better than 1%. Employing the internal standardization method, calibration-based analysis of Ni-Cr alloys was optimized. The effect of slopes and regression coefficients of the linear calibration curves on the analytical predictive capability of LIBS is studied through the correlation of the LIBS determined concentrations of Cr with its known values.
Chapter 5

5.1. INTRODUCTION

Pulsed laser-induced plasmas (LIPs) of metals and alloys formed at laser pulse irradiances near the plasma ignition threshold are of great interest since they have several important applications, e.g. material processing, thin film deposition and metal analysis in solid samples (1). Optical emission spectra of a LIP consist of atomic and ionic lines, superimposed on a continuum of radiation. Elemental analysis of the sample based on the optical emission spectra from a LIP is known as laser-induced plasma spectroscopy (LIPS), also called as LIBS. The LIBS technique, utilizing a pulsed LIP formed near the plasma ignition threshold as a spectroscopic source is a well-known analytical technique to provide remote, in-situ, rapid and multi-elemental analysis of bulk and trace sample in any phase (solid, liquid and gas) with no or minimal sample preparation (2-4).

The LIBS technique as mentioned earlier got several attractive features over other widely used analytical techniques of atomic emission spectroscopy. In particular, vaporization and excitation of samples are possible in a single step and no restriction has to be placed on the sample size or specific requirement of sample preparation. Moreover, simultaneous multi-element analysis can be performed irrespective of atomic number of elements and this technique can be employed for online analysis remotely in hostile environments. During the last two decades, LIBS has attracted a lot of attention, leading to an ever-increasing list of applications, both in laboratory and in industry. One of the major applications of this technique is in the composition analysis of metallic materials (5).

For the spectroscopic investigation of solid targets, several workers studied LIP from solid copper. Lee et al. (6) carried out time-integrated, space-resolved studies of laser-ablated plasma emission with Cu target in air at atmospheric pressure using a 193 nm pulsed excimer laser and determined T using the emission spectra. Mao et al. (7) characterized a LIP from a solid Cu target in air using a 248 nm pulsed excimer laser. They have employed time-integrated emission spectroscopy in the plasma characterization. Pietsch and his co-workers (8) studied the expansion of Cu plasma and its distribution, formed by a 308 nm pulsed excimer laser in air at reduced
pressure (20 mTorr), using a gated intensified charge-coupled device (ICCD) camera for spectroscopic applications. Wu et al. (9) investigated the dynamics of Cu plasma generated by a 308 nm pulsed excimer laser in air at reduced pressure (< 1 mTorr) by optically examining the plasma plume. Hafez et al. (10) studied the characteristics of Cu plasma produced by a 355 nm pulsed Nd:YAG laser interaction with a solid target in vacuum and argon buffer gas using the plasma spectroscopy and Langmuir probe methods. They determined T using the Boltzmann plot and ne using the Stark line broadening.

For quantitative elemental analysis of unknown samples, the calibration curve, which is a plot of intensity of an analyte emission line versus its concentration, is commonly made with standards of known elemental concentrations in a matrix close to that of the unknown samples. Although the calibration curve method is the convenient approach for quantitative analysis, it is most suited for matrix-matched samples. For achieving accurate quantitative results from the linear calibration curves, the experimental conditions affecting the analytical performance need to be carefully studied (11-13). The slope of the calibration curve that represents the sensitivity and the regression coefficient of the curve that represents the precision are the two important parameters affecting the analytical predictive capability of the LIBS technique to unknown samples. Several LIBS research papers on metallic solid samples in air at atmospheric pressure have been published where the calibration curves are obtained with varying slopes and regression coefficients (13-23). But, to the best of our knowledge, their effect on the correlation of the LIBS determined elemental concentration with that determined by any other analytical method has not been reported in many of these instances.

The calibration curve method is of limited application, because a matrix with composition similar to the unknown sample is required which is, in many cases, not possible. As an alternative method, the calibration-free LIBS (CF-LIBS) method has been initially developed by Ciucci et al. (24) for quantitative elemental analysis with LIBS spectra. In this method, the elemental composition of a sample is determined from the LIBS spectrum using computational methods in analyzing the basic physics of the plasma process through the estimation of the plasma temperature and electron
number density, assuming that the plasma composition represents exactly the composition of the sample, i.e. stoichiometric ablation and the plasma is optically thin and is in local thermodynamic equilibrium (LTE). Since its inception, the CF-LIBS method has been applied by several research groups across the world to the analysis of metallic alloys, such as Al-based (24, 25), Fe-based (25), Cu-based (20, 26-29) and Au-based (27, 30) alloys as well as non-metallic samples, such as soil, rock and glass (21, 26, 27, 29, 31). The advantage of this method is that the need for a matching matrix, a requirement for the calibration-based LIBS, is eliminated. A major drawback of the method is that one needs to detect at least one line of each element in the plasma with known atomic data. Gomba et al. (32) have developed a CF-LIBS procedure different from that of Ciucci et al. (24) to quantify the contents of the elements through the estimation of plasma temperature, electron density and relative number densities of the neutral and singly ionized ionic species in the LIBS plasma by making use of the experimental spectral line intensity values in the time window where the plasma is optically thin and in LTE.

In this chapter, the measurements of plasma temperature $T$ and electron density $n_e$ of copper plasma formed by irradiation of a solid Cu target in air at atmospheric pressure is reported. The laser irradiance of $4.5 \times 10^8$ W/cm$^2$ employed in this work was near the plasma ignition threshold. The aim of this investigation was to identify and optimize laser ablation parameters suitable for elemental composition analysis of samples using the LIBS technique. The Boltzmann plot method for determining $T$ and the Saha-Boltzmann equation method for determining $n_e$, was used instead of using Stark line broadening. From these measurements the time window where the plasma is optically thin and in LTE have been found, which is a necessary requirement for the applicability of the equilibrium equations as well as the applicability of emission signals to elemental analysis using the LIBS technique.

A detailed investigation has been carried out to show how the best analytical conditions for a given type of sample can be arrived at, by establishing calibration curves for Cr, using three samples of nickel alloys with known composition, and recording the LIBS spectra at five detector gate delays, employing the internal standardization (IS) method (16, 19). The ultraviolet laser was used because it
generates plasmas of samples in atmospheric air with improved emission characteristics (15). The effect of slopes and regression coefficients of the linear calibration curves which vary with the detector gate delays, on the quantitative elemental analysis was studied considering three certified samples as unknown samples. These results and the influence of the above two parameters of the linear calibration curve on the analytical predictive capability of LIBS are also discussed in this chapter.

Finally, the CF-LIBS technique, using the procedure developed by Gomba et al. (32), was applied to the quantitative analysis of a brass sample of known composition (70% Cu and 30% Zn) placed in air at atmospheric pressure, was studied and discussed in order to further evaluate the capabilities of the technique and establish the necessary conditions for accurate analysis by this procedure. For the quantification of elemental contents in the sample, an algorithm relating the experimentally measured spectral intensity values at a time delay where the plasma is optically thin and in LTE, with the basic physics parameters of the plasma determined by our methods described above. Using this algorithm we have determined the Zn and Cu concentrations in the brass sample. Our results show that with proper plasma conditions, determined from experimental measurements and theoretical considerations, reliable, quantitative, calibration free analysis can be done by the LIBS technique. This is of great importance from the point of view of remote analysis by LIBS, for applications like planetary surface exploration, analysis of hazardous materials and locations, remote environmental monitoring etc. These results are also presented and discussed in this chapter.

5.2 EXPERIMENTAL

A schematic diagram of the experimental set-up for LIBS, discussed in detail earlier (Chapter III) is reproduced in Figure 5.1.
High detector gate widths, which were found to be most advantageous in terms of the S/N ratio, was kept constant and used for all measurements. The continuum radiation from the LIBS plasma, which is intense at initial delay times of less than 300 ns decreases to negligible values at later times. The detector gate delay was therefore varied in the time span 300-2000 ns for optimization of experimental conditions. All LIBS spectra are derived from an integration of 120 laser pulses to minimize effects of pulse-to-pulse variations from run to run.

5.3 PLASMA CHARACTERIZATION

5.3.1 Calibration based LIBS

The ultimate goal of any analytical technique is to determine the concentration of a species in a sample with high precision and accuracy. A quantitative analysis begins with determining the response of a system for a given concentration or mass of the analyte of interest. This usually takes the form of a calibration curve as discussed earlier in this chapter. LIBS can be used to provide quantitative analysis of a variety of samples both in the laboratory and in the field. However, each application has some unique characteristics which must be dealt with in order to optimize performance (3).

5.3.2 Calibration free LIBS

For quantitative elemental analysis from the LIBS spectral line intensities, it is essential to characterize the time-evolution of LIBS plasma in terms of its temperature.
and electron number density and find out the time window where the LIBS plasma is optically thin and in LTE. Based on plasma spectroscopy, the Boltzmann plot method yields the temperature $T$ and the Saha-Boltzmann equation method yields the electron number density $n_e$ of LTE and optically thin plasmas (33). These methods as well as the criterion for determining the plasma to be optically thin and in LTE have been discussed in chapter II. Hence, the relevant equations for characterizing the LIBS plasma using line intensities of the LIBS spectrum are briefly mentioned for continuity sake.

5.3.2.1 Determination of plasma temperature $T$

The integrated spectral line intensity of the $k$-$i$ electronic transition of the species in charge state $Z$ ($Z = 0$ for neutral atoms, $Z = 1$ for singly-ionized atoms, etc.) of element $\alpha$ in optically thin and LTE plasma is given as (33)

$$I^\alpha_{ki, Z} = F n^\alpha_Z g^\alpha_{k, Z} A^\alpha_{k, Z} \lambda^\alpha_{ki, Z} P^\alpha_Z \exp\left(-\frac{E^\alpha_{k, Z}}{k_B T}\right),$$

(1)

where $F = \frac{hcL}{4\pi}$, $L$ is the characteristic length of the plasma, $h$ is the Planck constant, $c$ is the speed of light, $k_B$ is the Boltzmann constant, $E_{k, Z}$ and $g_{k, Z}$ are the energy and degeneracy of the upper energy level $k$ respectively, $A_{k, Z}$ is the transition line probability and $\lambda_{k, Z}$ is the transition line wavelength of the $k$-$i$ transition, $P_Z$ is the partition function and $n_Z$ is the number density of the species in ionization stage $Z$. By taking the natural logarithm, eq. (1) can be rewritten as

$$\ln\left(\frac{I^\alpha_{k, Z} A^\alpha_{ki}}{g^\alpha_{k, Z} A^\alpha_{ki}}\right) = -\frac{E^\alpha_{k, Z}}{k_B T} + \ln\left(\frac{F n^\alpha_Z}{P^\alpha}\right)$$

(2)

If the term on the left-hand side is plotted against $E_k$ for two or more transition lines, the linear plot obtained is called the Boltzmann plot where the integral intensity of each spectral line is represented by a point in the Boltzmann plane. The slope of the Boltzmann plot yields the plasma temperature $T$. 

5.3.2.2 Determination of electron density $n_e$

The electron density using atom and ion spectral lines emitted from the plasma is determined employing the Saha-Boltzmann equation for the line intensities of the species in two consecutive charge states $Z$ and $Z+1$ of a particular element as (32, 33)

$$
 n_e = \frac{I'_Z}{I_{Z+1}} \times 6.04 \times 10^{21} (T)^{3/2} \times \exp\left[\left(\frac{-E_{k,Z+1} + E_{k,Z} - \chi_Z}{k_B T}\right)\right] \text{cm}^{-3},
$$

(3)

where $I'_Z = \frac{I_Z A_{ki,Z}}{g_{k,Z}}$ and $\chi_Z$ is the ionization energy of the species in the ionization stage $Z$. The lowering of the ionization energy due to interactions in the plasma being negligibly small is omitted in eq. (3).

5.3.2.3 Determination of density ratio of the species of a particular element

The Saha Equation relating the concentrations in the two consecutive charge states $Z$ and $Z+1$ of a particular element $\alpha$ is written as (32)

$$
 \frac{n_e n_{Z+1}^\alpha}{n_Z^\alpha} = 6.04 \times 10^{21} T_e^{3/2} \frac{P_{Z+1}^\alpha}{P_Z^\alpha} \exp\left(-\frac{\chi_Z^\alpha}{T_e}\right) \text{cm}^{-3},
$$

(4)

where $T_e$ is the plasma temperature in eV. This equation determines the value of the density ratio of the species in two consecutive charge states of a particular element, using experimentally determined values of $T$ and $n_e$.

5.3.2.4 Determination of density ratio of the species of different elements

The density ratio of the species in different charge states of two elements is determined from the Saha-Boltzmann equation for the line intensities of the species in different charge states of two elements $\alpha$ and $\beta$ as (32)

$$
 \frac{n_e n_{Z+1}^\alpha}{n_{Z+1}^\beta} \times P_{\alpha,Z+1}(T) \times \exp\left(-\frac{E_{k,Z+1}^\beta - E_{k,Z}^\alpha}{k_B T}\right)
$$

(5)
5.3.2.5 Criterion for optically thin and LTE plasma

The criterion whether the LIBS plasma is optically thin as well as in LTE, necessary for the quantitative composition analysis of the elements from the LIBS spectra of a sample, is obtained from the intensity ratio of two lines of a particular element in the same charge state \( Z \) which is expressed as (34)

\[
\frac{I_1}{I_2} = \left( \frac{\lambda_{nm,Z}}{\lambda_{ki,Z}} \right) \left( \frac{A_{ki,Z}}{A_{nm,Z}} \right) \left( \frac{g_{k,Z}}{g_{n,Z}} \right) \exp\left(-\frac{E_{k,Z} - E_{n,Z}}{k_B T}\right),
\]

where \( I_1 \) is the line intensity from the \( k-i \) transition and \( I_2 \) is that from the \( n-m \) transition. If we consider two emission lines having the same upper level or as close as possible, the temperature effect of the Boltzmann factor on the reproducibility of the line intensity ratio is minimized and at the same time the consideration of the efficiency factor of the collecting system is avoided. Neglecting the exponential factor in that condition, one can find out the theoretical value of the intensity ratio of the two lines by using the atomic parameters of the transitions. By matching this theoretical intensity ratio with the measured values at different delay times, one can find out the time window where the plasma is optically thin and in LTE.

5.3.2.6 CF-LIBS for elemental analysis

For quantitative elemental analysis using the CF-LIBS method, procedure developed by Gomba et al. (32) have been followed where the concentrations of the elements are determined by matching theoretically obtained values of \( n_e \) and relative number densities of the neutral and singly ionized ionic species of a particular element as well as different elements in the plasma with those experimentally determined from eqs. (.3), (4) and (5) using the spectral line intensities in a time window where the LIBS plasma is optically thin and in LTE. The used procedure is mentioned in the following.

The total number density of element \( \alpha \) is written as

\[
n_{\text{tot}}^\alpha = n_0^\alpha + n_1^\alpha + n_2^\alpha + \ldots \ldots n_Z^\alpha
\]
\[ n_{c}^{\alpha} = n_{1}^{\alpha} + 2n_{2}^{\alpha} + 3n_{3}^{\alpha} + \ldots = \sum_{Z=1}^{Z_{\infty}} Zn_{Z}^{\alpha} \quad (8) \]

Let us define the functions \( S_{Z}^{\alpha} \) and \( R_{Z}^{\alpha} \) as

\[ S_{Z}^{\alpha} = \frac{n_{Z}^{\alpha} n_{Z+1}^{\alpha}}{n_{Z}^{\alpha}} = 6.04 \times 10^{21} T_{eV}^{3/2} \frac{P_{Z}^{\alpha}}{P^{\alpha}_{Z}} \exp \left( -\frac{Z_{eV}^{\alpha}}{T_{eV}} \right) \text{ cm}^{-3} \quad (9) \]

and

\[ R_{Z}^{\alpha} = \frac{n_{Z}^{\alpha}}{n_{0}^{\alpha}} \quad (10) \]

The function \( R_{Z}^{\alpha} \) can be rewritten as

\[ R_{Z}^{\alpha} = \frac{n_{Z}^{\alpha}}{n_{0}^{\alpha}} = \frac{n_{1}^{\alpha}}{n_{0}^{\alpha}} \frac{n_{2}^{\alpha}}{n_{1}^{\alpha}} \ldots \frac{n_{Z}^{\alpha}}{n_{Z-1}^{\alpha}} = \frac{S_{1}^{\alpha}}{n_{e}} \frac{S_{2}^{\alpha}}{n_{e}} \ldots \frac{S_{Z}^{\alpha}}{n_{e}} \prod_{j=1}^{Z} \frac{S_{j}^{\alpha}}{(n_{e})^{Z}}. \quad (11) \]

\( n_{c}^{\alpha}, \ n_{Z}^{\alpha} \) and \( n_{Z}^{\alpha}/n_{Z+1}^{\alpha} \) can be expressed in terms of \( R_{Z}^{\alpha} \) as

\[ n_{c}^{\alpha} = \frac{n_{0}^{\alpha} \sum_{Z=1}^{Z_{\infty}} ZR_{Z}^{\alpha}}{1 + \sum_{Z=1}^{Z_{\infty}} R_{Z}^{\alpha}} \quad (12) \]
The total electron number density $n_e$ of the plasma is obtained by summing up of electron contributions from all the elements:

$$n_e = \sum_{\alpha'=1}^M n_{e\alpha'}^d,$$

(15)

where $M$ is the total number of elements in the sample. Using $T$ obtained from the Boltzmann plot and a proposed (initial) set of $n_{\text{tot}}^{\alpha'}$ of all the elements, $n_e$ is calculated, incorporating electron contributions from all the elements, starting from its default value until convergence is reached. The converged value is taken as the theoretical value of $n_e$. Then, the values of $n_{Z+1}^\alpha$ and $n_{Z}^\alpha$ are calculated. These calculations are carried out for a variable set of $n_{\text{tot}}^{\alpha'}$ of all the elements to find out an appropriate set of $n_{\text{tot}}^{\alpha'}$ of all the elements that results in the theoretical estimates of $n_e$, $n_{Z+1}^\alpha$ and $n_{Z}^\alpha$ very close to the experimentally measured values. The relative concentration of element $\alpha$ is then obtained as

$$c^\alpha = \frac{n_{\text{tot}}^{\alpha}}{\sum_{\alpha'} n_{\text{tot}}^{\alpha'}},$$

(16)

in terms of molar fractions or as

$$c^\alpha = \frac{n_{\text{tot}}^{\alpha} \mu_\alpha}{\sum_{\alpha'} n_{\text{tot}}^{\alpha'} \mu_{\alpha'}},$$

(17)
in terms of mass abundance, where \( \mu_\alpha \) is the atomic weight of element \( \alpha \).

### 5.4 SAMPLES: COPPER, BRASS AND NICKEL ALLOYS

A 99.99% pure copper and brass (70% Cu and 30% Zn) plates (Alfa Aesar, USA) are used for plasma temperature and electron density measurements as well as CF- LIBS quantitative analysis. For calibration based LIBS experiments, we have employed three samples of Ni\(_2\) (Cr, Mo) alloys whose elemental compositions are listed in Table 7.

These nickel alloys are prepared by melting Ni (99.99 % purity), Cr (99.99 % purity) and Mo (99.99 % purity) in appropriate ratio in a non-consumable arc furnace with tungsten electrode and a water-cooled copper hearth under purified argon atmosphere. These compositions were chosen so that the alloys are in the single phase region in the ternary phase diagram. The alloys were homogenized at 1200 °C for 24 hours in flowing argon atmosphere followed by furnace cooling and then hot rolled to about 0.5 mm thickness.

**Table 7** Elemental concentrations (wt %) in three certified samples of Ni\(_2\) (Cr, Mo) alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.67</td>
<td>16.67</td>
<td>66.66</td>
</tr>
<tr>
<td>2</td>
<td>21.01</td>
<td>12.33</td>
<td>66.66</td>
</tr>
<tr>
<td>3</td>
<td>25.01</td>
<td>8.33</td>
<td>66.66</td>
</tr>
</tbody>
</table>

The specimens from these alloys of 5 mm x 5 mm dimension were solution treated at 1150 °C for two hours. X-ray diffraction as well as transmission microscopy studies confirmed that all the specimens are in single phase. Electron probe microanalysis also confirmed that the alloys have the same compositions as concentration of elements used for alloy preparation. The samples were supplied by Structural Metallurgy Section, Materials Group, Bhabha Atomic Research Centre, Mumbai.
5.5 RESULTS AND DISCUSSIONS

5.5.1 Plasma temperature and electron density

Using the neutral atom and ion emission spectra recorded at different delay times in the time span 300 - 2000 ns, we have characterized the LIP in terms of its transient T and n_e. Figure 5.2 shows a typical spectrum recorded using ICCD-based echelle spectrograph with a gate delay time of 700 ns, depicting Cu I and Cu II emission lines from the LIP. Five Cu I and two Cu II emission lines which are well resolved and free from spectral interference are chosen in the present work. These lines along with their spectroscopic parameters, taken from the NIST atomic database (35), are shown in Table 8.

![Figure 5.2 LIBS spectra of copper recorded using ICCD-based echelle spectrograph with a gate delay time of 700 ns at a laser irradiance of 4.5x10^8 W/cm^2, showing (A) Cu I atomic lines and (B) Cu II ionic lines used for characterization of the laser-induced Cu plasma.](image)

Fig 5.2 LIBS spectra of copper recorded using ICCD-based echelle spectrograph with a gate delay time of 700 ns at a laser irradiance of 4.5x10^8 W/cm^2, showing (A) Cu I atomic lines and (B) Cu II ionic lines used for characterization of the laser-induced Cu plasma.
Table 8 Wavelength, lower and upper energy levels, upper level degeneracy, transition probability for the Cu I and Cu II emission lines used in this work

<table>
<thead>
<tr>
<th>Atom/ion</th>
<th>Wavelength (nm)</th>
<th>Upper level energy (eV)</th>
<th>Lower level energy (eV)</th>
<th>Upper level degeneracy</th>
<th>Transition probability ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu I</td>
<td>510.55</td>
<td>3.817</td>
<td>1.389</td>
<td>4</td>
<td>2.0x10^6</td>
</tr>
<tr>
<td>Cu I</td>
<td>515.32</td>
<td>6.191</td>
<td>3.786</td>
<td>4</td>
<td>6.0x10^7</td>
</tr>
<tr>
<td>Cu I</td>
<td>521.82</td>
<td>6.192</td>
<td>3.817</td>
<td>6</td>
<td>7.5x10^7</td>
</tr>
<tr>
<td>Cu I</td>
<td>578.21</td>
<td>3.786</td>
<td>1.642</td>
<td>2</td>
<td>1.65x10^7</td>
</tr>
<tr>
<td>Cu II</td>
<td>268.93</td>
<td>13.392</td>
<td>8.783</td>
<td>7</td>
<td>4.1x10^7</td>
</tr>
<tr>
<td>Cu II</td>
<td>271.35</td>
<td>13.432</td>
<td>8.864</td>
<td>5</td>
<td>6.8x10^7</td>
</tr>
</tbody>
</table>

The value of $T$ is obtained from the Boltzmann plot made from the analysis of four Cu I lines (510.55, 515.32, 521.82 and 578.21 nm) at a given delay time. Figure 5.3 shows one such Boltzmann plot from the intensities of these Cu I lines at a delay time of 700 ns, the slope of which gives $T = 0.79$ eV.

In the Figure 5.3, the continuous line represents the result of a linear best fit. $I$ and $\lambda$ are the intensity and the wavelength of a transition from upper level $k$ of energy $E_k$ and statistical weight $g_k$ to lower level $i$ with $A_{ki}$ as the corresponding transition probability. The slope gives the temperature $= 0.79$ eV. The estimated values of $T$ at several delay times are presented in Table 9.
Fig 5.3 Boltzmann plot made from the analysis of four Cu I lines, considering the intensities at a delay time of 700 ns.

Table 9 Plasma temperatures and electron density as a function of delay time of the detector relative to the onset of the laser pulse on the sample:

<table>
<thead>
<tr>
<th>Delay time (ns)</th>
<th>Plasma temperature (eV)</th>
<th>Electron density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.78</td>
<td>2.0x10¹⁴</td>
</tr>
<tr>
<td>500</td>
<td>0.84</td>
<td>1.1x10¹⁵</td>
</tr>
<tr>
<td>700</td>
<td>0.79</td>
<td>5.7x10¹⁴</td>
</tr>
<tr>
<td>1000</td>
<td>0.75</td>
<td>2.9x10¹⁴</td>
</tr>
<tr>
<td>2000</td>
<td>0.69</td>
<td>4.5x10¹³</td>
</tr>
</tbody>
</table>

The variation of plasma temperature with detector delay is plotted in Figure 5.4. It is observed that after 500 ns delay time the plasma cools down exponentially.
Fig 5.4 Variation of plasma temperature with delay time

The value of $n_e$ is obtained from Eq. (3) using the measured intensity ratio of Cu I and Cu II lines at a given delay time. We have considered three intensity ratios: (i) 515.32 nm Cu I and 268.93 nm Cu II, (ii) 515.32 nm Cu I and 271.35 nm Cu II and (iii) 521.82 nm Cu I and 268.93 nm Cu II and obtained the values of $n_e$. As seen from Figure 5.2, Cu II lines at 277 and 279 nm are more intense than the chosen Cu II lines for the analysis. However, we could not use these more intense Cu II lines as the Cu II line at 277 nm overlaps with the three Cu I lines at 276.637, 276.639 and 276.888 nm and the transition probability of the Cu II line at 279 nm is not available in the NIST atomic database. The arithmetic mean of the three values of $n_e$ is represented as the average value of $n_e$. We have presented these average values as the electron density at several delay times in Table 8 and graphically in Figure 5.5. It is observed that after 500 ns delay the electron density decreases exponentially.

A comparison of Figures 5.4 and 5.5 shows that the plasma temperature and electron density follow similar decay rate with delay time. As mentioned earlier (Chapter 2) in other emission sources like D.C. Arc and ICP, the sample is first brought into the gas phase as atoms in the ground states get excited to the higher states in the plasma.
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Fig 5.5 Variation of electron density with delay time

But in laser-produced plasmas the sample is initially brought to the gas phase as highly excited ionic species which then undergo collisions with electrons and enter the highly excited atomic states. It is thus highly likely that the excited state population in LIBS will follow the electron number density, which itself, in view of the large number of collisions, distribute very fast, according to Maxwell-Boltzmann distribution. It is thus to be expected that the temperatures, calculated from population distribution as per Boltzmann distribution, and the electron number densities calculated from ion-atom intensities, show very similar behavior.

The time window where the plasma is optically thin and is also in LTE is inferred from the temporal evolution of the intensity ratio of two Cu I lines, 515.32 and 521.82 nm, which have upper levels having very close energy as shown in Table 7. Figure 5.6 shows the temporal evolution of the intensities of these lines and the intensity ratio between them. We have calculated the intensity ratio for this couple of lines using Eq. (6) which is equal to 1.85 and shown this theoretical value as a straight line in the same figure. Comparing the experimental data of the intensity ratio with the theoretical one, we have inferred the time window as 700-1000 ns where the LIP
produced is thin as well as in LTE though even at other delays up to, say 1500nsec the system deviates only little from LTE.

**Fig 5.6** Temporal evolution of intensities of two Cu I lines 515.32 and 521.62 nm and their intensity ratio

The straight line indicates the theoretical intensity ratio = 1.85 for this couple of lines, which is the condition of an optically thin and LTE plasma. The time window for thin and LTE plasma is 700-1000 ns.

**5.5.2 Calibration based LIBS**

**5.5.2.1 LIBS spectra**

Typical LIBS spectra of one of the certified Ni-alloy samples (sample 1) recorded at 2000 ns delay relative to the laser pulse are displayed in Figures 5.7 (a) and (b).
Fig. 5.7 Typical LIBS spectra of a Ni alloy (certified sample 1) at 2000 ns delay; (a) with inset showing Ni I line at 352.45 nm and (b) with inset showing Cr I line at 520.84 nm.

The spectral lines of Cr I and Ni I of interest are shown in the inset of the Figure 5.7. Three sets of such spectra are recorded for all the samples at each of the five delays of interest. A mean value calculated from the three spectra is used for the emission intensity of atomic lines, needed for obtaining the calibration curves.
5.5.2.2 Selection of spectral lines

The selection of the spectral lines of the analyte element as well as the internal standard (reference) element is required to be carefully made for the reproducibility of the analytical results using the internal standardization (IS) method (16, 19). As stated in (16, 19), the spectral lines of both the analyte element and the reference element selected for the calibration curves should fulfill the following four conditions: (i) they should be reasonably strong and isolated to avoid interference with other spectral lines, (ii) they should be non-resonant lines with lower levels much above the ground level particularly at higher concentrations of the elements of interest to avoid saturation of emission intensities due to self-absorption of the emission lines. It should be mentioned here that this condition is more relevant to the lower temperature sources like D.C. Arc and ICP, where the higher energy levels are populated by thermal excitation of ground and low lying atoms and will thus have lower number density compared to the ground state.

For the laser plasma source, this condition is more or less automatically fulfilled since the plasma first produces the material in highly excited ionic and atomic levels, from where they relax to other lower levels, and consequently the lower levels of almost all transitions will have very little population, making self absorption unlikely, (iii) they should have the upper levels with energies close to each other such that their energy level difference is near zero (< 2000 cm⁻¹) to minimize the plasma temperature effect on the reproducibility of the line intensity ratio and (iv) they should be simultaneously detected in a single laser shot to avoid complexities in the line intensity calibration. The foremost requirement of similar upper level energies of the analyte and reference lines is not fulfilled in many LIBS works based on calibration curves (13, 16, 19), affecting slope and regression coefficient of the calibration curves. For the calibration curves of Cr using the IS method, we have chosen the analyte Cr and the reference Ni lines as shown in Table 10. The related spectroscopic parameters of the spectral lines, taken from the NIST atomic database (35), are also shown in the table.
Table 10 Atomic emission lines used for quantitative analysis, along with the related spectroscopic parameters

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>Lower level energy (cm(^{-1}))</th>
<th>Upper level energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr I</td>
<td>520.84</td>
<td>7593.2</td>
<td>26787.5</td>
</tr>
<tr>
<td>Ni I</td>
<td>352.45</td>
<td>204.8</td>
<td>28569.2</td>
</tr>
</tbody>
</table>

These lines are non-resonant as well as interference-free, thus satisfying the first and second requirements. The energy level difference of the upper levels of the chosen line pairs is about 1780 cm\(^{-1}\), thus satisfying the third requirement. The fourth condition is automatically satisfied because the spectral range detected in a single laser shot using the present LIBS system is very large, covering the chosen line pairs.

5.5.2.3 Quantitative analysis using the IS method

The quantitative analysis using LIBS technique involves relating the plasma emission intensity of an atomic line of any element to the concentration of that element in the sample. It relies on the assumption that the plasma is optically thin and in local thermodynamic equilibrium (LTE). Under this assumption, the intensity ratio of an atomic spectral line emitted by an analyte element (denoted by subscript a) to that emitted by the internal standard (reference) element (denoted by subscript r), considered in the IS method, is given as (16, 19, 36)

\[
\frac{I_a}{I_r} = \frac{N_a}{N_r} \frac{g_a A_a Z_a \lambda_a}{g_r A_r Z_r \lambda_r} \exp[-(E_a - E_r)/kT].
\]  \hspace{1cm} (18)

Here I stands for the intensity of the spectral lines, N is the total atom number density, Z is the partition function, E and g are the energies and the degeneracies of the upper levels respectively, A and \(\lambda\) are the Einstein coefficient and the wavelength respectively for the observed line transitions, k is the Boltzmann constant and T is the plasma temperature.

Taking the natural logarithms in Eq. (18), one obtains:

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\[ \ln \frac{I_a}{I_r} = \ln \frac{N_a}{N_r} + \ln \frac{g_a A_a Z_a \lambda_a}{g_r A_r Z_r \lambda_r} - \frac{E_a - E_r}{kT} \]  

(19)

Thus, if the logarithm of the intensity ratio versus the logarithm of the concentration ratio is plotted, the calibration curve as a straight line with a slope of unity is obtained. Using the regression equation of the linear calibration curve one may obtain the analyte concentration from the measured analyte spectral intensity in unknown samples. Since the experimental data are normally subject to small errors, they may not fit perfectly on a straight line with regression coefficient equal to one. The slope values of the linear calibration curves are commonly observed to differ from the ideal slope of unity, owing to the inhomogeneity and matrix effect of the samples (36). Both the regression coefficient and the slope of the linear calibration curve affect the analytical predictive capability of the LIBS system. When the energy difference of the upper energy levels is much smaller as compared to kT, the effect of the last term in Eq. (19) that contributes only to the intercept of this straight line, affecting the reproducibility of the spectral line intensity ratio, is negligible. Under this condition the intercept is determined by the second term on the right hand side of Eq. (19). Here all the components except Z remain constant for the selected lines, whereas Z is dependent on the plasma temperature.

5.5.2.4 Calibration curves for chromium

Using the analyte Cr and reference Ni lines given in Table 9 and Eq. (19), we have produced the calibration curves for Cr at five delay times and depicted these in Figure 5.8. The logarithm of the relative intensity ratio of the analyte (Cr) element and the reference (Ni) element lines are plotted against the logarithm of the given relative concentrations of the three Ni alloy samples for the calibration curves of Cr. The linear regression equation and the regression coefficient for each of the calibration curves are also given in the figure. As seen from the figures, the calibration curves in our experiment are well characterized by a straight line without any saturation effect. The slopes and the regression coefficients of these linear calibrations curves are tabulated in Table 11.
Fig 5.8 Calibration curves for Cr at delay times (a) 300 ns, (b) 500 ns, (c) 700 ns, (d) 1000 ns and (e) 2000 ns. Linear regression equations and their coefficients are also given.

Table 11 Slope (m) and linear regression coefficient ($R^2$) of the calibration curves of Cr at five values of the detector gate delay using the three certified samples of Ni alloys

<table>
<thead>
<tr>
<th>Delay time (ns)</th>
<th>m</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.109</td>
<td>0.945</td>
</tr>
<tr>
<td>500</td>
<td>0.850</td>
<td>0.978</td>
</tr>
<tr>
<td>700</td>
<td>0.769</td>
<td>0.996</td>
</tr>
<tr>
<td>1000</td>
<td>0.286</td>
<td>0.966</td>
</tr>
<tr>
<td>2000</td>
<td>1.483</td>
<td>0.998</td>
</tr>
</tbody>
</table>

As evident from this table, the slope values differ from the ideal slope of unity, whereas the regression coefficient values of the linear fit are near unity with the best value equal to 0.998 at 2000 ns delay. From the regression equations, it is seen that
the intercept varies widely over the delay times of interest. The radiative lifetimes of electronic energy levels are in ns, and the observation time of 6 μs more or less ensures that, for any delay, we observe the emissions from all the atoms reaching the levels involved. This intercept is varying from a positive value to zero to slightly negative, and then to positive. This change is ascribed to the dependence of Z on the plasma temperature that varies significantly with the delay time.

5.5.2.5 Analytical results

For the demonstration of analytical predictive capability of the present LIBS system, we have used the linear regression equations of the produced calibration curves and determined the relative concentration of Cr in three nickel-alloy samples with known composition at 5 detector gate delays. We have also evaluated the accuracy of the elemental determinations using the LIBS method by their relative deviation from the certified values of the samples. Table 12 shows the correlation of the LIBS determined concentration ratio Cr/Ni with its certified value and the corresponding uncertainty of the three Ni-alloy samples using the produced calibration curves at 5 detector gate delays.

It is observed that the high regression coefficient with its value very close to unity (0.998) along with the slope (1.483) of the linear calibration curve close to the ideal value of unity, obtained at 2000 ns gate delay (Table 11) in the present experiment, yields the best LIBS analytical results in all the three samples. Thus, the analytical predictive capability of the LIBS system is strongly dependent on both the slope and the regression coefficient of the calibration curve, the best capability occurring at appropriate experimental conditions (gate delay) where both the slope and the regression coefficient of the linear calibration curve are close to the ideal value of unity.


Table 12 Correlation of the LIBS determined concentration ratio Cr/Ni with its certified values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified concentration ratio Cr/Ni</th>
<th>LIBS determined concentration ratio Cr/Ni (Correlation uncertainty, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Delay time (ns) 300  500  700  1000  2000</td>
</tr>
<tr>
<td>1</td>
<td>0.250</td>
<td>0.256  0.246  0.252  0.245  0.249</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2.4)  (1.6)  (0.8)  (2.0)  (0.4)</td>
</tr>
<tr>
<td>2</td>
<td>0.315</td>
<td>0.298  0.326  0.311  0.329  0.318</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5.4)  (3.5)  (1.3)  (4.4)  (1.0)</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.387  0.368  0.378  0.365  0.373</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3.2)  (1.9)  (0.8)  (2.7)  (0.5)</td>
</tr>
</tbody>
</table>

In Figure 5.9, the correlation of the LIBS determined concentration ratio Cr/Ni and certified concentration ratio Cr/Ni for the three Ni-alloy samples using the calibration curve at a delay time of 2000 ns is given. The correlation coefficient and the slope of the linear calibration curve are very close to the ideal value.

![Graph](image)

**Fig 5.9** Correlation of the LIBS determined concentration ratio Cr/Ni and certified concentration ratio Cr/Ni using the calibration curve at a delay time of 2000 ns

As seen from the Figure 5.9, the LIBS analytical results are fitted satisfactorily by a linear equation with the regression coefficient of 0.998 and the slope of 0.993.
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These results confirm high analytical predictive capability of the LIBS system provided the linear calibration curve is produced at an appropriate detector gate delay, having both the regression coefficient and the slope close to the ideal value of unity.

5.5.3 CF-LIBS

To demonstrate the capabilities of Calibration-Free analytical capabilities of LIBS, we developed the necessary algorithm as mentioned earlier and applied it brass, an alloy of copper and zinc. In order to arrive at the proper time window for quantitative analysis, where the LIBS plasma is optically thin and in LTE, we have recorded the LIBS spectra of brass (70% Cu and 30% Zn) at five values of detector gate delay (300, 500, 700, 1000 and 2000 ns) relative to the laser pulse as described earlier in the case of pure copper. A typical LIBS spectrum of brass at a delay time of 1000 ns is shown in Figure 5.10. Three sets of such spectra are recorded at each of the five delays of interest. A mean value calculated from the spectra is used for the emission intensity of atomic and ionic lines.

Fig 5.10 Typical LIBS spectrum of a brass sample at 1000 ns time delay

Plasma temperature and electron density were determined as before (Fig 5.3 and Table 8) and they have been found to be slightly different, indicating that it is better to determine the optimum window for each type of sample, especially when one wants to do CF-LIBS. The value of $n_e$ in the brass plasma at 1000 ns delay is obtained to be $1.10 \times 10^{15}$ cm$^{-3}$. 

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Using the measured values of T and ne at the time delay of 1000 ns and the corresponding partition function from the NIST atomic database (35) the density ratio \( n_{\text{Cu II}} / n_{\text{Cu I}} \) was determined from eq. (4) to be 65.7. The density ratio \( n_{\text{Zn I}} / n_{\text{Cu II}} \) was determined from eq. (5) using the intensities of Zn I and Cu II lines at the time delay of 1000 ns and their spectroscopic parameters, taken from the NIST database (35). The atomic and ionic lines chosen in the present work are well resolved and free from spectral interference. We have considered three intensity ratios, 636.23 nm Zn I and 268.93 nm Cu II, 636.23 nm Zn I and 271.35 nm Cu II and 328.23 nm Zn I and 271.35 nm Cu II and obtained the values of \( n_{\text{Zn I}} / n_{\text{Cu II}} \). The average value of \( n_{\text{Zn I}} / n_{\text{Cu II}} \) as the arithmetic mean of the three values is determined to be equal to 1.163\times10^{-2}. These experimental results are shown in Table 13.

**Table 13** Values of T, ne, \( n_{\text{Zn I}} / n_{\text{Cu II}} \) and \( n_{\text{Cu II}} / n_{\text{Cu I}} \) in the LIBS plasma determined from the LIBS spectral line intensities as experimental results

<table>
<thead>
<tr>
<th>T (eV)</th>
<th>ne (cm(^{-3}))</th>
<th>( n_{\text{Zn I}} / n_{\text{Cu II}} )</th>
<th>( n_{\text{Cu II}} / n_{\text{Cu I}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.77</td>
<td>1.10 \times 10^{15}</td>
<td>1.163 \times 10^{-2}</td>
<td>65.7</td>
</tr>
</tbody>
</table>

For the quantification of elemental contents in the sample, an algorithm based on the procedure discussed in section titled CF-LIBS for elemental analysis was developed by Laser Plasma Technology Division, Bhabha Atomic Research Cebtre, Mumbai. A schematic diagram of the CF-LIBS algorithm used in this work is shown in Figure 5.11.

We have varied the values of \( n_{\text{tot}}^{\text{Cu}} \) and \( n_{\text{tot}}^{\text{Zn}} \) in the range \( 10^{13} - 10^{15} \) cm\(^{-3}\) in the algorithm and calculated the values of \( n_{\text{ne}}, n_{\text{Zn I}} / n_{\text{Cu II}} \) and \( n_{\text{Cu II}} / n_{\text{Cu I}} \) in the LIBS plasma as the theoretical results, which match well with the experimental results when \( n_{\text{tot}}^{\text{Zn}} = 3.3 \times 10^{14} \) cm\(^{-3}\) and \( n_{\text{tot}}^{\text{Cu}} = 8.0 \times 10^{14} \) cm\(^{-3}\) are considered.
Using these density values we have determined the fractional molar concentrations of Zn and Cu in the brass sample. The values of Zn and Cu concentrations in the brass sample obtained from the CF-LIBS analysis along with their certified values are shown in Table 14.

**Table 14** Values of Zn and Cu concentrations obtained from the CF-LIBS analysis along with their certified values and accuracy errors of the LIBS analytical results

<table>
<thead>
<tr>
<th>Zn concentration (wt %)</th>
<th>Cu concentration (wt %)</th>
<th>Accuracy error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF-LIBS</td>
<td>Certified</td>
<td>CF-LIBS</td>
</tr>
<tr>
<td>29.794</td>
<td>30</td>
<td>70.206</td>
</tr>
</tbody>
</table>
The accuracy of the LIBS analytical results are also given in the table. It is noted from the table that the analytical results obtained from CF-LIBS agree very well with the certified values of the elements in the sample, with accuracy better than < 1% thus confirming the suitability of LIBS for Calibration-Free analysis of major components without externally introduced "internal" standards. As already mentioned, this is of great importance for remote/in situ analysis where there is no direct access to the sample other than through observed, remotely recorded spectra. Planetary exploration, Industrial (eg, Nuclear Power-related) accidents, un-removable components in heavy material Industrial Plants (fertilizer, oil, thermal power etc) etc are examples of such situations.

5.6 CONCLUSION

From the studies discussed in this Chapter, it is seen that accurate quantitative analysis can be done by the technique of LIBS with suitable choice of laser and instrumentation and optimization of experimental parameters. The main factors affecting the accuracy and reproducibility are: laser pulse energy, observation window determined by delay and gate width of detector and choice of suitable spectral lines. Once these are appropriately determined, quantitative analysis of major components can be achieved with ± <1% error, in a very short time, without any prior sample preparation.

5.7 REFERENCES

copper plasma by time-resolved spectroscopy of neutral atom and ion emissions," Pramana 74(6), 983-993 (2010)