Development of Laser-induced Breakdown Spectroscopy for the Measurement of Toxic Elements in the Solid and Liquid Samples

Summary

A Thesis Submitted to the University of Allahabad, Allahabad For the Degree of Doctor of Philosophy in Science

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Summary of Thesis

The present thesis focuses on the development of the LIBS technique, including experimental configuration, calibration and quantification and its application in environmental monitoring.

Laser-induced breakdown spectroscopy (LIBS)

LIBS is increasingly under consideration as a method for rapid elemental analysis applied to multiple media such as solid, liquid, colloidal or gas that means in any phase of matter [1-5]. Applications of LIBS typically employ a pulsed laser with a high peak power to form a spark (plasma) in the medium to be examined [6, 7]. The hot plasma dissociates molecules into their constituent atoms, excite the electrons in the neutral atoms and ions into their excited atomic states. As the plasma cools, the excited electrons and ions relax back into their ground states, emitting light at their characteristic atomic frequencies, which is the signature for the elements present in the sample volume. The quantification of the elemental species concentration requires the quantification of the intensity of the atomic emission spectral lines via different methods of quantification, which are discussed in the subsequent chapters.

The main advantage of LIBS over other analytical methods is that nearly every element in the periodic table can be detected simultaneously with this method, with varying detection limits. This makes LIBS suitable for rapid and real time analysis, with minimal sample preparation. LIBS is non-destructive in nature which provides online, in-situ monitoring of the elements and this capability of LIBS technique makes it a very strong analytical tool [8]. Chapter 01 deals with the detailed description of LIBS, plasma formation and the whole process behind the spectral emission from the laser-induced plasma as well as the problems handled. Particularly, the focus is on the application of LIBS for the detection and quantification of toxic heavy metals present in samples of environmental interest by means of the development of different quantitative methods.

Heavy metals are extremely persistent in the environment; they are nonbiodegradable and nonthermodegradable and thus readily accumulate to their toxic levels. Heavy metal emissions from various anthropogenic sources and waste water
irrigation are known to contribute significantly to the concentration level of heavy metals, mainly Pb, Cr, Cd, Zn, Co etc, in the soil [9]. The important dietary uptake pathway of these toxic heavy metals could be through crops grown in such contaminated soil grounds. These heavy metals impact on the health either directly or through food chain [10].

**Chapter 02** outlines the experimental design which consists of fabrication and experimental development in setting up LIBS technique. In our experimental setup, Nd:YAG laser source with high pulse power at 532 nm is employed, to form plasma. Plasma is formed on the surface of target, when the power density at the point of focus exceeds $10^9$ W/ cm$^2$, followed by the removal of material from the surface, a mechanism known as laser ablation [11, 12]. The emission from the plasma is collected through the fiber bundle having lens at its tip and then detected and analyzed using spectrometer along with CCD. One of our experimental photograph related to plasma generation on soil sample surface and the emission collected from the plasma through FO cable is shown in Fig. 1.

![Figure 1: Photograph of plasma generation](image-url)
Laser shots at same location of the sample surface result in the formation of crater, which may change lens to sample distance. In order to avoid the formation of deep craters on the sample surface, motorized translation and rotational stage with adjustable height are fabricated and the sample is placed onto it so that every time laser shot introduces to fresh sample surface.

Number of parameters including laser wavelength, laser energy, lens focal length etc. are optimized in a LIBS experiment before performing the qualitative and quantitative estimation of elements present in any matrix in order to accurate and precise analytical measurements.

**Vertical migration of heavy metals in soil**

In the present day scenario, where the pollution is spread by human activities, a better understanding of heavy metals accumulation at the soil surface requires the monitoring of contaminated land to identify the trends of pollution. Therefore, Chapter 03 outlines the suitability of LIBS to monitor the gradual change in the concentration of heavy metals moving deep into the interior of soil surface. To study the rate of migration of heavy metals below the surface of the soil, samples are collected from Naini agricultural area near Allahabad, India, that had received heavy application of municipal sewage sludge, at different depth is investigated to observe the rate of penetration of heavy metals (Mg, Al, Fe, Cu, Hg) deep into the soil. LIBS spectra of the soil sample collected from the different depth (0 -15 cm, 15 cm -30 cm and 30 cm - 45 cm) are recorded. Numerous atomic lines present in the LIBS spectra of soil sample indicate the presence of large number of elements present. The LIBS intensity of the spectral line is proportional to the concentration of the element. Intensity of any chosen atomic line is obtained by measuring the peak area of that spectral line present in the LIBS spectra of soil samples. Our study clearly reveals that the intensity of the spectral lines and hence concentration of the elements; Mg, Al, Fe, Cu, Hg is greater at soil surface and it decreases as we move deep into the soil. A graph (Fig. 2) between the LIBS intensity of chosen atomic spectral line of element of interest versus the depth of soil ground clearly reveal that less the slope, more the efficiency of heavy metal to move deep into the soil.
Thus, the leaching of heavy metals into the soil varies in the order Hg > Al > Mg > Cu > Fe.

![Graph showing vertical distribution profile of Fe, Mg, Cu, Al and Hg](image)

**Figure 2: Vertical distribution profile of Fe, Mg, Cu, Al and Hg**

**Quantification of Pb using Calibration curve method**

EPA has decided the lower safe limit for each heavy metal concentration above which the particular element shows toxic effect, therefore after the recognition of heavy metal presence in LIBS spectra of soil samples, our next step of interest is to determine the exact concentration of that heavy metal. **Chapter 04** describes the one possible approach, named as, calibration curve method for the quantification of heavy metal, Pb, in the Indian agricultural soil, in the vicinity of brick-kiln area, Phaphamau, near Allahabad, India.

In this method, there is an establishment of a curve which relates line intensity of atomic line of element of interest and the corresponding elemental concentration, provided that several certified reference material of known elemental concentration is available. By comparing the line intensity measured for an unknown sample, the corresponding unknown elemental concentration is directly inferred from this curve. For the quantitative determination of Pb in the soil sample, LIBS spectra of reference samples having known amount of analyte (Pb) is recorded (Fig. 3) and the three different
calibration curves at different wavelength of Pb (220.3 nm, 363.9 nm, 405.7 nm) are drawn.

In order to improve the LIBS accuracy by minimizing the experimental fluctuations, calibration curve is drawn using the intensity ratio of an analyte line with that of adjacent reference line versus the analyte concentration (Fig. 4). It is observed that 220.3 nm, which is observed in the UV region of LIBS spectra, completely interference free, is best suited for the quantification of trace amount of Pb in soil instead of any other Pb lines, because it has best linear correlation coefficient and smallest standard deviation of the background signal. Based on the present work, the concentration of Pb in agricultural soil of brick-kiln area in Phaphamau is found to be $\approx 570$ ppm, which is more than the regulatory standards imposed by US EPA for the presence of lead in soil, therefore, it is of great concern to us.

Similarly, for the quantification of heavy metals Cd and Zn in soil sample of Kanpur industrial area, calibration curves for Cd line at 226.5 nm and for Zn line at 206.2 nm are obtained. The limit of detection for Cd and Zn in soil are found to be 0.2 ppm and 1.0 ppm respectively.

![Figure 3: LIBS spectra of different Pb concentration contaminated soil](image-url)
Development for algorithm for Calibration-Free (CF) LIBS method

The non-availability of standard samples and the matrix effects are two major factors affecting the quantitative analysis of environmental and biological samples using LIBS. Therefore, in order to quantify traces as well as major constituents in any sample matrix, a model is developed known as Calibration-Free (CF) LIBS method. **Chapter 05** consists of the description of CF-LIBS method for quantitative determination of a wide range of elements present in any materials with no need of CRM, internal standards and calibration curves. The CF-LIBS procedure, is based on the physical parameters that characterize the plasma conditions such as plasma temperature, electron density etc. Stoichiometric ablation, self absorption and local thermal equilibrium (LTE) are the essential hypothesis for applying CF protocol and have been checked posteriori in LIBS measurements. After determination of plasma temperature and verification of the existence of LTE, the LIBS data is used for the quantitative estimation of each element present in the target. A data processing algorithm is developed based of the CF-LIBS model given by Ciucci et. al. [13] with the help of MATLAB, which directly reads the LIBS intensity and other spectroscopic data stored in the excel file and finally calculated the concentration of elements present (Fig. 5).
To validate our CF-LIBS method the LIBS spectra of pure Pb powder (Merck Pvt. Ltd.) has been recorded. The results obtained from the CF-LIBS have been compared with the certified results obtained from the manufacturer and good agreement has been observed.

**Input parameters:**
- Total number of species present
- Their Integrated Intensity
- Corresponding transitional probabilities,
- Degeneracy factors,
- Upper energy levels

**Figure 5: Flow Diagram of the algorithm for the CF-LIBS procedure**
Application of CF-LIBS in environmental sample (soil)

Chapter 06 deals with the detection and quantification of pollutants including Cd, Co, Pb, Zn, Cr etc along with major constituents present in the environmental sample (soil) by using CF-LIBS approach. Investigated soil samples are obtained from Jajmau, Kanpur, India, to determine the extent and nature of elemental pollutants using LIBS and CF-LIBS techniques. In this area, a serious environmental disaster is brewing on account of the supply of hazardous irrigation water to the farmlands near it.

Prior to the application of CF protocol, the essential hypothesis, stoichiometric ablation, self absorption and local thermal equilibrium (LTE) are checked. For CF-LIBS, this MATLAB program has been used to determine the concentrations of pollutants like Si, Ti, Al, Fe, K, Mg, Ca, Cd, Co, Cr, Mn, P, Sn, Sr, V, W, Na, Pb, Cu etc. in industrial area soil. The quantitative analysis for Cd and Zn in these soil samples is also performed by using calibration curve by preparing different CRM samples and using the same experimental data points as used in CF-LIBS approach. And the results obtained are compared with that of obtained by CF-LIBS (Table 1). Thus, LIBS based on calibration curve in combination with CF-LIBS can be utilized as an authenticated technique for monitoring of toxic heavy metals in environmental samples. It is also clear that the concentrations of the toxic elements are much more than the regulatory standards imposed by US EPA, for the area under investigation. In addition to this, CF-LIBS method is easily utilized to obtain the quantitative information of one of the major matrix element like Si, which is not possible by calibration curve method.

Application of CF-LIBS in biological sample (coral skeleton)

In Chapter 07, our study demonstrates the applicability of CF-LIBS in the area of biological sample which is a sea organism called coral. Corals contain organic constituents identical to that of human skeleton, therefore used in natural therapies, for treatment of osteoporosis and in strengthening bone growth. Calibration curve should have Certified Reference Material (CRM) having similar matrix as that of sample, which is difficult to obtain in the case of such as sea organism. Coral contains an organic composition identical to that of the human skeleton, including strontium, calcium, magnesium etc essential to human life [14]. Laser induced plasma emission at the coral
skeleton sample surface, without any pretreatment, has been used for recording the spectra. The temperature of Laser-induced plasma, ignited on the surface of coral skeleton sample, is evaluated by using Boltzmann plot method. The quantitative estimation of the constituents present including Ca, Sr, Mg, C, O, Na, K and Fe is obtained in the coral skeletons using CF-LIBS and the results are summarized in the bar chart in Fig. 3. It is evident from the bar chart that the concentration of each element in all three samples is nearly comparable. The results of CF-LIBS analysis have also been compared with those obtained by ICP-MS but the results are not in agreement with the results obtained using CF-LIBS. The reason for this disagreement may lie in the fact that CF-LIBS data relate to the coral surface whereas that of ICP-MS relates to its whole mass.

Table 1: Comparison of concentrations of heavy metals (Co, Cd, Pb, Zn and Cr) in four soil samples estimated using conventional calibration curve method, CF-LIBS method and ICP analysis

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Co (ppm)</strong></td>
<td><strong>Cd (ppm)</strong></td>
<td><strong>Pb (ppm)</strong></td>
<td><strong>Zn (ppm)</strong></td>
</tr>
<tr>
<td>CF-LIBS</td>
<td>Calibration LIBS</td>
<td>ICP</td>
<td>CF-LIBS</td>
</tr>
<tr>
<td>6.5</td>
<td>-</td>
<td>4.55</td>
<td>3.6</td>
</tr>
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<td>529</td>
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<td>-</td>
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</tr>
<tr>
<td>22335</td>
<td>-</td>
<td>21100</td>
<td>18254</td>
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</table>

*Limit of Quantification (LOQ) = 3.3 X LOD = 0.6 ppm

The present study reveals that with the help of CF-LIBS method, quantitative analysis of numerous elements may be performed easily in any kind of sample without any pretreatment. And hence the present study also has a direct consequence of applicability of CF-LIBS procedure in biomedical field which is rather difficult even for ICP because of in-situ limitation.
Figure 6: The concentration of elemental constituents present in coral skeleton samples

Development of new working calibration curve

Chapter 08 includes the development of a new working calibration curve which reduces the problem of matrix effect which is an extension in the traditional calibration curve approach. Traditional calibration curve method is based on the assumption that the distribution of elements among the different excitation and ionization states are same for both the certified and unknown samples. But the soil samples collected from different area have substantial difference in their matrices in terms of structure, morphology etc. Therefore, in this newly developed working calibration curve, a plot between intensity of one neutral atomic line and one ionized atomic state line of an element versus its concentration in the sample is drawn. As in this model, the spectral lines corresponding to neutral atom and ionized state atom are introduced therefore, any variation in the distribution of atomic population between the neutral atom and ionized state atom in the laser induced plasma of unknown and standard samples does not introduce any error in measurement of total concentration of an element in unknown sample using newly developed calibration curve and thus reduces the matrix effect.

This working calibration curve is now used for the quantitative estimation of heavy metal, Cd, in the industrial area soil. The traditional calibration curves are drawn at Cd neutral atomic line (226.5 nm) and Cd singly ionized state atomic line (228.8 nm) and
selecting Si (221.0 nm) as reference line. The working calibration curve is also drawn using both these Cd lines and Si (221.0 nm) as reference line (Fig. 7). The merit of different calibration curves are compared by estimating the limit of detection (LOD) of the contaminants as the LOD depends on the slope of calibration curve.

The limit of detection using working calibration curve is found best as obtained using both of its constituent calibration curves (i.e. individual calibration curves) this is because this working calibration curve is the result of the combined effect of effect of its constituent’s calibration curves. Also the results obtained using working calibration curve are found to be more close to that of obtained by ICP in comparison to the results obtained by the traditional calibration curve.

Thus, the LOD as well as analytical results obtained by working calibration curve are found better. Hence, we can say that our working calibration curve is more suitable for the quantitative determination of contaminants in environmental samples as it reduces the influence of matrix in which analyte element are embedded, on the intensity of LIBS signal.

Chapter 09 presents the summary of the thesis and expansion/ extension of LIBS, when integrated with various techniques.

![Figure 7: Ratio working calibration curve using ratio of intensity of analyte lines at 228.8nm plus at 226.5 nm with intensity of the internal reference Si line at 221.0 nm versus concentration of Cd in standard soil sample.](image-url)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
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<tr>
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<tr>
<td>R</td>
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Bibliography


