

Screening of brick-kiln area soil for determination of heavy metal Pb using LIBS

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Received: 22 May 2007 / Accepted: 14 January 2008 / Published online: 9 April 2008
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Abstract Rapid measurement of heavy metals in soil is an important factor in modeling the effect of industrial pollution on agricultural soil. Conventional methods of heavy metal analysis are relatively slow in terms of measurement/analysis time and sample preparation time with the requirement of skilled manpower. Our results highlight the quantitative analysis of toxic metal lead (Pb), for the first time, in an Indian agricultural soil, in the vicinity of brick-kiln area, Phaphamau, near Allahabad, India, by using a novel technique named as Laser-induced breakdown spectroscopy (LIBS). LIBS spectra of soil has been recorded in the wavelength range from ultraviolet (UV) to infrared region (200–1,100 nm). The suitability of Pb lines for drawing the calibration curve is checked and realized, for the first time, that 220.3 nm, which is observed in the UV region of LIBS spectra, is completely interference free and best suited for the quantification of trace amount of Pb in soil instead of any other Pb lines, because it has best linear regression coefficient and smallest standard deviation of the background signal. In the present work the

detection limit for Pb in soil is found to be 45 ppm. Based on the present work the concentration of Pb in agricultural soil of brick-kiln area in Phaphamau is found to be $\cong 570$ ppm, which is more than the regulatory standards imposed by US Environmental Protection Agency (400 ppm) for the presence of lead in soil, therefore, it is of great concern to us.

Keywords Laser-induced breakdown spectroscopy · Soil · Brick-kiln · Phaphamau · Heavy metal · Pb

Abbreviations

Al	aluminum
Ba	barium
C	carbon
Ca	calcium
Ca I	calcium first excited state atom
CCD	charge-coupled device
Cr	chromium
CRM	certified reference material
DRDO	Defense Research and Development Organization
Fe	iron
Fe I	iron first excited state atom
K	potassium
Li	lithium
LIBS	laser-induced breakdown spectroscopy
LOD	limit of detection
Mg	magnesium
Mn	manganese
N	nitrogen

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Na	sodium
Nd:YAG	neodymium-doped yttrium aluminum garnet
O	oxygen
Pb	lead
Pb I	lead first excited state atom
R	linear regression coefficient
Si	silica
Ti	titanium
UV	Ultra violet
US EPA	United States Environmental Protection Agency

Introduction

Soil, whether in urban or agricultural areas, acts as major absorber for metals released into the environment from a variety of anthropogenic sources e.g. emissions from high temperature processes such as coal combustion, mining, smelting, brick-kiln, use of biosolids in agricultural and the past use of antiknock gasoline additives and waste excretion etc (Badawy et al. 2002). In soil, some of these metals persist for longer time like Pb because of their fairly immobile nature, while other metals, migrate to either ground water aquifer or plants due to its mobile nature.

Lead is a common component of municipal and medical waste, whose undesirable increase in soil and water find their way into the human body through respiration or through ingestion of water and food i.e. through food chain. Pollution due to Pb, irrespective of source, is a matter of major concern because of its long residence time (mean residence time evaluated is hundred to thousands of years) in the soil and it causes developmental problems in children and developing fetuses (Buckley et al. 2002; Manceau et al. 1996).

The use of Pb by our society has been started before the Christian era, but after the industrial revolution such as mining and brick-kilning, acid battery recycling, synthesis of tetra alkyl lead and lead paints and combustion of leaded gasoline ([EPA-HQ-OPPT-2005-0049; FRL-8116-6], RIN 2070-AC83, 40 CFR Part 745), the accumulation of Pb in environment has tremendously increased. Lead, airborne from the kiln foundries, falls on the ground in the period of few days and become distributed in soils and water sources. As time passes, enormous amounts of anthropogenic lead

have been started storing in the biosphere, as its removal rate is much lesser (approximately 20 times) than its loading rate and this results in continuous increase of Pb concentration. The bioecological cycle of Pb has been affected to man to a greater extent than that of any other toxic metals. Ample amount of literature exist that show how lead is effecting children in many folds (Extreme Health USA 2007; Blackman et al. 2006).

Therefore, it is clear that the impact of Pb on the environment would be deleterious to our society. Children, exposed to lead, can have serious health effects such as the hematologic, endocrinologic, nervous, renal and reproductive systems. Lead has been linked to learning disorders, behavioral problems and deficits in intelligence in children, including delayed development also.

Thus, the monitoring of Pb contaminated land is of particular importance to identify the trends of pollution and to apply controlling activities. Monitoring of toxic heavy metals, in contaminated lands, require development of novel analytical detection systems that can rapid, online, in situ analysis, for their quantitative determination in matrices of different complexity including ground waters and soils of different genesis. Conventional analytical technique such as atomic absorption/emission spectroscopy, X-ray fluorescence, polarographic techniques, molecular methods, Chemical analysis etc. (Palumbo et al. 2004) require lengthy sample preparation, trained operator or chemical technician and long measurement time. In addition to this, these techniques are unable to perform online analysis of heterogeneous sample. In this situation, the solution to this task is Laser-induced breakdown spectroscopy (LIBS).

LIBS is a method in which elemental analysis of any kind of sample (Rosenwasser et al. 2001; Cho et al. 2007; Samek et al. 2000; Rai et al. 2002) even having heterogeneous composition can be easily done with minimal disturbance. LIBS works by firing an intense pulse of laser light on the sample surface. The laser beam ablates a spot on the target sample that's roughly of the size of a pencil point. The collecting optics captures light emitted from the plasma and directs it to a spectral analyzer. Each element creates its own spectral fingerprint i.e. specific wavelengths of the light in the plasma correspond to spectral lines of specific elements present in the soil. In LIBS, the plasma can be formed at almost any material sample

surface, but the important issue is the translation motion of sample to reduce crater effect (Song et al. 1997).

Thus, detection, quantification and controlling the accumulation of Pb in environment (soil and water) are important from health point of view. Hence, our main objective in the present paper is to determine the concentration of toxic heavy metal (Pb) in the agricultural field, adjacent to brick-kiln area, using LIBS technique.

Experimental

Sample preparation

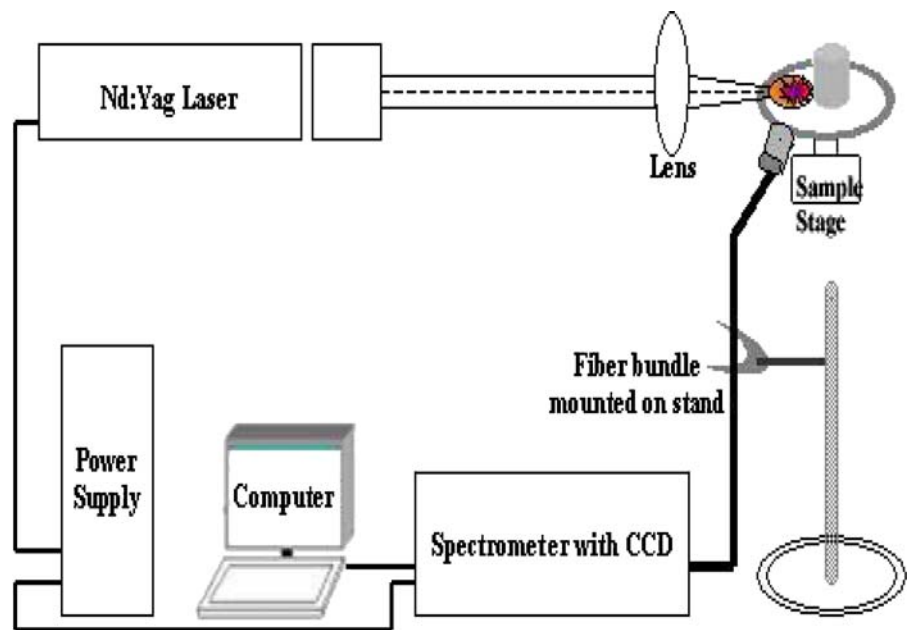
Quantitative analysis of soil always remains a major challenge because of its higher degree of inherent spatial heterogeneity. Detection of heavy metals using LIBS, provides data in few seconds from soil with little preparation (Wainner et al. 2001). In LIBS technique, the sample handling is minimal because the plasma can be formed on almost any sample surface, kept in any phase. But the distance between the focusing lens and sample surface should be constant. To achieve this condition pellet formation of the soil is necessary. Soil is dried, ground to grain size, sieved and finally, pressed at 2.5 ton by hydraulic machine to form the pellet.

Calibration curves are required for quantitative determination of heavy metal in soil. To get the calibration curve, a set of standard soil samples containing the known amount of element of interest are needed. As it is difficult to find certified reference material of the similar matrix, therefore such samples are artificially prepared by spiking the alluvial soil with known amount of pure $Pb(NO_3)_2$ salts and then pellet of these samples are made.

Layout

LIBS is a form of atomic emission spectroscopy in which a pulsed laser is used as the excitation source. The basic principle is illustrated in the schematic diagram (Fig. 1). The output of a frequency doubled Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Continuum Surelite III-10), having variable pulse energy up to 450 mJ, 3–4ns pulse duration and 10 Hz repetition rate, is focused by using a lens of focal length $\cong 15$ cm, onto the surface of the material to be analyzed. The position of beam waist was 9 mm before focusing. After focusing the diameter of the beam at the sample surface becomes 0.02 mm. Thus, for a short duration of time, which is typically few nanoseconds, the power density at the surface of the material can exceed 1 GW/cm^2 . At these power densities, a fraction of a microgram of material is

Fig. 1 A schematic diagram of LIBS experimental setup



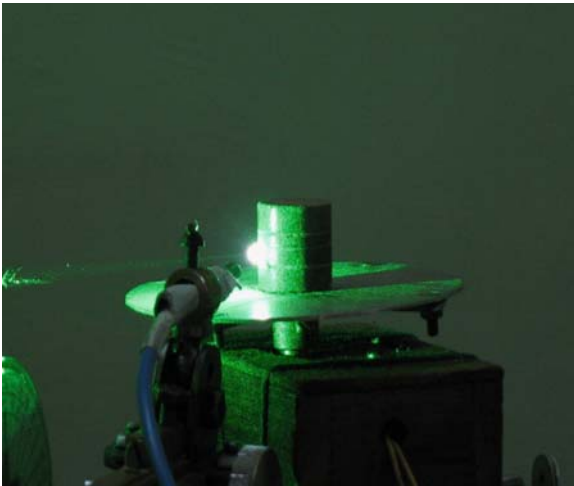


Fig. 2 Photograph of plasma generation on a soil pellet and collection through fiber optic bundle

ejected from the surface by a process known as laser ablation and a short-lived but highly luminous plasma with instantaneous temperatures reaching thousands of Kelvin, is formed at the surface of the material (Fig. 2). Within this hot plasma, the ejected material is dissociated into excited ionic and atomic species. At the end of the laser pulse, the plasma quickly cools as it expands outwards at supersonic speeds. During this time the excited ions and atoms emit characteristic optical radiation as they revert to lower energy states (Body et al. 2001). The plasma optical emission was guided to a LIBS2000 spectrometer via fiber optics bundle. A fiber optic bundle is, therefore positioned at

Fig. 3 Map of Allahabad district, indicating Phaphamau area from where the soil is collected



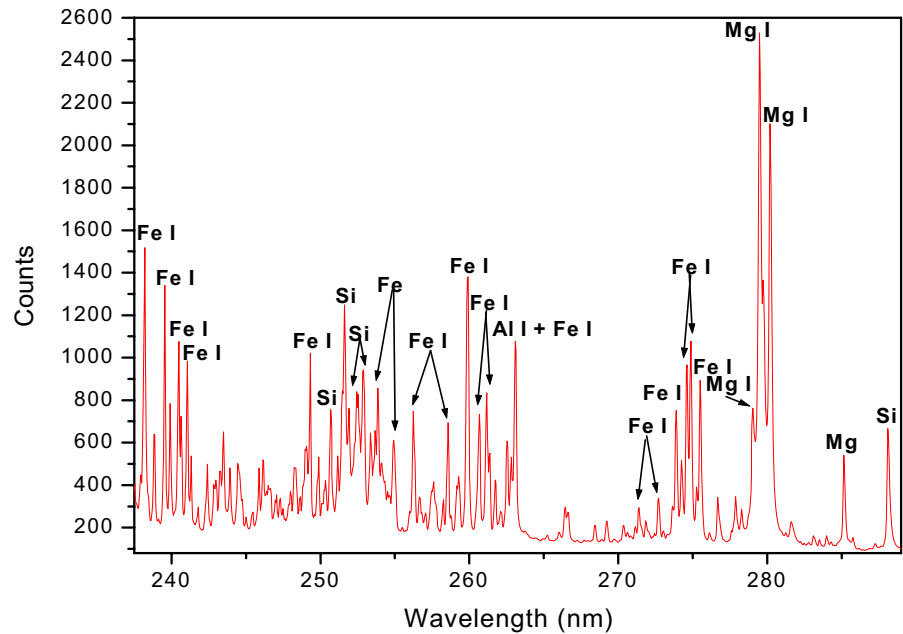
a distance of nearly 10 cm from the plasma, having a small lens on its tip, kept normal to the target surface, making an angle 45° to the laser beam. Since laser shots at same location result in the formation of crater and hence the sample is placed on a motorized translation/rotational stage with adjustable height to get fresh sample surface for every laser shots, in order to avoid the formation of deep craters on the sample surface that may change lens to sample distance, an important parameter regarding LIBS. The LIBS spectrometer (Ocean Optics, model No. LIBS2000+) equipped with CCD is used for the simultaneous detection of all elements present in sample. The spectrometer has wavelength range from 200 to 510 nm with 0.1 nm resolution, simultaneously the data is collected by another grating having wavelength range 200–1,100 nm and resolution 0.75 nm. This whole setup is controlled by the OOLIBS multi channel software.

Results and discussion

LIBS spectra and identification of Pb

Soil samples are collected from the agricultural area adjacent to brick-kiln foundry Garapur, Phaphamau (shown in Fig. 3) near Allahabad, India. LIBS spectra of prepared brick-kiln soil pellet is recorded within the whole spectral range 200–1100 nm as shown in Figs. 4,

Fig. 4 LIBS spectra of brick-kiln area soil in 232–290 nm region using high resolution grating



5 and 6. 100 laser pulses have averaged in order to get each LIBS spectra and this procedure is repeated in duplicate and such two resulting spectra are averaged. Thus, every LIBS spectra given in this paper is the average of 200 individual spectrums. Care has been taken in keeping all the experimental conditions (laser energy, position of the focusing and collecting optics etc.) constant, during all the measurements.

During the course of experiment, a very highly intense signal is observed at 532 nm due to reflection of laser light from the pellet surface, therefore, atomic lines which lie adjacent to this wavelength (532 nm) region become overlapped/hidden due to the strong signal at 532 nm. But, in this paper we are mainly interested in the atomic lines corresponds to heavy metal Pb, and almost all spectral lines of Pb, (i.e. the

Fig. 5 LIBS spectra of brick-kiln area soil in 310–455 nm region using high resolution grating

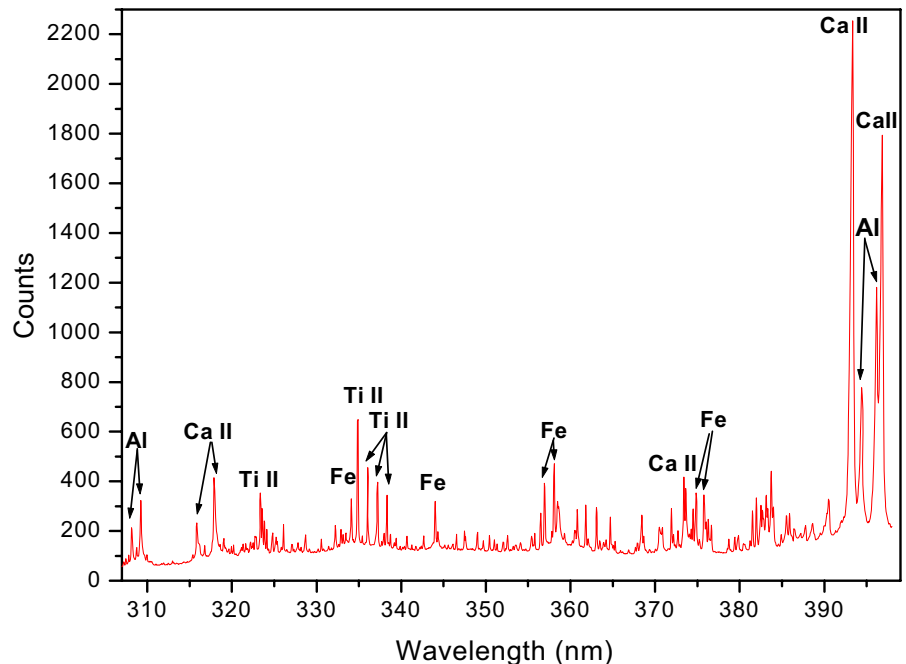
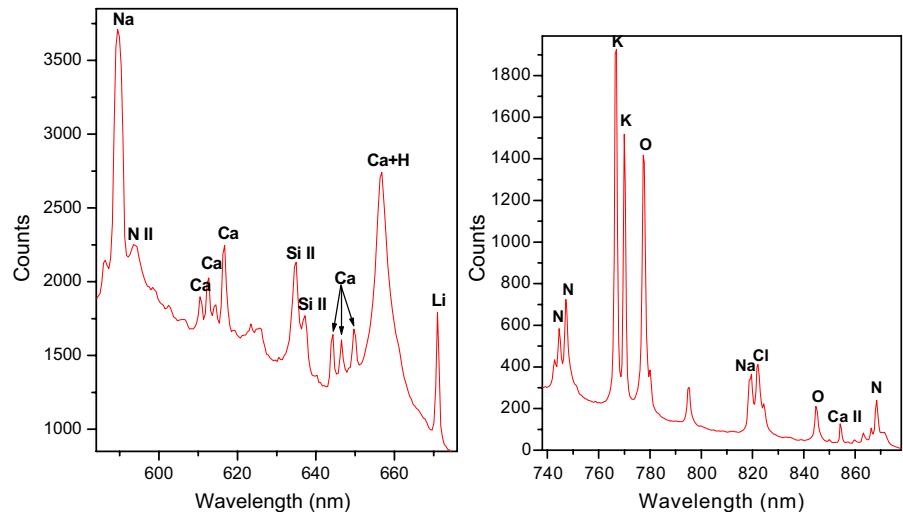


Fig. 6 a Zoomed LIBS spectra of brick-kiln area soil in 585–675 nm region using low resolution grating
b Zoomed LIBS spectra of brick-kiln area soil in 700–880 nm region using low resolution grating

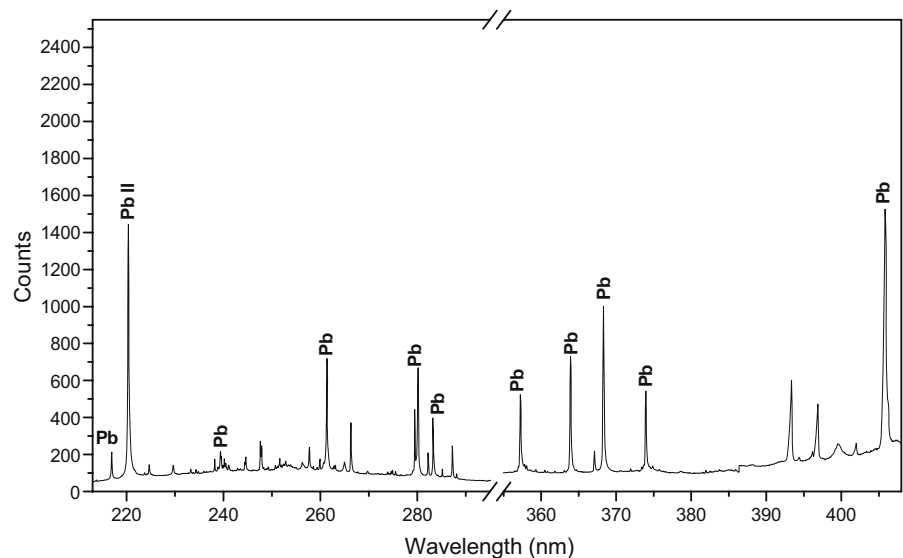


persistent line of Pb) lie in the wavelength range below 500 nm or beyond 560 nm, i.e. excluding the region of strong reflected signal.

The presence of Al, Ba, Mg, Si, Ti, C, Mn, N, O, Fe, Ca, Na, K, Li, etc. are confirmed by the numerous spectral lines of those elements present in LIBS spectra of soil sample as shown in Figs. 4–6. The presence of huge number of spectral lines makes the task of identification of atomic lines, which are the fingerprint of particular heavy metal (say Pb), difficult. To overcome this, we have recorded the LIBS

spectra of pure $\text{Pb}(\text{NO}_3)_2$ pellet and a portion of it is shown in Fig. 7, where Pb lines at 205.3, 205.9, 208.8, 211.5, 213.8, 217, 220.3, 239.3, 261.4, 280.2, 283.3, 357.2, 363.9, 368.3, 373.9, 405.7 nm are clearly seen. To identify these Pb lines in LIBS spectra of soil sample, we have superimposed the LIBS spectra of pure $\text{Pb}(\text{NO}_3)_2$ with that of soil as shown in Fig. 8a,b. This clearly shows the presence of Pb line at 220.3 and 405.7 nm in brick-kiln soil sample. Both are the most intense lines of Pb neutral atom and Pb singly ionized atoms respectively, which clearly demonstrates the

Fig. 7 LIBS spectra of pure $\text{Pb}(\text{NO}_3)_2$ sample



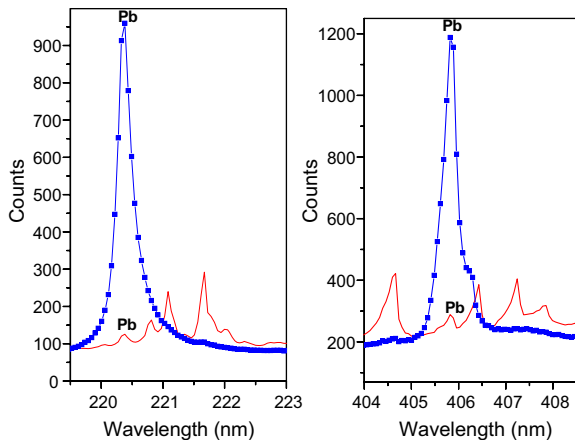


Fig. 8 **a** Pb I spectral line (220.3 nm) in the LIBS spectra of brick-kiln area soil (represented by *solid line*) overlapped with Pb spectral line in the LIBS spectra of pure $Pb(NO_3)_2$ pellet having 99% Pb (represented by *dotted line*). **b** Pb spectral line (405.7 nm) in the LIBS spectra of brick-kiln area soil (represented by *solid line*) overlapped with Pb spectral line in the LIBS spectra of pure $Pb(NO_3)_2$ pellet having 99% Pb (represented by *dotted line*)

presence of Pb in appreciable amount in agricultural soil near brick-kiln area.

Calibration curve

Our next step of interest is to determine the concentration of Pb in soil. For quantitative analysis, a calibration curve (a graph between concentration of analyte element (Pb) in reference soil and intensity of spectral line of that element in LIBS spectra of soil) is required. In order to draw the calibration curve, the LIBS spectra of different reference soil samples (whose preparation is already described under experimental section) are recorded as shown in Figs. 9 and 10. Intensity of any atomic line is obtained by measuring the peak area of that spectral line present in the LIBS spectra of soil samples.

For good calibration curve, the line of the analyte element (Pb) should be free from interference of other lines of elements present i.e. be well isolated. As soil contains large number of elements, its LIBS spectra has dense atomic lines (Figs. 9 and 10) and most of the atomic lines of Pb are affected by the adjacent

Fig. 9 LIBS spectra of different Pb concentration contaminated soil

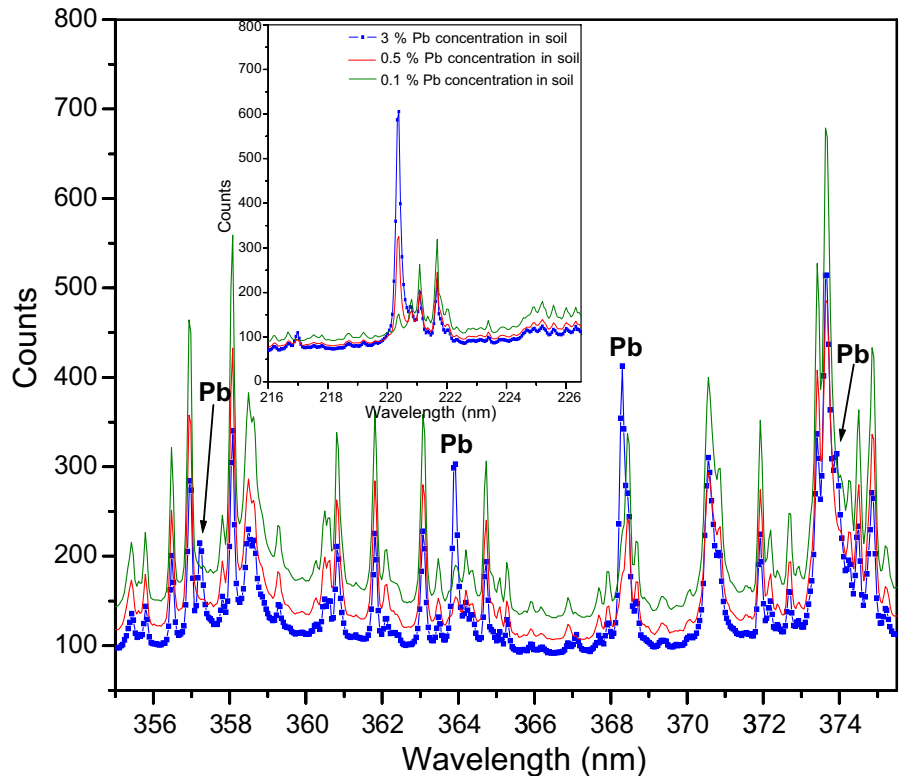
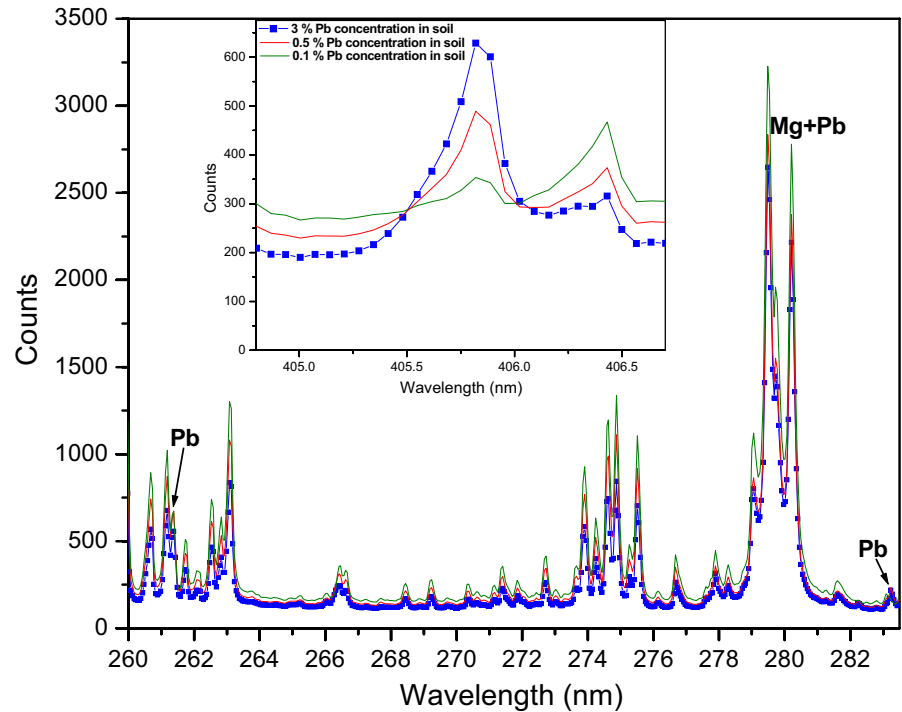


Fig. 10 LIBS spectra of contaminated soil having different Pb concentrations



atomic emission lines of other elements present in the soil (261.4 nm is affected by the adjacent Fe I line at 261.2, 280.2 nm Pb line is overlapped with the Mg most intense line at 280.19, 283.3 and 357.2 nm Pb line have very low intensity, 368.3 nm spectral line have appreciable intensity, but its spectral shape is affected because of the presence of Fe I (368.4 nm) in the vicinity, the intensity of the 373.9 nm is influenced by Ca I atomic line). Therefore, we have chosen three distinct interference free emission lines (405.7, 363.9 and 220.3 nm) of Pb to get the calibration curve.

First of all the calibration curve is drawn by taking the absolute intensity of these Pb lines then a linear curve is fitted to the data points and the linear regression coefficient (R) is obtained. The R of the calibration curve for 363.9 nm Pb line (Fig. 11) is found to be 0.91. Similarly, the calibration curve is obtained for 220.3 nm (Fig. 11), which is the intense line of Pb I and linear regression coefficient is found to be 0.94. The calibration curve is also drawn for 405.7 nm, which is the intense line of Pb neutral atom (Fig. 11), but instead of linear curve, a second order polynomial is fitted to the data points. This shows that

the Pb 405.7 nm line suffer from self-absorption effect (the line is broadened at higher concentration as shown in the inset of Fig. 10). Hence the intensity of Pb line is not increased linearly as the concentration of Pb atom increases.

It is the well known fact that the intensity of any atomic line is directly proportional/related to the laser power, small fluctuation in laser power while recording the LIBS spectra of all reference soil samples may reflect change in the absolute intensity of the analyte line. Therefore, in this situation, a calibration approach is used, to reduce the effects of such power fluctuations in order to improve the LIBS accuracy by obtaining the calibration data using the intensity ratio of an analyte line with that of adjacent reference line versus the analyte concentration. The most important criterion for selecting the reference line for the intensity ratio calibration curve is that the upper energy level of the interference free reference line should be very close to that of analyte line. Figure 12 represent the calibration curves for Pb 363.9/Ti 334.9 nm; Pb 220.3/Fe 249.3 nm and Pb 405.7/Ca 442.6 nm. It is clear from the Fig. 12 that R is 0.99 for 220.3 nm and 0.95 for

Fig. 11 Calibration curves for different wavelengths of Pb in soil

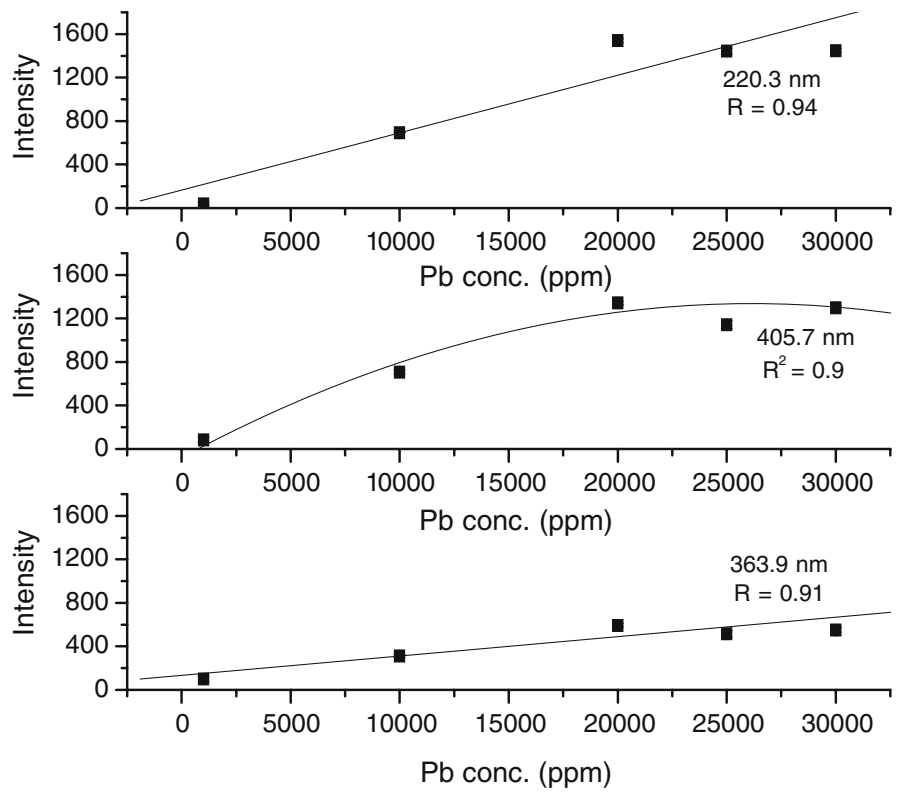
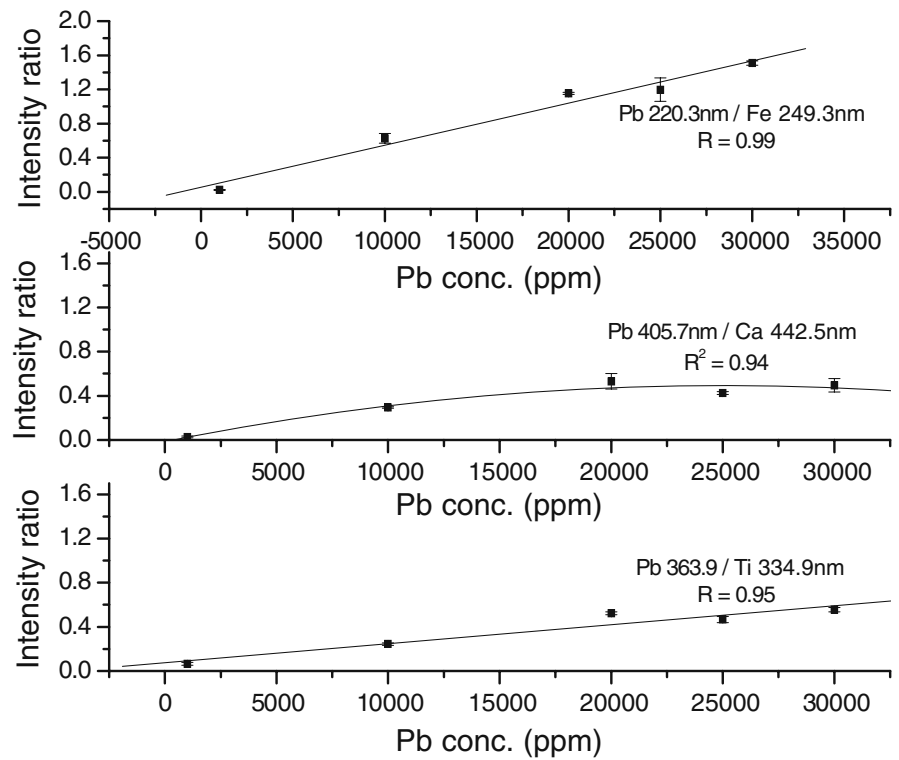


Fig. 12 Calibration curves for different wavelengths of Pb using intensity ratio with adjacent wavelength



363.9 nm, therefore, 220.3 nm is preferred in comparison to 363.9 nm line for drawing the calibration curve.

In our analysis, we have chosen 220.3 nm line instead of 405.7 nm, because at high concentrations of Pb, the line at 405.7 nm wavelength is showing nonlinear behavior (as shown in Figs. 11 and 12). Therefore, present study clearly reveal that the 220.3 nm line of Pb is suitable to get the calibration curve when plasma is produced by using 532 nm wavelength of Nd:YAG laser.

Limit of detection (LOD) calculation and quantitative analysis

The LOD is defined as the concentration that produces net line intensity equivalent to three times the standard deviation of the background and it is evaluated with the expression:

$$\text{LOD} = 3 \sigma_B / m,$$

where σ_B is the average of the standard deviations of the background measurements (adjacent to the analyte line) for the reference samples and m is the slope of calibration curve (Sabsabi et al. 1995). It is clear from the expression that if the slope of the calibration curve is large and the standard deviation of background is small than the detection limit is low.

It is clear from the Fig. 12 that the slope of the calibration curve for 220.3 nm line is large in comparison to 363.9 nm spectral line. In addition to this, 220.3 nm line is completely free from interference effects and also the standard deviation to the background signal, adjacent to this line, is small in comparison to other lines. The detection limit computed by using calibration curve for 220.3 nm spectral line is 45 ppm Pb in soil.

We have used this line for the quantitative analysis of Pb in brick-kiln area agricultural soil, near Allahabad. The LIBS spectrum of the soil of that area is recorded and is shown in Figs. 4–6. The intensity of Pb lines at 220.3 nm, present in the LIBS spectra of brick-kiln area soil, is measured and by using the calibration curve for 220.3 nm, the concentration of Pb in the above area sampled soil is found to be ≈ 570 ppm ($\pm 9.78\%$). This value is much more than the regulatory standards imposed by United States Environmental

Protection Agency (US EPA) for the presence of lead in soil (400 ppm), therefore, it might be harmful to us.

Conclusion

On the basis of the results and discussions presented above, it is concluded that to determine the concentration of Pb in soil, calibration curve by using Pb line at 220.3 nm is more suitable in comparison to other Pb lines as it lies in interference free UV region as well as it has best linear regression coefficient. Based on this calibration curve, Pb concentration in agricultural soil adjacent to brick-kiln area near Allahabad, India is calculated for the first time and found to be much more than the defined non-toxic standard concentration of Pb in soil by US EPA. This increased amount of Pb in soil display the alarm of danger therefore controlling activities should apply as soon as possible.

Acknowledgement The financial assistance from the Defence Research and Development Organisation project (No. ERIP/ER/04303481/M/01/787) is duly acknowledged.

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