Laser Ablation Technique for Estimation Lead Level in Soil Samples near Power Station

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***Abstract*—** This paper reports the analysis of heavy metal from contamination soil using laser ablation technique. The soil samples were taken at various distances (200-1000 m) and depths (10-50 cm) from Tanjung Bin Power Station area in Johor-Malaysia. All samples were dried and pelletized prior to excitation. Calibration was carried out by injected pure powder of Pb into the soil matrix. A Q-switched Nd:YAG laser was employed to ablate the sample. Maya spectrometer with resolution of 0.2 nm was utilized to record the emission spectrum of fluorescence beam. The quantitative results of laser induced breakdown spectroscopy (LIBS) technique were validate via flame atomic absorption spectroscopy (FAAS) analysis which shown in a good agreement. The detected heavy metal element of lead also identified to be lower than the threshold limit set by DOE and Europe standard and yet the studied area is established to be among the lowest pollutant area in worldwide.

***Keywords*—** Power station, Lead, Soil, LIBS.

I. Introduction

The main of the environmental problems in industrialized countries is the environmental impact, especially with heavy metals. Increased the concentration of heavy metals constitute a serious health threat of people and animals. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystems through direct ingestion or contact with contaminated soil, the food chain, drinking of contaminated ground water, reduction in food quality via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems [1].The elevation of the content of these elements in the soil can be treated as one of the indicators of human influence on the environment. In large urban areas, the most important origins of emission of heavy metals are industrial plants, power stations and motor transport [2].

In order for assessing the impact of toxic metal pollution on different environments by using various pollution calculation methods, several works have been done [3]. But those researchers were using analytical techniques like atomic absorption spectroscopy (AAS), inductively couple plasma (ICP) and Energy-dispersive X-ray spectroscopy (EDX) for determination concentrations of heavy metals in the soil, most of the available methods are generally time-consuming due to sample preparation, require special chemicals and are not cost effective [4]. Other alternative techniques are desired, amongst them is laser ablation technique.

Laser ablation technique involves the formation of optical breakdown. The emission spectrum induced from the laser interaction were recorded using spectrometer. This system commonly known as laser induced breakdown spectroscopy, in short LIBS. It is a relatively new atomic emission technique that has found great utility in the elemental analyses of a variety of materials. It is an emerging technique for elemental determination in a wide range of environmental samples, metallurgical, metallic and non –metallic solid, sewage sludge, liquid, aerosol, gases and biological samples etc. [5].

In the present paper, contamination soil from Tanjung Bin Power Station area was investigated using laser ablation technique. Initially calibration of Pb was established. The quantitative estimation of tested soil was validated with conventional method using FAAS. Furthermore, the safety level of tested soil was compared with professional agency and the degree of safety level.

II. Experimental

2.1 Sample Collection and Preparation

In this work the soil sample were taken from Tanjung Bin Power Station at Pontian Johor-Malaysia (1°20′3″N 103°32′55″E). 25 soil were taken from 5 different distances within the range of 200-1000 m from the tower of power station. On each site the depth is varied from 10-50 cm from the surface as shown in figure 1. Pellets were prepared by transferring 10 g each of powdered material to Herzog pelletizing press with applying pressure of 40 kPa in 5 minutes. The dimension of each final pellet is 5 mm thickness and 40 mm in diameter.

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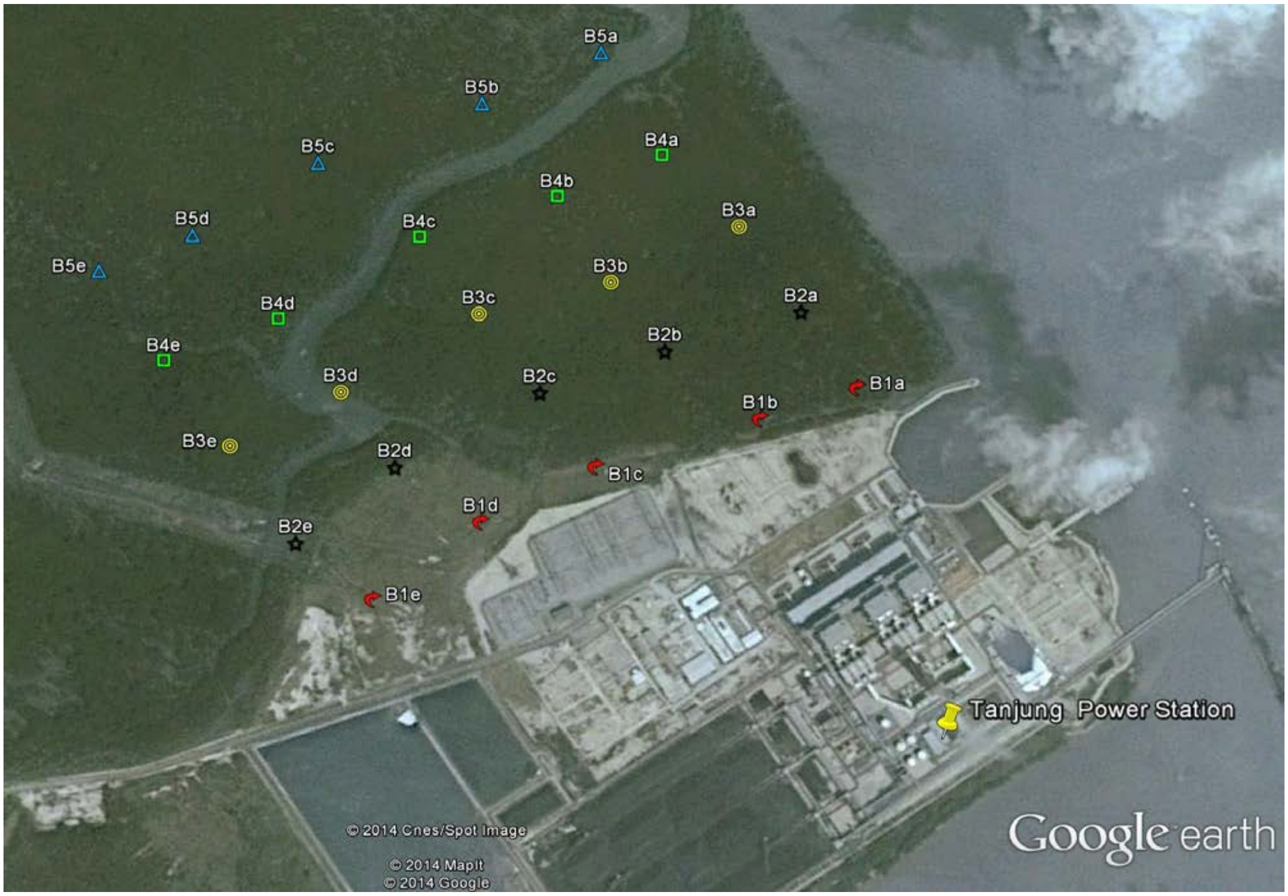

Fig. 1 Map of Malaysia a location of soil sampled sites at Tanjung Bin power station.

2.2 LIBS Setup

In this work a Q-switched Nd:YAG laser at wavelength 1064 nm and pulse duration of 10 ns was employed. The laser is operated in repetitive mode with a rate of 1 Hz.The output energy remained constant at 90 mJ per pulse. The laser pulse was focused using a lens with focal length of 10 cm.The pellet was placed in a xy-axes translation stage in a plane orthogonal to the laser propagation direction. A model Maya2000PRO spectrometer manufactured by Ocean Optics, USA, which equipped with Hamamatsu S10420 CCD detector having enternace aperture of slit-5 (5 µm wide x 1 mm high) coupled to a 600 µm core fiber optics was deployed to collect the plasma emission. The spectrometer collection angle with respect to the laser optical axis was set at 450. 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. The schematic diagram of experimental set-up, is shown in figure 2.

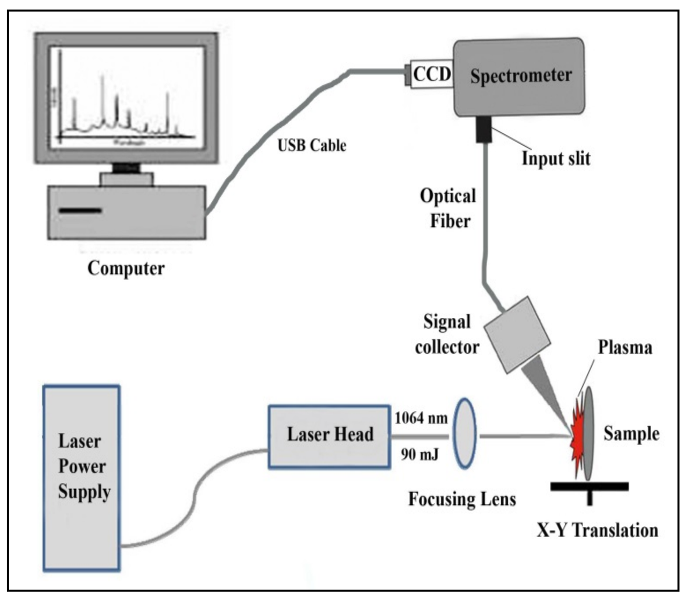

Fig. 2 Schematic diagram of LIBS experimental set-up.

III. Results And Discussion

A. LIBS Analysis and LOD

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 standard samples of known concentration of Pb were record. Each spectrum on the average of 10 single 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 illustrate the detail of LIBS spectrum. The lead peaks and other peaks for elements existing in soil sample appeared in the spectra. Several emission lines of Pb are observed in the spectrum including 257.72, 261.36, 283.3, 363.95, 368.34, 373.99, 405.78 and 500.65 nm.

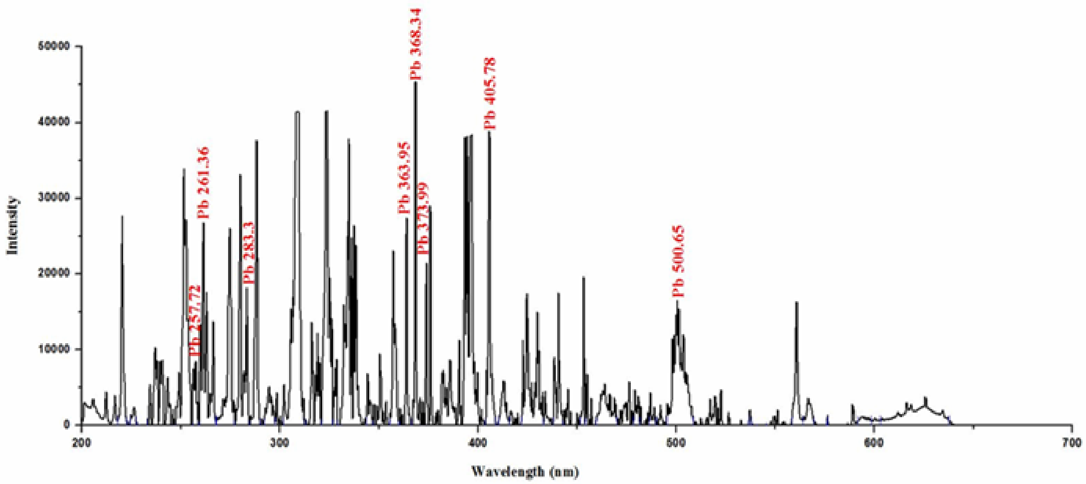

Fig. 3 LIBS spectrum for sample collected at a depth 20 cm from the soil surface

The calibration curve for Pb is achieved after following the adopted procedure. Seven amounts of known concentration are chosen to provide the calibration curve. The concentration of the element deposited in the soil matrix is comprised of Pb in the range of 50-600 ppm. The LIBS spectra for each range of concentration of the Pb are recorded. The calibration curve was established as shown in figure 4.

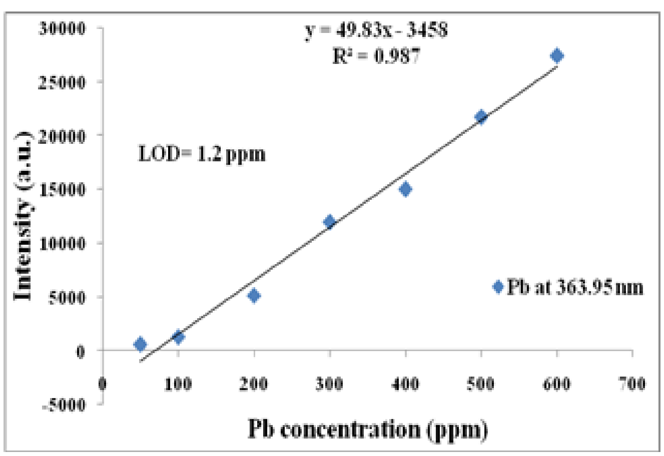

Fig. 4 Calibration curve of Pb in soil sample at wavelength 363.95 nm.

The limit of detection (LOD) is defined based on the 3σ IUPAC as a lowest concentration that can be detected in LIBS technique [6]:

$$LOD=3\sigma/m \quad (1)$$

where, σ is the standard deviation of the background, and m is the slope of the calibration curve. The limit of detection of each element in soil matrix calculated by using Eq. (1). In general the calibration curve is linear. The limit of detection of Pb metal in LIBS method is 1.2 ppm.

B. Heavy Metal Concentrations in Soils

Heavy metal (Pb) concentrations in the soil samples collected from each sampling site of the power station were determined. Figure 5 shows the distribution of element with respect to the distance and the depth from the soil surface. The concentrations of heavy metal are observed decreasing with distance from the source of contamination. Maximum concentrations found to be at sites B1 and B2 which about 200 and 400 m away from the tower station at corresponding depth of 20 cm from the surface.

This power station using coal firing method to generate the electricity. In this case, all the atoms of heavy metals are exposed on the soil surface nearby the towers area and coal storage tanks. It is better to note that minimum concentration of heavy metals have been found at sites B4 and B5 which about 800 m and 1000 m away from the station at corresponding depth of 40 and 50 cm from the soil surface respectively. This figure describes the decreasing trend of concentration of metal levels with respect to distances and depths of the nearby area.

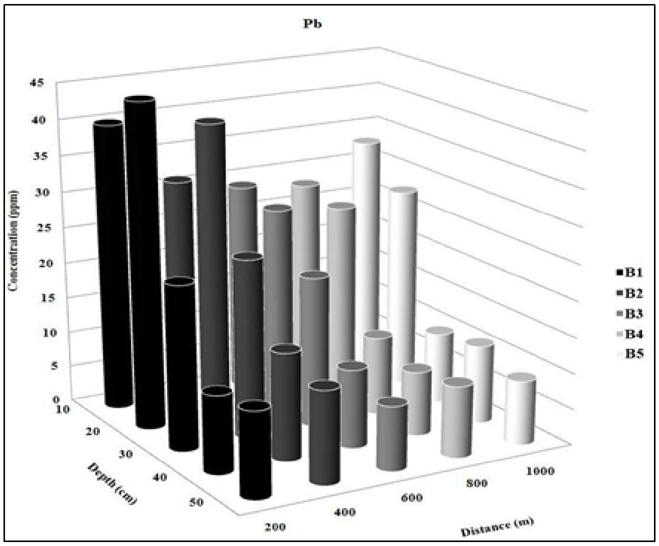

Fig. 5 The concentration of Pb against distance and depth of soil samples from Tanjung Bin power station.

TABLE 1.
COMPARISON THE CONCENTRATION VALUES OF LIBS WITH FAAS TECHNIQUE.

Sample	Concentration of Pb (ppm)	
	LIBS	**FAAS**
B1	56.2	55.29
B2	45.0	44.20
B3	39.6	35.28
B4	27.0	24.47
B5	19.2	16.10

In order to confirm the validity of LIBS measurement the results of analytical of soil sample are compared with conventional technique by using a flame atomic absorption spectroscopy (FAAS).The comparison results are summarized in Table 1. In general the results from LIBS technique shown in good agreement with the FAAS. However, some differences still arise attribute to the instrumental noise of the LIBS itself and the variation of intensity induced by difference in soil properties at different sampling sites. On the other hand, the quantitative analytical ability of LIBS for heavy metal in soil is promising technique to be performed in situ, and in easy way comparable to that of FAAS.

In general Pb concentrations of all soil samples of Iskandar power station are in the allowable limits as published by Department of Environment, DOE of Malaysia. According USEPA and European standard [7], the permissible limit of Pb is about 400 ppm and the maximum concentration in B1 is 56.2 ppm.

IV. CONCLUSIONS

The analytical ability of laser induced breakdown spectroscopy was validated by the FAAS measurement. In this study, the contamination soil sample from power station sites is confirmed to be safe because the concentration of heavy metal are mostly under the permissible limit set by DOE and Europe standard. In comparison to amongst other cities in the world obviously shown that Tanjung Bin power station area far safer than the rest of cities in the world. Laser ablation technique has a promising technique to be portable and compact system to be able to performe in situ and simple way in determining the safety level of environmental.

ACKNOWLEDGEMENT

The authors like to express their thanks to government of Malaysia through MOHE, UTM, GUP grant vote no.(00G79) for the financial support in this project. Thanks also due to UTM through RMC for financial management and monitoring the progress of the project.

REFERENCES

[1] M. J., McLaughlin. R. E., Hamon. R. G., McLaren. T. W., Speir. and S. L., Rogers. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Soil Research, 2000.38(6), 1037-1086.

[2] B., Jankiewicz. and D, Adamczyk. Assessing Heavy Metal Content in Soils Surrounding the Łódź EC4 Power Plant, Poland. Polish J. of Environ. Stud, 2007.16(6), 933-938.

[3] T., Nasrabadi. G. N., Bidhendi. A., Karbassi. and N., Mehrdadi. 2010. Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. Environmental monitoring and assessment, 171(1-4), 395-410. http://dx.doi.org/10.1007/s10661-009-1286-x

[4] R. S., Harmon. F. C., De Lucia. A. W., Miziolek. K. L., McNesby. R. A., Walters. and P. D., French. Laser-induced breakdown spectroscopy (LIBS)–an emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis. Geochemistry: Exploration, Environment, Analysis, 2005.5(1), 21-28.

[5] S., Gupta. P., Pandotra. A. P., Gupta. J. K., Dhar. G., Sharma. G., Ram. and Y. S., Bedi. Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of< i> Zingiber officinale</i> collected from different locations of North Western Himalayas by Atomic Absorption Spectroscopy. Food and Chemical Toxicology, 2010.48(10), 2966-2971.

[6] J. D., Ingle. and S. R., Crouch.. Spectrochemical analysis. New Jersey. 1988.

[7] Guideline. Malaysian Recommended Site Screening Levels for Contaminated Land. Department Of Environment DOE Malaysia. 2009. No.1, 1-59.

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