Laser-induced breakdown spectroscopy: A versatile tool for monitoring traces in materials

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Abstract. Laser-induced breakdown spectroscopy (LIBS) is an emerging technique for simultaneous multi-elemental analysis of solids, liquids and gases with minute or no sample preparation and thus revolutionized the area of on-line analysis technologies. The foundation for LIBS is a solid state, short-pulsed laser that is focused on a sample to generate a high-temperature plasma, and the emitted radiation from the excited atomic and ionic fragments produced within the plasma is characteristic of the elemental composition of the sample that can be detected and analyzed using a suitable optical spectrograph. In the present paper, the applicability of LIBS for different solid samples having homogeneous (silver ornament, aluminum plate) or heterogeneous composition (soil) using nanosecond laser pulses is discussed. Nanosecond pulse laser makes plasma at the sample surface even at very low pulse energies and also allows for precise ablation of the substrate material with little damage to the surrounding area. We have also studied the penetration of different heavy metals inside the soil surface.

Keywords. Laser-induced breakdown spectroscopy; nanosecond pulse laser; leaching; heavy metals; soil.

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1. Introduction

LIBS is a spectrochemical method which emerges as a powerful tool for determining the elemental composition of various samples present in any phase (solid [1–3], liquid [4,5] and gas [6]), by simultaneously vaporizing and exciting the sample and thus it improves the spectrochemical techniques by eliminating the requirement of sample pre-treatment. When an intense pulsed laser beam is focused onto a sample surface, breakdown of the sample occurs, which eventually results in the creation of spark, frequently called laser-induced plasma, and rapidly heats the sample region to extremely high temperature. The light emitted from the plasma is collected and analyzed to determine the elemental constituents of the sample.

LIBS has proved to be a powerful laser-based analytical technique due to its simplicity and versatility. Practically any kind of sample such as soil having heterogeneous nature, can be analyzed with minor sample preparation.

Soil is the major source through which heavy metals can be absorbed by the vegetable and crops via their roots or foliage [7,8]. Therefore, a better understanding of heavy metals accumulation at the soil surface and their leaching inside the soil seems to be particularly important in the present scenario, where pollution is spread by human activities. Conventional analytical techniques for the analysis of soil, such as, atomic absorption/emission spectroscopy, X-ray fluorescence, polarographic techniques, molecular methods, chemical analysis etc. [9], require lengthy sample preparation, trained operators or chemical technicians and long measurement time.

But 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 [10]. This makes LIBS suitable for rapid on-line analysis, with minimal sample preparation. Recently, a compact LIBS set-up is developed which is readily transportable for monitoring explosives [11].

Although the LIBS technique has been extensively used as an analytical tool for the analysis of traces in different materials, literature on the use of LIBS technique by the scientists working in Indian Universities/laboratories is sparse. Therefore, we have developed the experimental facility for LIBS [12] and the purpose of the present article is to assess the potentials of the LIBS technique in the qualitative and quantitative analysis of the traces present in soil, precious alloys etc. with better sensitivity and reproducibility. The suitability of LIBS to monitor the gradual change in the concentration of heavy metals moving deep into the interior of soil surface is also demonstrated.

2. Experimental set-up

The experimental set-up, sketched in figure 1, consists of Q-switched Nd:YAG (neodymium-doped yttrium aluminium garnet) laser (continuum lasers, Surelite III-10) which delivers maximum energy up to 425 mJ at 532 nm (2nd harmonics of Nd: YAG emission), within 3–4 ns pulse duration, at 10 shots per second repetition rate, for the ablation of sample material and generation of LIBS plasma. The laser beam is focused by using fused silica quartz lens having a focal length of 15 cm onto the sample placed on a suitable rotating stage with an adjustable height. The optical emission from the plasma is collected and guided to LIBS2000+ spectrometer via fiberoptics, to yield information on the elemental make-up of the material. The fiber bundle is positioned at a distance of nearly 1.0–1.5 cm from the plasma, making an angle 45° to the laser beam. A small lens is mounted at the tip of fiber bundle. The spectrally dispersed signal from the spectrometer is automatically sent to charge-coupled device (CCD), in-built within the spectrometer, which converts the spectral signal into digital signal. The LIBS2000+ spectrometer allows us to acquire laser-induced breakdown (LIB) spectrum ranging from 200 to 1100 nm. The present LIBS2000+ spectrometer has four gratings; one having 0.75 nm resolution and covering the wavelength range from 188.7 nm to 1096.06 nm and
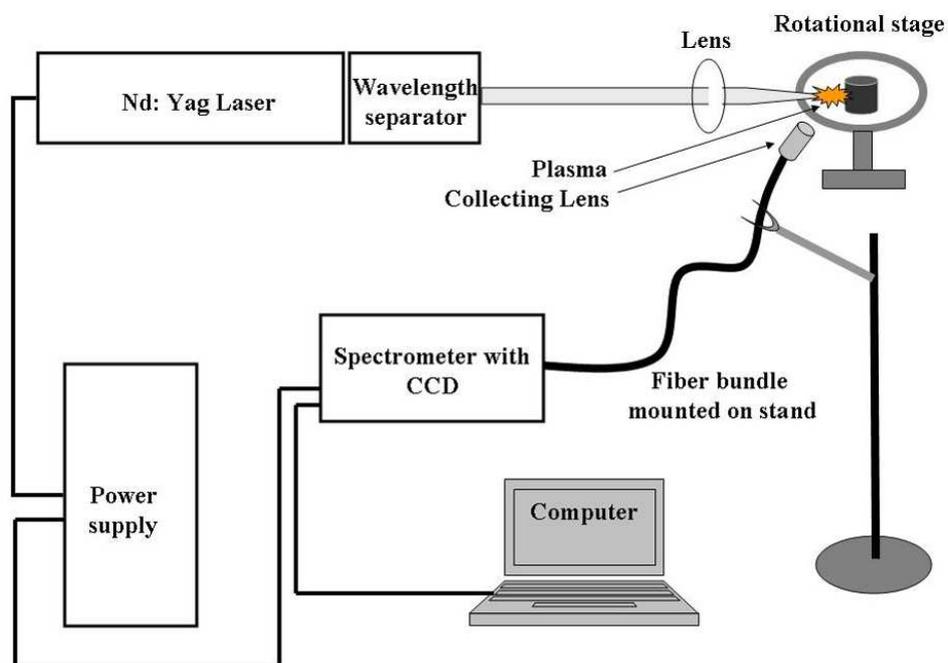
Figure 1. Experimental set-up for LIBS.

the other three gratings have 0.1 nm resolution covering the wavelength range from 198.07 nm to 302.07 nm, 295.7 nm to 391.78 nm and 384.64 nm to 512.47 nm. This whole set-up is controlled by a software.

3. Result and discussion

In nanosecond laser heating of metals, the absorbed laser energy first heats up the target to the melting point and subsequently vaporize that melted portion. In this case evaporation occurs from the liquid metal, and heat conduction into the solid target is the main source of energy loss.

The LIB spectra consist of spectral lines which give information about all the constituting elements as well as elements in trace amount present in that sample. Nearly every element in the periodic table can be detected with LIBS method with different detection limit.

3.1 *LIB spectra of homogeneous sample*

LIB spectra of silver ornament is recorded by pointing laser beam on the flat surface of that ornament, without any pre-treatment. Only a single shot of the laser beam is sufficient to get the LIB spectra of the above sample. Figure 2 represents a
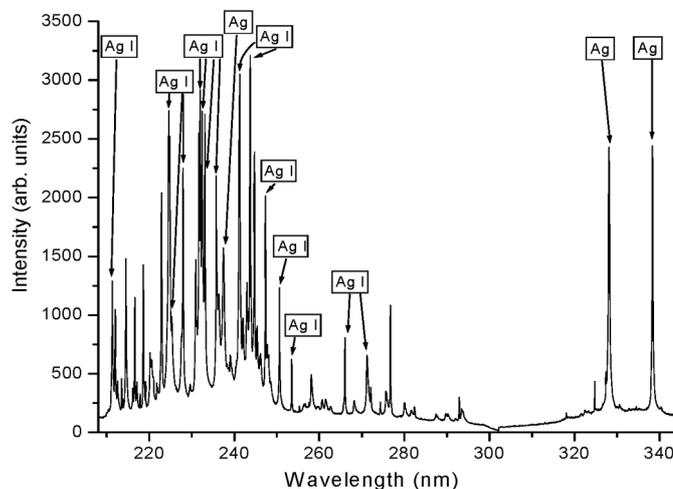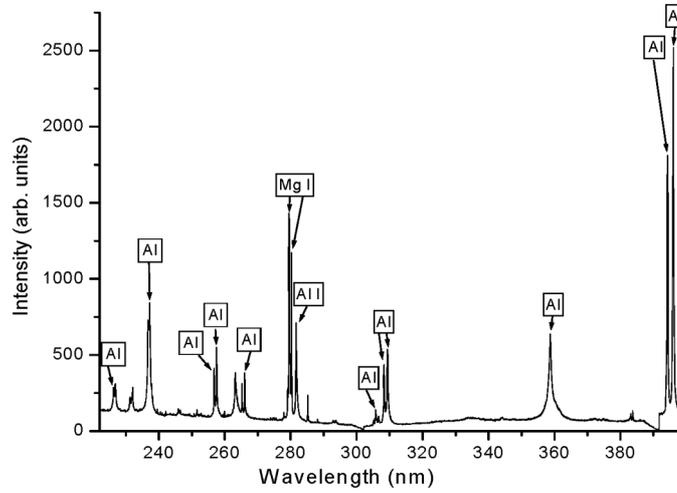
Figure 2. Single-shot LIB spectra of silver ornament without any sample preparation.

small portion of the single shot LIB spectra of silver ornament, in which almost all intense lines of neutral and excited state atoms of silver (Ag) are visible. The lines of Ag neutral and first excited state lines are identified with the help of peak identification facility in the OOILIBS software and by wavelength tables of Brodey *et al* [13]. The distinctive atomic lines of Ag atoms at 328.0, 338.2, 211.3, 214.5, 216.6, 218.6, 224.6, 224.8, 227.9, 232.0, 232.4, 233.1, 235.7, 237.5, 241.3, 243.7, 247.3, 250.6, 253.5, 266.0, 271.2, 276.7 nm etc. are identified.

Similarly, the single shot LIB spectra of aluminum (Al) sheet is recorded using the same experimental set-up and same experimental conditions. The atomic lines of Al neutral atom at 226.9, 237.3, 256.8, 257.5, 266.0, 305.7, 308.2, 309.2, 394.4 and 396.1 nm and atomic lines of first excited state of Al atoms at 281.6, 358.6 nm are observed in the LIB spectra of Al sheet. In addition to these atomic lines of Al, the persistent lines of Mg at 279.5 and 280.2 nm, are also observed in the LIB spectra of Al sheet (figure 3) and this clearly shows the presence of magnesium (Mg) in this Al sheet as an impurity at trace level. Thus our experimental result clearly demonstrates that LIBS technique is able to detect traces of any element present in any matrix.

3.2 *LIB spectra of heterogeneous sample*

Soil is an inhomogeneous matrix. It is difficult to maintain the distance between the focusing lens and sample surface when loose soil sample is used. Sample-to-lens distance is an important parameter while performing the LIBS experiment. Thus, to maintain the sample-to-lens distance constant, soil should be made as pellets. Soil is dried, ground to grain size, sieved and finally, pressed at 2.5 ton pressure by hydraulic machine so that the pellet is formed. Soil is a matrix that has ample

Figure 3. Single-shot LIB spectra of aluminum plate without any sample preparation.
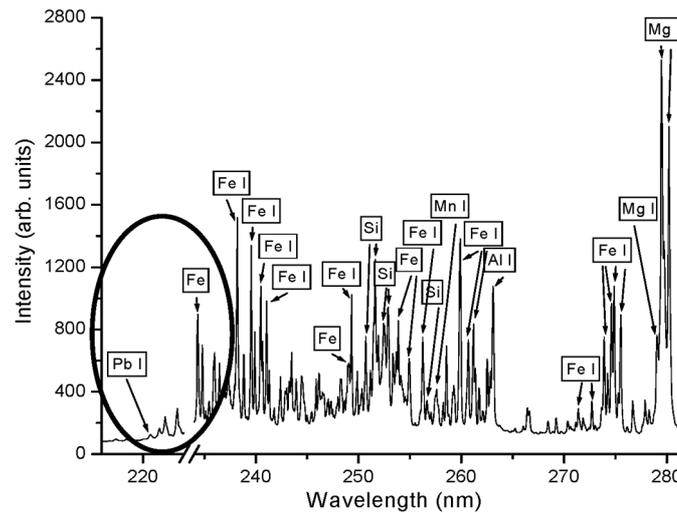
Figure 4. Single-shot LIB spectra of soil sample without any sample preparation, encircling the lines used for drawing the calibration curve.

amount of elements present and therefore LIB spectra of the soil shows dense atomic lines. Figure 4 represents only a small portion of the LIB spectra of the soil sample. Figure 4 clearly indicates the presence of Al, Ba, Mg, Si, Ti, C, Mn, N, O, Fe, Ca, Na, K, Li, Pb etc., i.e. heavy metals are also present in the soil sample, which is dangerous for all living creatures, as these heavy metals are transported to crops and vegetables grown in this soil.

Figure 5. Map of Allahabad district, indicating Naini area (within squares), where leaching effect is studied.

3.3 *Leaching of heavy metals*

In recent decades, an increasing accumulation of heavy metals in the upper soil layer, due to atmospheric deposition has been observed. Leaching of heavy metals from the top soil to the deep soil is a way by which heavy metals can be migrated to the plants through roots and foliages, and therefore it is an important source of trace elements in human diet. Vertically migrated pollutants creat a real threat to the human society also because of the potential contamination of the ground water supplies [7]. Therefore, we have planned to study the rate of migration of heavy metals below the surface of the soil. Soil samples, collected from Naini agricultural area near Allahabad, India (figure 5) that had received a great quantity of municipal sewage sludge, is investigated to observe the rate of penetration of heavy metals (Mg, Al, Fe, Cu, Hg) deep into the soil. Total elemental composition of soil samples collected is measured by LIBS technique [14]. In this article we have compared the leaching of Mg, Al, Fe, Cu and Hg inside the soil surface by using LIBS technique. LIB spectra of the soil sample collected from different depths (0–15 cm, 15–30 cm and 30–45 cm) are recorded and are shown in figures 6a–6c.

We have measured the intensity of atomic lines of Al at $\lambda = 281.6$ nm, Hg at $\lambda = 253.6$ nm, Mg at $\lambda = 285.2$ nm, Fe at $\lambda = 238.2$ nm and Cu at $\lambda = 249.2$ nm in the LIB spectra of the above soil samples (figures 6a–6c). It is clear from the bar chart of figure 7 that the intensity of the spectral lines and thus concentration
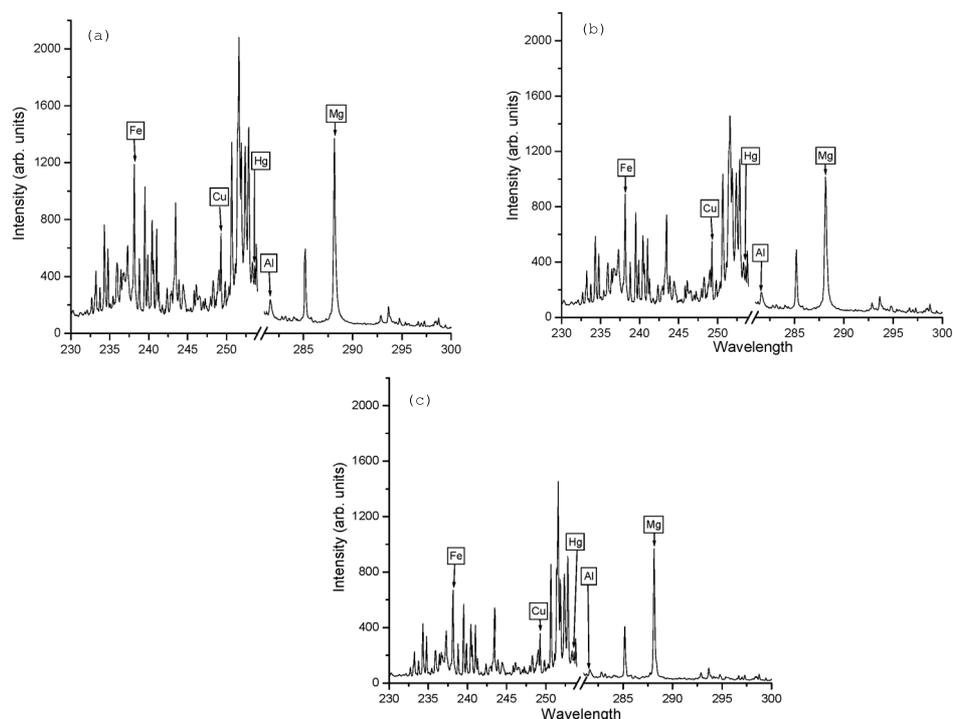
Figure 6. LIB spectra of Naini area soil sample at (**a**) 0–15 cm depth, (**b**) 15–30 cm depth and (**c**) 30–45 cm depth.

of the elements Mg, Al, Fe, Cu, Hg is greater at soil surface and it decreases as we move deep into the soil. The variation of intensity of the spectral line, which is also proportional to the concentration of the element at different depth, is summarized in table 1 and figure 8. Table 1 and figure 8 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. Thus, the present result clearly demonstrates that leaching effect (penetration) of Hg is more in comparison to other metals, i.e. it can leach deep into the soil. Hg is hazardous in comparison to other heavy metals and hence its uptake by the roots and foliage of the plants is ultimately dangerous for human health.

It also appears that large fractions of heavy metals present due to pollution is moved out of the soil surface by physical-chemical or biological processes. Even then there is potential for groundwater and surface water contamination. Excess uptake of these heavy metals in vegetable crops can produce severe toxic effects. It is a well-known fact that Cu, Hg, Pb, Zn etc. ions invariably affect photosynthesis functions of plants either directly or indirectly [15]. Figure 7 clearly demonstrates that these heavy metals can penetrate into deep interior of the soil and can affect the production of crops and vegetables.
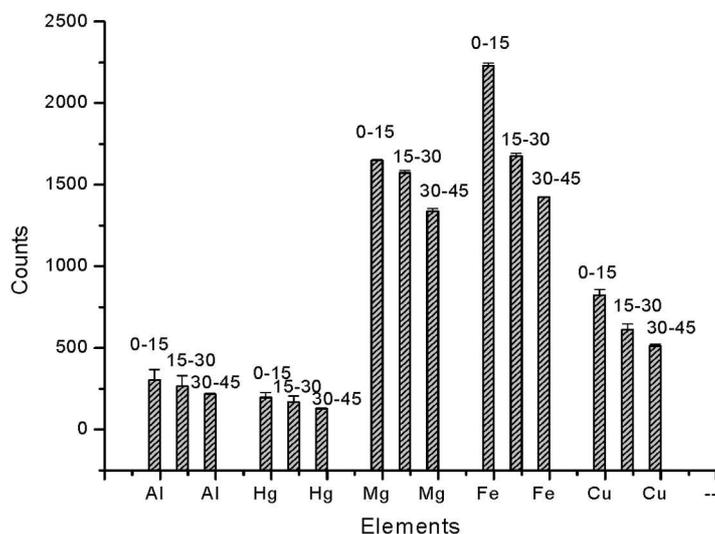
Figure 7. Variation of heavy metals (Al, Hg, Mg, Fe, Cu) at different depths (cm) from the soil surface in terms of LIB spectral intensity.
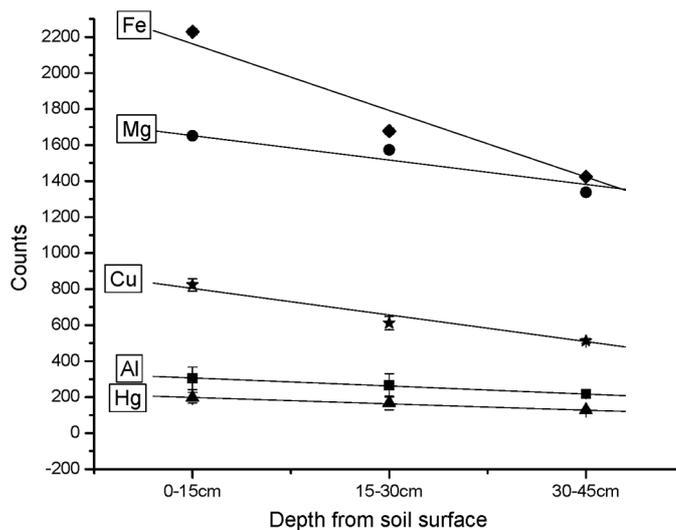
Figure 8. Vertical distribution profile of Fe, Mg, Cu, Al and Hg.

3.4 *Quantitative analysis and LOD calculation*

The emission intensity of an atomic line of any element is proportional to the amount of the elements present in the sample. For quantitative analysis of elements present in any sample, a calibration curve is required. To get the calibration curve, one has to have a set of reference samples, whose constituents are known and
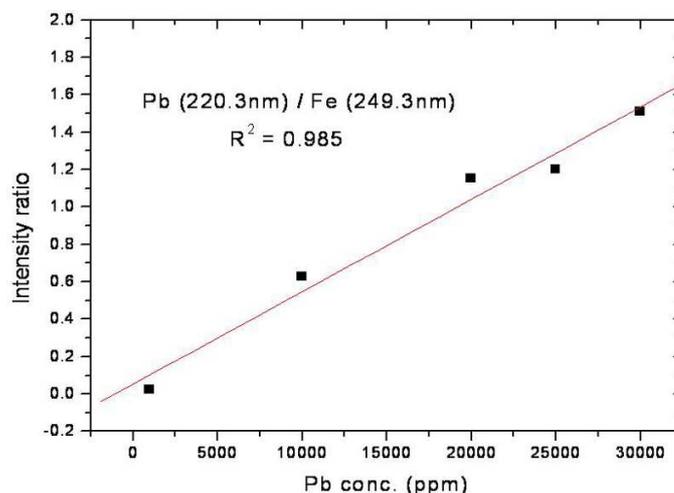
Figure 9. Calibration curve for quantitative analysis of Pb in soil.

Table 1. LIBS intensity and relative standard deviation (RSD) of the chosen atomic line of heavy metals detected in the soil sample of Naini area at different depths.

		Depth (cm)						
		0–15		15–30		30–45		
	λ used (nm)	Int. (arb. units)	RSD	Int. (arb. units)	RSD	Int. (arb. units)	RSD	Slope
Al	281.6	304.25	62.6	266.00	64.3	217.62	4.30	44.2
Hg	253.6	196.87	29.5	167.62	37.8	127.50	4.71	35.4
Mg	285.2	1652.00	1.79	1573.00	14.4	1338.00	17.8	135.7
Fe	238.2	2228.75	17.7	1677.50	16.5	1424.00	2.83	370.0
Cu	249.2	823.75	34.8	611.00	37.3	512.25	13.5	147.4

have the same matrix as that of the unknown samples. In the present article we concentrate on the quantitative analysis of Pb, which is another toxic element present in the soil. To perform this analysis, reference soil samples having varying concentration of Pb are prepared artificially by spiking the soil with known amount of pure $Pb(NO_3)_2$ compound and then pellets of these samples are made. The LIB spectra of all reference soil samples are obtained and the intensity of spectral lines corresponding to Pb (220.3 nm) and Fe (234.3 nm) in all the LIB spectra are measured. A calibration curve (graph between concentration of Pb in reference soil samples and intensity ratio of spectral line of Pb at 220.3 nm with Fe at 234.3 nm) has been plotted (figure 9). The concentration of Pb in any unknown soil sample may be easily obtained by recording the LIB spectra of unknown soil sample and by using calibration curve. We have recorded the LIB spectra of Pb-contaminated soil sample and the atomic line corresponding to Pb is shown in figure 4. The

intensity of the spectral line at 220.3 (Pb) and 234.3 (Fe) nm shown in the inset of figure 4 are measured to calculate the Pb concentration in the soil sample. Finally, the concentration of Pb in the soil sample is calculated using the calibration curve (figure 9) and found to be 570 ppm. The limit of detection (LOD) of Pb in soil sample is also calculated using the equation

$$\mathrm{LOD} = 3\sigma_{\mathrm{B}}/m,$$

where σ_{B} is the standard deviation of background of replicate measurements and m is the slope of calibration curve [16]. The detection limit of Pb in soil calculated by the above equation is equal to $\approx$45 ppm.

4. Conclusion

Laser-induced breakdown spectroscopy technique has opened a new door for simultaneous multi-elemental detection and has revolutionized the area of on-line analysis technologies by rapid material characterization. Our present study clearly reveals that LIBS technique may be utilized for the detection of traces in the environment and thus this technique is useful for monitoring the pollutant in matrix like soil, water etc. Work is in progress to study the behavior of leaching effect beyond 45 cm depth by taking the soil sample at small depth intervals and up to 1 m.

Acknowledgement

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