Chapter 6

Trace elemental analysis in soil by LIBS


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ABSTRACT

Direct analyses of trace elements in complex matrices like minerals, soil, alloys etc., by Laser Induced Breakdown Spectroscopy (LIBS) are considered difficult, since the major components of these samples (alkali and alkaline earth metals, transition metals, Al etc.) will give extremely complex spectra in the plasma making it very difficult to isolate suitable spectral lines of elements present at trace levels for quantitative analysis. With the aim of quantifying trace elements in such materials, a fast, sensitive, high resolution, broad range LIBS system has been set up and optimized. Conditions for getting good quality LIBS spectra for multi-elemental trace analysis of soil samples have been standardized. Different data processing techniques were tested to optimize best possible method for achieving low limits of detection. Methods were standardized for analysis of copper, calcium, iron, magnesium and zinc in soil samples. The results show that these elements can be quantified directly in complex matrices like soil, routinely at ppm levels by LIBS, without any pre-concentration to remove the major elements in the sample. The technique was validated by comparing LIBS results to conventional AAS measurements.
6.1. INTRODUCTION

With the tremendous increase in industrial output to meet the ever increasing consumer needs, enormous growth of heavy industries like automobile, oil, and fertilizers, highly increased power generation (thermal, nuclear) programs, and need for much larger amounts of advanced materials (semiconductors), etc, the environment is being overloaded with numerous pollutants. Currently, the synergy between trace metal pollutants in the environment and in living systems, and its impact on human health, has evoked considerable interest. The versatility of LIBS technique for simultaneous multi-element analysis and its applicability in different phases of matter (solid, liquid and gas) finds its use very attractive in quantifying the concentration of pollutants/trace elements in environmental samples like water, soil and agricultural/dairy products (1-7).

Recent studies using soil samples proved that, as time goes by, the lack of rigorous control on environmental contamination can infect the soil with heavy metals resulting in contamination of food and water in these areas (5, 6, 8-11). Chen et al (12) has done extensive studies on surface soils and found that soil is not only a medium for plants to grow or a pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface water, groundwater, atmosphere, and food. Although not much attention has been paid to soil compared with food, water, and atmospheric pollution, soil pollution has been emphasized increasingly by many environmental protection agencies and communities (12).

LIBS has been explored as a multi elemental, continuous emissions monitor (CEM) to detect toxic metals in soil and paint (13). Remotely operated LIBS systems can carry out such monitoring even under extreme hostile conditions. It can perform rapid, on-site analysis in those environments and can significantly reduce the time and cost associated with sample preparation required by conventional analytical techniques and is therefore a promising technique for environmental monitoring and process control (13). It may be mentioned here that such remote-operated LIBS systems can even be employed for planetary surface studies in space exploration (14-16) to derive important information on isotopic composition and origin of surface
Samples. Combination of echelle spectrographs with sensitive ICCD are being preferred for LIBS experiments currently, since these provide high resolution, broad wavelength range, high dynamic range (15, 17, 18), and possibility of in situ analysis of relatively inaccessible samples (19).

Low concentrations of some metals such as Cu, Zn, Mn, and Mo are necessary for all living organisms, while many of these present toxicity hazard at higher concentrations (20). Capitelli et al (1) used LIBS technique to determine heavy metal contents in soils and compared this data with results from conventional Inductively Coupled Plasma (ICP) spectroscopy. The agreement, though only partial, between the two sets, suggested the potential applicability of LIBS technique for analysis of heavy metals in soils. Some of the sample preparation methods have also been investigated and it was found that pellet samples give better results compared to powder samples (21).

Though the applicability of LIBS for soil analysis has thus been investigated, it has also been suggested that LIBS may not be suitable for trace element analysis in soils, because of the complex nature of the matrix and the resulting possible interference from the major constituents (22). But the availability of commercial echelle-ICCD spectrographs with their high resolution, wide range, and time-gating capabilities make the LIBS technique a very attractive option for multi-elemental trace analysis even for highly complex matrices. Instrumental advances have enabled novel data processing options which can overcome the many drawbacks of conventional emission spectrographic analysis methods.

Using our LIBS system, which has been optimized through extensive studies as discussed earlier, we have developed a method for quantitative, multi-elemental trace analysis of soil samples. The flexibility of the spectroscopy system with improved data processing techniques like background subtraction, multi-line signal addition, and correlation spectroscopy has been investigated. Results show that analysis of ppm levels of trace elements in complex matrices can be routinely achieved by LIBS. The results are presented and discussed in this chapter.
6.2 MATERIALS AND METHODS

6.2.1 Experimental

The experimental setup used in the present studies is discussed in detail in earlier chapters and is shown in Figure 6.1.


Fig 6.1 Experimental layout of LIBS system used for soil analysis

6.2.2 Sample Preparation

Soil samples were obtained from Krishi Vigyan Kendra, Udupi, Karnataka, India. The elements have been chosen in discussion with soil scientists at this centre. Generally elements in soil are classified into primary nutrients, secondary nutrients and micro/trace nutrients. This is done based on the quantity of nutrients required for a good crop. Copper, zinc and iron (micronutrients) and magnesium and calcium (secondary nutrients) were chosen as analytes for the current study. All soil samples were collected and processed for analysis according to standard procedures (23).

6.2.2.1 Soil pellet preparation

The soil samples in our study were in the sand category with particle size 0.02-2.0mm. The samples were dried and ground using agate pestle and mortar, and
filtered through 0.2mm sieves to facilitate pellet making. 3gms of the sample was placed in a stainless steel (SS) die (20mm diameter) and pelletized using M15 model press (Technosearch Instruments, India), applying 150 kg/cm² pressure for 15 minutes. The 20mm diameter, 3mm thick pellets were used for LIBS studies. A photograph of the press and prepared soil pellets are shown in Figure 6.2.

Fig 6.2 Photograph of the press and die used for soil pellet preparation. Inset shows the soil pellets prepared using this press.

6.2.2.2 Soil standard preparation

To standardize the method of analysis, several parameters have to be optimized. These include method of preparation of standards and samples, laser power, laser focusing parameters, delay, collection conditions, element line(s), number of pulses required to achieve the desired sensitivity, best method of data processing, and other variables. One also has to test the effect of background subtraction, signal addition for multiple lines etc. This will require several runs with synthetic standards somewhere in the middle of the concentration range of interest (say around 200-300ppm). After finalizing analytical conditions, standards and blank have to be run for establishing the standard calibration curves. Each run means 5-10 trials. So there should be enough soil to make pellets of these standards and blank.
Hence both sides of the pellets were used to reduce the number, as well as to make sure that either side of a pellet can be used routinely.

To begin with, we have chosen copper as the element of our interest in soil. 1000ppm standard solution of copper sulphate was prepared by taking 50mg copper sulphate (Sigma Aldrich, India) in 50ml HPLC grade water. With 50mg copper sulfate we have 19.905mg of copper i.e. (63.54/159.61)X 50. This was dissolved in 50ml water i.e. (19.905/50) X 1000, gives 400 mg/ml copper solution. Since 50mg copper sulphate in 50ml water will give you 1000 ppm, one can consider the sample as 400 ppm in copper. 1ml of this solution was taken and mixed with 1gm of blank soil (see below) and ground thoroughly after drying to prepare 400ppm standard (400 mg/gm) of soil. Similarly 200, 100 ppm etc standards have also been made as standards for calibration. Standards for other elements were also prepared same way. A soil sample, tested for absence of the required elements (see later) was used as blank, as well as for preparation of calibration standards. Standards were prepared for other elements of interest like zinc, magnesium, calcium and iron, by adding the required amounts of solutions as explained above of suitable compounds of the element to the soil blank and grinding the mixture thoroughly after drying to a uniform consistency.

6.2.3 Gate delay and Gate width

Soil spectra have been recorded with delays of 100, 200, 300ns etc and gate widths 500, 1000, 2000ns etc, keeping all other conditions same. Unless otherwise stated, 400 laser pulses in 40 seconds (laser power $8.2 \times 10^{11}$ W/cm$^2$) were averaged for any single run.

Figure 6.3 shows typical LIBS results of a blank soil. It can be seen from the figure that at shorter delays the spectra are dominated by continuum spectra, and as the plasma decays the continuum decreases giving good quality LIBS spectrum, dominated by atomic lines, which can be used for quantitative analysis.
Fig 6.3 Gated spectrum of LIBS plasma from soil as a function of delay

Similar trial runs for other parameters, namely laser power, number of laser pulses (number of accumulations set in ICCD) and gate width were also optimized (Figure 6.4). We have chosen 396.2nm line of iron in the soil for these studies. Each point in the graph indicates average of three runs. It is evident from the figure that intensity of the collected signal increases linearly with increasing values of these parameters. This is significant since, when these parameters are kept constant in any particular analytical application, reproducibility can be improved by keeping the parameters same from run to run over periods of several weeks at least, since the linearity of the plots indicates that effects of small day-to-day variations can be minimized by suitable normalization. This is of great importance for remote applications, since in many such applications –for example planetary surface spectroscopy- it is not possible to add appropriate internal standards as in laboratory measurements, and one may have to depend only on observed intensities.

The optimum conditions for soil analysis were found to be: laser power 4 x $10^{12}$ W/cm$^2$; delay 500 ns; gate width 6000 ns and number of laser pulses for each run, 400. A typical soil spectrum with these conditions is shown in Figure 6.5, indicating how complex such a spectrum can be due to the major matrix elements.
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Fig 6.4 Optimization studies of (i) Laser power (Delay 500ns and Gate width 6000ns), (ii) Number of Laser pulses (Laser power $2 \times 10^{12}$ W/cm$^2$, Delay 500ns and Gate width 6000ns) and (iii) Gate width (Laser power $2.5 \times 10^{12}$ W/cm$^2$ and Delay 500ns) using soil sample.

Fig 6.5 Typical LIBS spectrum of a soil sample.
6.2.4 Data processing

For samples like soil and minerals, the LIBS technique can be used routinely in the lab, but more important, it is highly suitable for remote (mineral exploration, planetary surfaces) analysis. A comparison of the LIBS spectrum of the typical soil sample with spectrum of a prospective analyte element, copper, (Figure 6.6), shows that the presence of the many strong lines of the major constituent elements (Fe, Mg, Si, etc), makes it very difficult to select suitable spectral lines for quantitative analysis of elements present at trace levels. Normally, in the laboratory, in other conventional analytical methods, this problem is solved by extracting the element of interest by chemical methods and analyzing it in a suitable matrix like graphite, which give only few additional spectral lines. But this is not possible for remote analysis and also involves considerable time and effort for lab measurements. We have investigated the possibility of using various data processing techniques for reliable analysis without any pre-concentration, for such samples, and this is discussed below, taking copper in soil as an example.

![LIBS spectra](image)

**Fig 6.6** LIBS spectra of pure copper and soil blank to indicate copper line positions. Inset shows 520nm region of both spectra in expanded scale.
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The strong lines of copper fall in the regions around 270, 325, 360, 465, 520, 580, 780 and 810 nm. The high resolution and wide range of the echelle system used for these studies enable one to choose interference-free lines for analysis even with highly complex spectra. It was found that the 500-530nm region is suitable for analysis as seen from the fact that the copper line at 521.82nm can be clearly seen without any interference from matrix lines. The very weak peak at 520nm range (shown inset of soil spectrum) comes from ultra-trace amounts of copper in the blank soil (see later).

Figure 6.7 shows a spectrum of 400 ppm copper in soil in the 520nm region, in expanded scale, after background subtraction with a polynomial fit of the general background points. If we look at the 521.82nm line, it can be seen that even at 400 ppm level the copper line seems weak, and quantitative analysis at still lower levels may be deemed as not very easy in this sample. However, as can be seen from the figure, the signal/noise ratio is high enough (>1000) so that analysis of parts per million (ppm) levels is possible.

![Graph showing copper lines in the 520nm region](image)

**Fig 6.7** LIBS spectrum of 400ppm copper in soil after background subtraction
Thus it may be presumed that trace analysis below this level may be difficult with the LIBS technique, because of the enormously large number of lines generated by the variety of atomic and ionic states of any given atom in the high temperature plasma. The plasma will contain multiply ionized states of the atom, continuum states, and highly excited atomic states, all of which decay to different ionic and atomic levels.

The total emission from all atoms of a given element in the sample is thus distributed over many lines, compared to a D.C. Arc (~3000°C) or ICP (6000°C) where all the atoms together give much fewer lines. Furthermore, in a D.C. Arc or ICP source, the excitation mechanism is available all the time and signal is usually collected for about 20-30 seconds or more (that is, same atoms can get excited and emit radiation several times, so long as they remain in the source), whereas in LIBS the total exposure time (time in which the atoms can emit) for several hundred pulses is only a few micro- milliseconds. All this may be thought to lead to low emission intensities of single lines in the plasma making trace analysis difficult. But one has to remember that at the low temperatures of the D.C. Arc and ICP, much smaller numbers of the emitting atoms only will be populating the upper levels.

There are two methods available to further increase the intensities of the lines of interest. One is by increasing exposure time, which has practical difficulties beyond a certain range. The second method is to use the idea that the total trace element excited in the plasma is represented by the total number of lines emitted by that element. That is, make use of as much emission (as many atomic and ionic lines) as possible. For example, if we can add the intensities of four lines, (of more or less same intensity), the signal will increase 4 times while noise which increases as square root, will increase only twice, giving an increase by 2 in signal/noise ratio. We adopted a technique to achieve this purpose by adding the intensities of many lines for preparation of calibration curve.

Data processing details employed for this study can be illustrated by taking copper as the example. The aim is to measure the intensity of a weak line in a very complex array of lines. Since it may be difficult to even locate this line from spectra
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to spectra at very low concentrations, we have to adopt indirect methods. All we know is, this line has to be, say around 521 (Strongest line of copper is at 521.82nm), but not the exact line in the observed spectrum, which will correspond to that. Moreover, as concentration decreases further, we may not be able to locate the line correctly since its intensity may change not only because of decrease in concentration, but also due to changes in experimental conditions (delay, laser power etc). Even after seeing a peak, it is not sure it is due to the line we want, since there are so many weak peaks around it from the major components of the matrix.

So we consider the possibility that if any weak line is there, in addition to the regular matrix lines the total intensity in the region should increase, provided all lines of matrix more or less are coming with same intensity, which can be expected as explained earlier, when excitation conditions are kept constant. The criterion may be difficult to satisfy, but may be achieved under suitable conditions as discussed below.

1) Restrict the wavelength range for data processing to a minimum, i.e. take only wavelength range essential to include the analyte line.

2) Reduce line shifts from run to run, which can be achieved by accurate calibration over the short range selected. For example, for the 528nm line, chose 5-6 intense soil lines in the 505-525nm nm range, and calibrate all spectra in this range with same mean values for the chosen lines. It should be noted that it is not necessary for the calibration to be very accurate in wave length. What is required is that all spectra should be calibrated by the same values for calibration lines so that analyte and matrix lines in samples and standards match as exactly as possible, for further data processing. For this we can use the mean of several blank soil runs, and choose 5-6 lines from the mean to calibrate all spectra. This minimizes errors due to line shift from run to run.

3) To compensate for variations in operating conditions (laser power, collection, jitter in pulses etc) we normalize all spectra with respect to a suitable matrix line in one spectrum, say the mean "Blank" soil. This is equivalent to using the chosen matrix line as an internal standard and will be useful under conditions of remote analysis,
where it is not possible to externally add an element as an internal standard. This is justified in view of the linear relations shown earlier to exist between the intensities and the various experimental parameters, and the quite low probability of change in composition of major components in a given type of mineral/soil, from site to site. Any small changes in the major element’s concentrations will produce only permissible errors in estimation of trace elements.

Theoretically, the above pre-processing will have all soil lines (lines from the major components in the matrix) aligned at same positions with same intensity in all spectra. Practically this may not happen, but we observed that random errors are minimized by these operations.

To get an idea of the concentration of the trace element, several options are available. The simplest is, add the signal in all the pixels in the wavelength range both in the mean blank, standards, and sample spectra, and subtract the blank spectrum value from the values for standards and samples. This gives us the excess signal in standards due to the added analyte, which can be plotted to make a calibration curve and concentrations in samples can be determined from this curve. The disadvantage is, we are adding large number of signal counts to give a very large total and any small difference (arising from trace levels) may be swamped by errors in this large background.

In short, the initial data processing involves background subtraction, calibration, normalization, and matrix - that is blank - subtraction to give the so-called “Difference Spectra”. The magnitude of the integrated signal in these difference spectra are attributed to the analyte spectrum.

In addition to the above two methods –single line intensity measurement and addition of intensities of multiple lines- a third method that is usually suggested for trace analysis is the calculation of correlation function (24), a technique employed to extract weak signals from high background noise. In the present work, this also has been attempted, as discussed below. All data processing-background subtraction,
calibration, normalization, and difference spectra calculation- have been done with GRAMS PLSplusIQ (Thermo Galactic, USA).

6.3 RESULTS AND DISCUSSION

Figure 6.8 (a) shows the spectrum of soil blank, (b) soil sample with known concentration (400ppm) of copper, and (c) the “Difference Spectrum”, after background correction, calibration, and normalization. It is to be noted that though there are 3 strong lines of copper in the 500-530 nm region, they are hardly noticeable at this concentration. However, once a “Difference Spectrum” is obtained, one can add the signal around each copper line, using as many lines as possible to get the excess emission from copper.

![Fig 6.8 Soil sample analysis using LIBS](image)

Table 14 below show this for the spectrum in Figure 6.8 (c). The three regions here correspond to one with the strong copper line (521.82nm), the second (515.324nm) and third (510.554nm) weaker copper lines. In principle adding the counts for the three lines should increase the sensitivity of the technique compared to
using a single line. The echelle system is ideal for this because it covers a wide range and can give many lines from any single analyte. In the fourth row of Table 15 the total counts in the Difference Spectrum is given for a wave length range where no (or only very weak) copper lines are there to indicate the magnitude of any background contribution to such a sum. It is clear that the total counts in this case are noticeably less than for corresponding range where copper lines are present, showing the viability of the technique of “Matrix Blank” subtraction, and improved sensitivity that can be achieved by signal addition from several lines.

Table 15 Excess emission signal from the elements of our interest

<table>
<thead>
<tr>
<th>Wavelength Range (nm)</th>
<th>Excess Intensity (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>520-524</td>
<td>17992.575</td>
</tr>
<tr>
<td>513-517</td>
<td>13404.116</td>
</tr>
<tr>
<td>508-512</td>
<td>12665.036</td>
</tr>
<tr>
<td>550-555</td>
<td>9289.383</td>
</tr>
</tbody>
</table>

The “Difference Spectrum” discussed above, in principle, will contain only spectral lines of elements which are not present in the blank. Under conditions in the high temperature plasma, it is likely that any element will give, most probably, very similar spectrum when it is present in the pure state, or when in a matrix, since the plasma conditions are determined by the very high electron temperature as discussed in Chapter V. The “Difference Spectrum”, will thus contain lines of an element not present in the blank, and will be thus highly correlated to the spectrum of the same element in the pure form. We can thus calculate the cross correlation between the “Difference Spectrum” and spectrum of the pure element. From elementary statistics, the standard statistical cross-correlation function between two signals $x_i$ (pure copper spectrum) and $y_i$ (difference spectrum) is defined as
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\[
\rho = \frac{1}{N} \sum_{i=1}^{N} \frac{(x_i - \bar{x})(y_i - \bar{y})}{\sigma_x \sigma_y}
\]

where \(N\) is the number of points, \(\bar{x}\) and \(\bar{y}\) are the means of pure copper spectrum and difference spectrum respectively, \(\sigma_x\) and \(\sigma_y\) are the standard deviations of \(x_i\) and \(y_i\). The function \(\rho\) takes values from \([-1, +1]\), where values near +1 mean good correlation (i.e. when one function increases, the other also does in proportion), values near 0 mean uncorrelated (i.e. there is no relation between changes in one function and the other) and values near -1 mean anti-correlated (i.e. when one function increases, the other decreases in proportion). In the case of matching pure copper spectrum and difference spectrum, we got good correlation in 520-524nm range with \(\rho = 0.6\) and practically zero correlation in 508-512nm range indicating that the latter weaker line may not be suitable for quantitative analysis. There could be several reasons for this, like more noise or interference from matrix, random changes in intensity due to varying plasma conditions from run to run, differences in dynamics of excited states in pure material and complex matrix etc. The point to note is that a good cross correlation coefficient is an indication about the suitability of that region for quantitative analysis.

In order to investigate the LIBS capabilities for quantitative analysis of trace elements in complex matrices, we have recorded the spectra of soil standards with known concentrations of copper. Spectra were generated for 400, 200, 100 and 60ppm of copper. To test the sensitivity when only a single line is used, a calibration graph was prepared by taking the corresponding peak intensities for 521.82nm line of copper as shown in Figure 6.9. LOD was calculated from this plot (\(3\sigma/\text{slope}\), where \(\sigma\) is the standard error) and it was found to be 0.256ppm.

To investigate whether better sensitivity can be attained by using multiple lines, we have taken the regions with relatively strong copper lines i.e. 254, 263, 272, 324, 370, 450, 458, 465, 468, 481, 521, 578, 809nm. The spectra were calibrated and normalized section wise, and blank soil values were subtracted from (soil+ copper). Calibration plots were made with 10-13 lines, 3-5 lines, and so on.
Fig 6.9 Calibration curve for copper in soil (Single line)

13 copper lines were used first and 6 trials were carried out. The intensity values of respective lines for each concentration were averaged and added together. The calibration graph plotted from this result is shown below in Figure 6.10. The LOD in this trial was found to be 0.225ppm.

Fig 6.10 Calibration curve for copper in soil (Multiple lines- 13 copper lines)
Further examination of the results showed that, out of the thirteen lines, results of five lines (254.48nm, 324.75nm, 450.74nm, 521.82nm and 578.213nm) for different concentrations were found to be same as compared to the remaining eight lines. Hence we averaged and added peak intensities of these five lines and plotted a calibration curve (Figure 6.11). The LOD in this case was 0.225ppm.

![Calibration curve for copper in soil (Multiple lines- 5 copper lines)](image)

**Fig 6.11** Calibration curve for copper in soil (Multiple lines- 5 copper lines)

A comparison of the slopes and corresponding standard errors of the three calibration curves shows that usage 5 strong lines marginally improves the sensitivity, while additional lines do not give any better results. It is therefore necessary to determine the optimum number of lines to be combined if one wants to increase sensitivity. With better noise reduction (better detector, signal enhancement etc.), and further data processing, (for example curve fitting, see below), it may be possible to improve the signal-to-noise ratio.

To average out any noise contribution we can fit the spectra in the regions of interest with suitable curve fitting techniques and use the intensity values from this fitted peaks or areas (total intensities) of the curves. Using same regions (after calibration, normalization and background subtraction), curve fitting was done for 13 lines. For this, sections (or part of it containing the copper line and one or two soil lines on either side) were taken and curve fit was done with Gaussian, Lorentzian, or
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Gaussian + Lorentzian shapes to see which is best. Trial runs showed that Guassian shapes gave best fit and this was used for final calculations. The curve fit will give automatically area, peak position, intensity, and half width. We found that using 4 copper lines out of 13 yielded best results.

The areas and intensities of copper lines can now be added for four lines (254, 324, 450 and 521) and plotted as shown in Figure 6.12. Curve fit need to be run only for a section with the copper line and one or two lines on either side. The curve fit technique has the advantage that the total counts for the line (area) can be obtained, and noise will be reduced since a best fit to observed values is done. The LODs measured in this case were 0.353ppm (peak height) and 0.498ppm (area under the curve).

**Fig 6.12** Calibration curve for copper in soil (Curve fit method)

Another method, which is a modification of the curve fit, in that total counts are taken, also was tried by calculating the total counts for the regions mentioned above. For this the 13 lines of copper were taken and blank soil total counts were subtracted from (soil + copper) total counts. Effectively we are integrating over the lines, that is, taking the area of each line (Figure 6.13). This has the advantage that any errors introduced by small shifts from background will be reduced and signal to noise ratio can improve. The LOD was found to be the best in this case (0.182ppm).
Fig 6.13 Calibration curve for copper in soil (Total counts method)

It was observed from the graph that the line intercepts y-axis around 250000 counts. The possible reasons are explained as follows:

(a) The base line correction may not be good enough.

(b) There may be an overlap of some other elemental line with one or more of the copper lines. In this case there could be some counts from the soil at those lines. However, we can see what are the major elements in the soil (Al, Si, Fe, etc) and check in the NIST database whether any of them have strong lines near the copper lines we have chosen.

(c) If there is contamination from the solution-water used- (either of copper or some element with line near copper line) then a constant background can come.

Similarly calibration curves for other major elements in soil like calcium, magnesium, iron and zinc were constructed and these are shown in Figure 6.14. This has been done by adding known amounts of the required element to the soil and then recording LIBS spectra as explained earlier.
Fig 6.14 Calibration curve for copper, iron, magnesium, zinc and calcium in soil

After making the working curves for all these elements, LIBS spectrum of a blank soil has been recorded and extrapolated the observed intensity of characteristic lines of each element to see their concentration in soil which is shown in Table 16.

**Table 16 LIBS intensity of elements in blank soil**

<table>
<thead>
<tr>
<th>Element</th>
<th>LIBS intensity (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (521.82nm)</td>
<td>120</td>
</tr>
<tr>
<td>Zinc (472.21nm)</td>
<td>444</td>
</tr>
<tr>
<td>Iron (495.76nm)</td>
<td>13223</td>
</tr>
<tr>
<td>Magnesium (518.36nm)</td>
<td>12359</td>
</tr>
<tr>
<td>Calcium (428.93nm)</td>
<td>260</td>
</tr>
</tbody>
</table>

As we mentioned earlier in all these cases the working curves have been prepared after subtraction of the Blank spectrum from the standard. Theoretically this means they should extrapolate to zero signal for zero added concentration of the
analyte. For copper, zinc, and calcium this is more or less observed. Theoretically the signal after blank subtraction has to be attributed to the added amount of the analyte element. If the “Blank” contains residual analyte, any intensity due to this is supposed to be subtracted out and the counts after subtraction should be proportional to the added concentration only of the analyte. In other words, the Calibration curve is a “TRUE” curve, of actual concentration against spectral intensity. To see how far this argument holds, after making the working curves for all these elements we recorded LIBS spectrum of a blank soil has been recorded and the observed intensity of the characteristic lines of each element (Table 16) were extrapolated to estimate their concentrations in the blank soil. We then measured the concentrations using the Atomic Absorption Spectroscopy (AAS) technique (GBC 932 PLUS, MERC, Australia). The results are shown in Table 17. It is seen that the agreement is quite satisfactory.

Table 17 Comparison of LIBS results with AAS for elemental analysis in blank soil

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration using LIBS (ppm)</th>
<th>Concentration using AAS (ppm)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>60</td>
<td>50</td>
<td>7.07</td>
</tr>
<tr>
<td>Zinc</td>
<td>45</td>
<td>60</td>
<td>10.61</td>
</tr>
<tr>
<td>Iron</td>
<td>Out of range</td>
<td>51250</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>920</td>
<td>930</td>
<td>7.07</td>
</tr>
<tr>
<td>Calcium</td>
<td>25</td>
<td>16</td>
<td>6.36</td>
</tr>
</tbody>
</table>

According to scientists at the Krishi Vigyan Kendra, soil in South Karnataka, India is rich in iron. Even though iron is considered as a micronutrient in soil, it is often found in large concentration in soil and cause toxicity which in turn makes the soil deficient in calcium as evident from LIBS and AAS results. This may be the reason why calcium, being secondary nutrient in paddy soil, found in low concentrations. Calcium deficiency can affect the growth, appearance, and health of
plants. The cause is usually the inability of the plant roots to carry calcium to the growing parts. Although trace amounts of iron are required for plants to grow properly, exposure to too much of the element can cause as many problems as its absence. Excessive iron not only proves toxic to plant tissues, but it also displaces other nutrients that plants need. Plants that absorb too much iron have inefficient roots and difficulty regulating photosynthesis, the process by which light is converted usable energy. Unbalanced levels of many other important nutrients like zinc and manganese often arise with iron poisoning, compounding problems in unpredictable ways. Leaves stained red, orange or dark green that develop spots of rot are among the first visible symptoms of excessive iron uptake in plants. This reaction begins in the tips of leaves, spreading inward to cover the plant if high-iron conditions persist. Excessively iron-rich soil causes many plants to develop sparse, ragged root systems. Large sections of the roots will die, and the weakened portions that survive will often be stained brown or black. High levels of iron are known to reduce the yield of fruit, vegetable and cereal crops by promoting stunted growth. The importance of simultaneous analysis of major, minor, and trace elements is thus obvious. The ability of LIBS to carry out such analysis is thus highly advantageous.

6.4 CONCLUSION

As is evident from the above results and discussion, rapid elemental analysis, minimum sample preparation, low detection limits of the order of ppm, possibility of high resolution measurements for isotopic composition etc make LIBS a preferred tool for trace analysis of complex samples in situ/remote conditions. Broad spectral coverage and high resolution of the echelle system give further advantages to the LIBS technique as many lines can be used for cross checking, signal addition, and isotopic compositions can be studied to understand the origin of the samples etc. Different data analysis methods have been attempted like use of a single strong line, integrated area of one strong line, counts added for as many lines as possible, integrated area of as many lines as possible and correlation method. The results showed that adding intensities of selected strong lines, or using total counts of blank-subtracted, normalized spectra, can give good sensitivity for ppm level quantitative analysis. The LIBS results are found to be in good agreement with results of
conventional AAS technique. Measured low limits of detection (LOD) of copper, zinc and calcium in soil sample show the robustness of the LIBS technique for trace analysis of complex samples like soils and minerals.

6.5 REFERENCES