LEAD ASSESSMENT BY LASER ABLATION METHOD OF SOIL SAMPLE ON BOTH SIDES OF HIGHWAY IN JOHOR, MALAYSIA

M. ARAB, N. BIDIN[*], Z. HAIDER, SALEHA SAFIE
Advanced Photonic Science Institute, Universiti Teknologi Malaysia, Johor, Malaysia

Laser induced breakdown spectroscopy (LIBS) technique was employed to determine the heavy metal (lead) in soil samples. The Q-switch Nd:YAG laser pulse operating at 90 mJ and fundamental wavelength of 1064 nm was utilized as energy source. Soil from nearby southern highway of Malaysia was collected at several distances. The soils were prepared in the form pelletized prior to use as target sample. The laser was focused on pelletized soil to induce optical breakdown associated with plasma formation. The spectroscopy properties of the sample were studied via Maya spectrometer system. The LIBS signal was optimized based on the laser energy, integration time, distance and angle of optical fiber from the fluorescence emission of plasma. Two atomic lines of Pb (at 363.95 and 373.99 nm) are selected to estimate the lead concentration as well as limit of detection (LOD). Pb concentrations are found to be 358 ppm and 336 ppm at a distance of 100 m, and reduces to 75 ppm and 88 ppm at a distance of 500 m for respective lines. These lead concentrations are still in allowable limits according to a standard set by USEPA and European (32–400 ppm). Furthermore the LOD of this technique at Pb line 363.95 nm is about 44 ppm.

(Received December 23, 2013; Accepted February 18, 2014)

Keywords: Heavy metal, Pb, LIBS, limit of detection

1.Introduction

Lead (Pb) is a physiological and neurological toxin that can affect almost every organ and system in the human body [1]. It is a chemical element in the carbon group with symbol Pb and atomic number 82. The lead element exist in two types in nature is a soft and malleable metal, which is regarded as a heavy metal and poor metal. Lead occurs naturally on Earth exclusively in the form of four isotopes: lead-204, -206, -207, and -208[2]. The health effects of lead are a highly poisonous metal. The exposure to lead and lead chemicals can occur through inhalation, ingestion and dermal contact. The main target for lead toxicity is the nervous system, both in adults and children.

The main exposure to Pb of the general non-smoking adult population is from food and water, whilst for infants and children, food, air, water and dust or soil are the main potential sources of exposure[3] . Foods may contain Pb from the environment or from food processing and storage. Human Pb intake in developed countries has declined significantly during the last two decades due to the ban use of Pb from the smoke induced by the combustion of the gasoline [4]. There are some speculations those high soil-lead concentrations typically available in older, inner-city neighborhoods to high-traffic routes.

The soil-lead concentrations diminished within a distance from the city center. Another study claimed that soil-lead concentrations are 10 to 100 times higher in old communities in large cities than in comparable neighborhoods in smaller cities, perhaps because traffic volume is high and vehicles remain inside the city longer[5]. All studies assumed that the lead from the atmosphere

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[*] Corresponding author: noriah@utm.my

or soil can end up to the plants, groundwater and surface water and transferring to the human body through eating the vegetables or drinking water[6].

Conventional off-line chemical analyses, such as inductively coupled plasma (ICP), X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS), have been used to determine Pb concentration in soils[7][8]. However, these conventional methods require a series of sample preparation steps, making their use expensive and time-consuming.

As a means to measure Pb contents, a laser-induced breakdown spectroscopy (LIBS) can be used[9], as it can provide a less-destructive, cost effective and faster screening of contamination levels in vast and numerous polluted sites[10]. However, an accurate quantification of metals in soils by the LIBS was hindered due to the complex matrix in soils. It requires many standard reference samples having a similar compositional matrix to target sample to establish calibration lines for quantification of metals[11].

Laser-induced breakdown spectroscopy (LIBS) is an emission spectroscopy technique that used high-energy laser pulse to simultaneously ablate and excite the sample. It is important analysis to assessing the contamination elements in environment (liquid, soil, etc.)[12][13]. Recently laser induced breakdown spectroscopy (LIBS) has become to play an important role in environmental analysis[14][15].

LIBS is depend on the principle work of the spectral emission analysis of photons emerging from the spark caused by incident a laser beam on the surface of the target. The information from these emission photons can be give us guide to the elements existing inside the sample according to emission intensity for each element. The special thing in this technique is not need to sample preparation and can use in any area in the situ field[16][17]. While another chemical analysis need to more time for preparing the sample and can be used only in laboratory field. So Laser induced plasma for any phase of material (liquid or solid) are also of more benefit, especially for the part of laser diagnostic, thin film growth, and pollution elements test[18][19].

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[20]. 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[21].

The aim of present work is to measure the concentrations of Pb element in soil samples taken from area closed to southern highway of Malaysia by using laser applications technique. The most of the available analysis methods are generally expensive or time-consuming due to sample preparation, require special reagents/chemicals and are not cost effective[22], therefore LIBS technique is conducted to analyze and characterize the Pb concentration in soil.

2. Experimental

2.1 Sample collection and preparation

A 50 soil samples were collected by using Saga GIS software from five different sites located near the highway in Johor city, Pulai Jaya (+1° 34' 0.77", +103° 35' 40.99") for different distances (0-500 m) at fix depth 10 cm under the surface as shown in figure 1. Samples were prepared for LIBS analysis in the form of pressed pellets. Initially the soil samples were finely ground into powder before filtering with a 100 μm sieve. Pellets were prepared in a pelletizing press by transferring 10.0 g of powdered material to Herzog pelletizing press and applying 40 kN in 5 minute. Pellets were approximately 5 mm thickness and 40 mm in diameter.
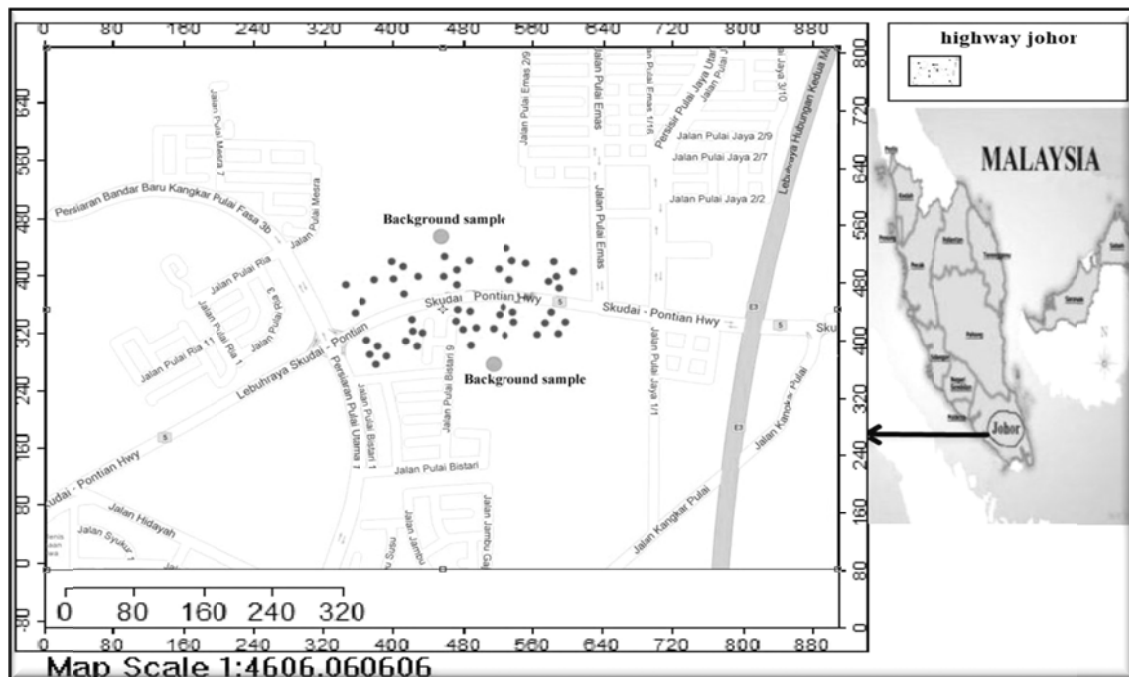
Fig. 1. Map of soil samples collected from different sites located along the highway in Pulai Jaya, Johor city-Malaysia for different distances and the background sample selected at 500 m using Saga GIS software.

First five shots of laser pulse is focused on the soil samples for cleaning purpose before the measurements were taken. All Measurements were performed at five various positions (sampling spots) for same pellet face in order to minimize problems linked to sample microheterogeneity and the average of these measurements was used as dataset. The number of accumulated laser pulses of each sampling spot was optimized. Spectral lines were identified using the NIST Atomic Spectra Database [23].

2.2 LIBS setup

A Q-switched Nd:YAG laser (AL-14 FP6000, China) was used in this experiment with fundamental wavelength λ=1064 nm, duration time 10 ns and operating at repetition rate of 1 Hz with pulse energy of 90 mJ. The distance from the lens to sample was fixed at 10 cm with beam diameter of 2 mm. In this arrangement the energy density was optimized at 2.3 Jcm^{-2}. The two-axes translation stage was using to put the sample on it in plane perpendicular with the laser orientation. The arrangement of LIBS experiment was shown in the figure 2.
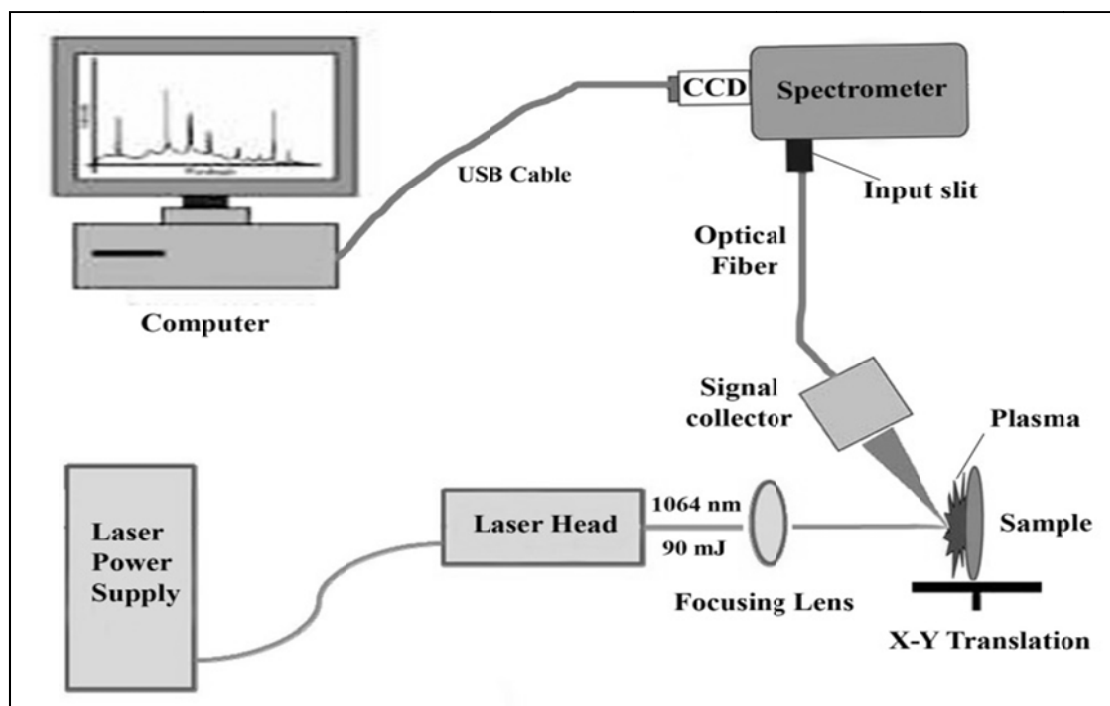
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Fig.2. Experimental setup for recording the LIBS spectra of soil sample

A Maya2000PRO spectrometer (Ocean Optics, USA) provided with Hamamatsu S10420 CCD detector at spectrum range of 165-1100 nm and entrance aperture of slit-5 (5 μm wide x 1 mm high) was used in this experiment. The optical resolution FWHM for this spectrometer is about 0.2 nm. The fiber optic connector is SMA 905 with numerical aperture of 0.22. Optical fiber with core 600 μm is used to collect the plasma emission and send it to the spectrometer. The spectrometer collection angle estimate with the axis of laser beam was 45°. The features of using spectrometer equipped with inner CCD detector for LIBS analysis can be found from previous researchers [24].

3. Results and discussions

3.1 LIBS spectrum and calibration curve

Optimizing LIBS for lead soil pellet was done by optimizing all the experimental conditions in the same spectral range of 200-700 nm. The pulsed laser beam was focus on the soil sample to produce plasma on its surface. LIBS spectra of seven different reference samples with known concentrations of Pb were record. Each spectrum on the average of 10 laser shots, the first five shots for cleaning the surface of the pellet from the impurities and the second part of five shots were average to represent the data for the spectrum. Figure 3 illustrates the detail of LIBS spectrum. The lead peaks and other peaks for elements existing in soil sample appeared in the spectra. Some of emission spectral lines of Pb are appeared in the spectrum including 257.72, 261.36, 283.3, 363.95, 368.34, 373.99, 405.78 and 500.65 nm.
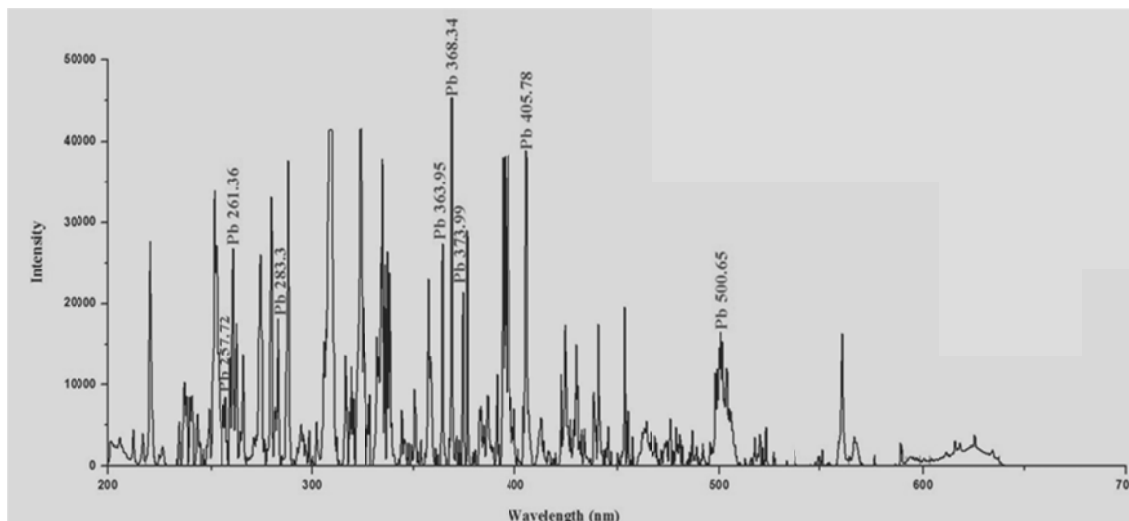
Fig. 3. LIBS spectrum of (soil + Pb) pellet with repetition rate 1 Hz and the energy remained constant as 90 mJ per pulse.

The calibration curve for **Pb** has achieved after following the adopted procedure. Seven samples of known concentration comprised of 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 in weight percent (wt. %) of lead were mixed in the soil matrix. The spectra of LIBS experiment for these seven concentrations of the elements have recorded. All these spectra were record with take the mean of 10 times shots by laser pulses, at five various positions on the surface of sample. The calibration curve of the lead metal was determined by drawing the intensity of LIBS signal of Pb at two wavelengths 363.95 nm and 373.99 nm with the concentration wt. %. The calibration curves for the Pb element at those two wavelengths are presented in Figure 4. For pulse energy 90 mJ the signal intensity for different concentration of Pb 363.95 nm in soil sample was linearly with correlation coefficient ($R^2 = 0.993$) better than the line of Pb at 373.99 nm with ($R^2 = 0.965$).
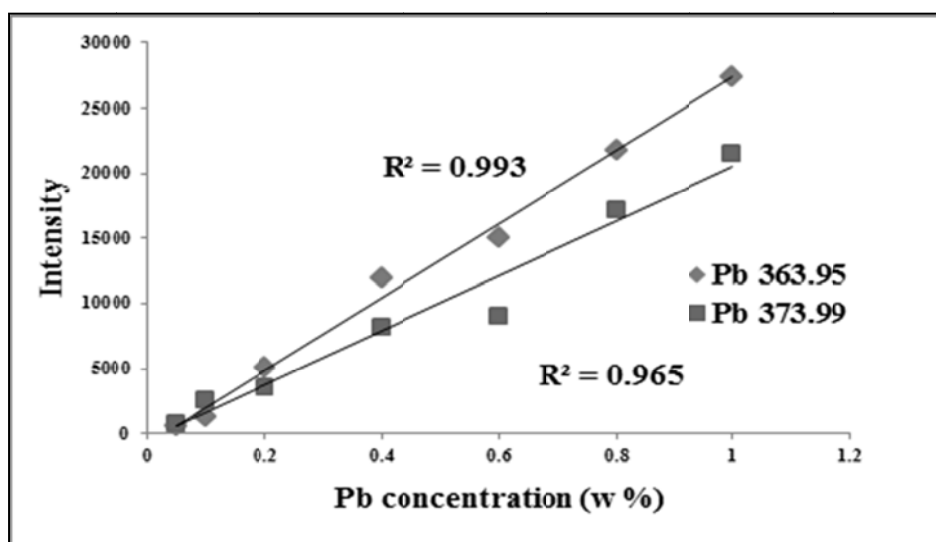

Fig. 4. Calibration curves of the Pb at 363.95 nm and 373.99 nm emission lines for various known concentrations in soil sample.

3.2 Limit of detection and Pb concentration

For quantitative analysis, the detection limit measurement is important for Pb in soil sample in this experiment. The mean of detection limit here the minimum concentration that can be detected by LIBS technique. The limit of detection (LOD) can be calculated by using the following formula[25].

$$\text{LOD} = \frac{3\sigma_b}{S} \tag{1}$$

where, σ_b is the background standard deviation, and S is the slope of the calibration curve. The limit of detection for LIBS analysis of lead soil pellet was calculated by using the previous formula and are listed in Table 1. The LOD of the Pb at wavelength 363.95 nm in soil matrix is 44 ppm better than Pb at 373.99 nm with LOD about 79 ppm. Limit of detection also related to the slope of calibration curve. A large slope means the high sensitivity of the technique and the lower limit of detection can be achieved.

Table 1. Limit of detection for lead element lines in the soil sample.

Element	Wavelength (nm)	R^2	σ_b (a.u.)	LOD (ppm)
Pb I	363.95	0.993	5241	44
Pb I	373.99	0.965	5584	79

By using the calibration curves of the Pb at 363.95 nm and 373.99 nm, Pb concentrations in the soil samples collected from each sampling site were determined. The Pb concentrations of 363.95 nm and 373.99 nm are found to be the high at the site in distance 0-100 m about 358 ppm and 336 ppm respectively. As the distance is far away from the highway the lower the Pb concentration as indicated at the distance about 500 m whereby the value are 75 ppm and 88 ppm at respective tested lines. As shown in figure 5, it was observed that the Pb concentration decreased with increasing distance from the source regions of contamination because those sites are near to highway where the main source of lead is due to cars exhaust. It was also noted that Pb concentrations in all soil samples in the allowable limits established by USEPA and European standard (32–400) ppm for soils[26]. This means the site closer to the road is still safe to live on humanity because the Pb concentration is within the permitted limits, but may be this concentration will be increased in the next feature years due to the increasing number of vehicles and the heavy traffics on the road.
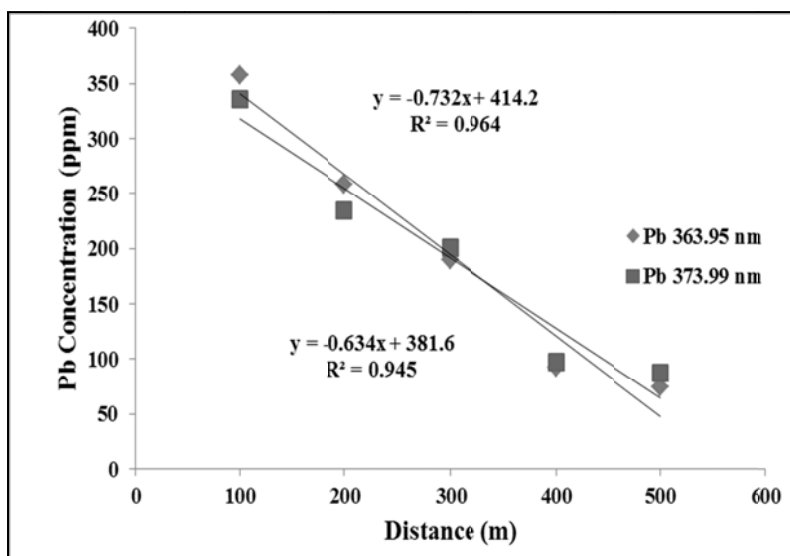
Fig 5. Relation between the distance of the soil sample from the highway road and Pb concentrations.

Table 2 explain the comparison of results from some different studies from different cities worldwide is complicated due to the variation in sampling methods, the different sample preparation methodologies and sample analysis methods. The mean Pb concentrations obtained in this study were found to be higher than the mean concentration from another cities. The general comparison of results from Johor site across all the cities suggests that the sources of Pb in the urban street dust could be traced to common urban sources.

Table 2. The concentrations of Pb in street dust from different cities in the world[27].

City, Country (year of study)	Number of samples	Site description	Pb concentration (ppm)
Singapore (2009)	—	Three locations (residential, commercial and industrial)	68.6 ± 25.9
Ulsan, Korea (2009)	12	Three locations (traffic rotary stations, circulation road, highway and downtown)	92.1 ± 12.3
Dhahran, Saudi Arabia (2010)	5	Mean values from a residential camp	40.3 ± 34.9
Dhanbad and Bokaro, India (2011)	13	Four zones (rural, urban, mining and industrial)	48 ± 29 (17–128)
Mutah, Jordan (2010)	24	One zone (major roads)	143 ± 109 (26–368)
Nanjing, China (2011)	35	Eight urban districts with different land	103 ± 48 (37.3–204)
Coventry, UK (2003)	49	Three locations (industrial, residential and parks),	47.1 ± 8.4 (0.0–199)
Massachusetts, USA (2011)	85	Three locations (Fenway, Somerville and Greenfield)	73 ± 181 (0–1,639)
Our work Johor, Malaysia (2013)	50	Five different sites located on both side of the highway	196 ± 133 (75-358)

4. Conclusion

The southern highway area currently still safe for living because the Pb level in that area is still under the permitted concentration as suggested by the standard body such as USEPA and European (within 32 -400 ppm). However due to heavy traffic and frequent used of vehicle at the highway in Johor, the level of concentration might be increased, because currently the highest level of Pb is already achieved up to 358 ppm. The optimum Pb line at 363.95 nm is found better than line at 373.99 nm and the best limit of detection obtained from this LIBS technique could be achieved down to 44 ppm.

Acknowledgements

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