Salloom et al. *Iraqi Journal of Science, 2022, Vol. 63, No. 6, pp: 2523-2531*
DOI: 10.24996/ijs.2022.63.6.19

ISSN: 0067-2904

Laser-Induced Breakdown Spectroscopy for Determination of Toxic Metals in Fertilizers: emphasis on Lead

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Received: 26/5/2021 Accepted: 6/8/2021 Published: 30/6/2022

Abstract

The present work aims to evaluate the content of some toxic metals in chemical and organic fertilizers purchased from local markets in Baghdad, Iraq. The analysis was performed by laser-induced breakdown spectroscopy (LIBS) system. The emission spectral lines of lead (Pb), chromium (Cr), cadmium (Cd) and cobalt (Co) have been recorded to determine the best peak representing each element according to the NIST database. The validity of the LIBS procedure was checked by cross-validating the obtained results using atomic absorption spectroscopy (AAS) with a maximum relative error of 5.3%. Moreover, for qualitative analysis, Pb I 296.64 nm emission line was determined to be superior for the evaluation of lead content in terms of three calibration methods: the external standard (ES), the internal standard (IS), and the multiple linear regression (MLR). The linear correlation coefficient values were : 0.94, 0.97 and 0.992, respectively. LIBS results based on the multiple linear regression (MLR) model have demonstrated better performance and were adopted in the assessment of the Pb content in solid fertilizer samples.

Keywords: LIBS, Quantitative analysis, Fertilizers, Lead, Multiple linear regression

التحليل الطيفي للانهيار المحتث بالليزر لتحديد المعادن السامة في الأسمدة: التركيز على الرصاص

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الخلاصة

يهدف العمل الحالي إلى تقييم محتوى بعض المعادن السامة في الأسمدة الكيماوية والعضوية المشتراة من الأسواق المحلية في بغداد – العراق. من خلال التحليل الطيفي للانهيار الناجم عن الليزر (LIBS). سُجلت خطوط طيف الانبعاث للرصاص (Pb) والكروم (Cr) والكادميوم (Cd) والكوبالت (Co) لتحديد أفضل قمة طيفية ممثلة لكل عنصر وفقًا لقاعدة بيانات العالمية NIST. تم التحقق من صحة إجراء LIBS من خلال النتائج التي تم الحصول عليها باستخدام التحليل الطيفي للامتصاص الذري (AAS) مع أقصى خطأ نسبي بنسبة 5.3 ٪. علاوة على ذلك ، من أجل التحليل النوعي لعنصر الرصاص ، تم تحديد خط انبعاث Pb I 296.64 نانومتر ليكون متفوقًا في تقييم محتوى الرصاص من خلال طرق المعايرة الثلاث: المعيار الخارجي (ES) ، والمعيار الداخلي (IS) ، والانحدار الخطي المتعدد (MLR). وكانت قيم معامل الارتباط الخطي هي:

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0.94 و 0.97 و 0.992 على التوالي. أظهرت نتائج LIBS المستندة إلى نموذج MLR أداءً أفضل وتم
اعتمادها في تقييم محتوى الرصاص في عينات الأسمدة الصلبة.

1. Introduction

With the continuous increase in the use of fertilizers in agriculture, which in turn achieves a high growth rate for agricultural products, these fertilizers are a significant source of soil and water pollution [1-3]. Fertilizers are generally divided into two groups: organic and inorganic; both are used to supply essential elements for the plant (such as nitrogen, phosphate, and potash) [4]. It is required for all types of crops to achieve good yield levels. These elements are necessary not only to enhance the fertility of the soil but also to improve food quality[5]. There are many problems related to the overuse of fertilizer, particularly when the manufacturer does not disclose precise information about the concentrations and/or presence of harmful ingredients. Studies on the impact of fertilizer on soil and water are being performed worldwide due to the lack of accountability on behalf of certain producers[6]. Even though not all fertilizer metals are inherently harmful, some are harmful if they are present in high concentrations, such as Mn, Zn, Fe and Mg; there are also certain metals that can be dangerous even in small amounts, such as Ni, Pb, Co, Cd, and Hg [2].

It is of great importance to determine the composition of the fertilizer; many techniques are carried out for this purpose, such as flame atomic absorption spectrometry (AAS) [7] and inductively coupled plasma (ICP)[8]. Typically, with these methods, the processes need the dissolving of solid samples into solutions and then diluting. Thus, it is difficult to obtain direct and real-time measurements due to the time-consuming and complex sample preparation steps. Recently, laser-induced breakdown spectroscopy (LIBS) has become a common tool for direct solid sample analysis in various fields [9, 10]. Potential applications of LIBS for the fertilizer analysis have motivated many efforts to enhance new quantitative and qualitative analytical methods capable of obtaining fast measurements with no need for sample preparation [11, 12]. In this sense, Andrade et al. [13] determined the major (Ca and Mg) elements, the minor (B, Cu, Mn, Na, and Zn) elements as well as the trace elements(Cd, Cr and Pb) in solid fertilizer samples using LIBS method and the reference values obtained with ICP.Farooq et al.[14] applied LIBS technique for the elemental analysis of fertilizer samples; they detected a very high quantity of hazardous health elements like Cd, Ni, and Pb. Several works have used mathematical processing of LIBS spectral data to improve its sensitivity. The external standard (ES) and internal standard (IS) calibration methods are widely used for quantitative analysis by LIBS[15]. However, these models need further investigation to achieve the best results for analyzing fertilizer complex matrix. On the other hand, the Multiple Linear Regression (MLR) method could be a possible solution to compensate for the matrix effect of complex solid fertilizer [16, 17].

This study aims to apply LIBS analytical method for multi-element analysis of solid fertilizers. Moreover, the research is focused on accurate evaluation of the percentage of some toxic elements in the chemical and organic fertilizers available in the local markets, with particular emphasis on lead. The contents of elements of interest in fertilizers were also determined by the atomic absorption spectroscopy(AAS).

2. Experimental Part

2.1 Sample Collection

Eight compound fertilizers (three organic and five chemical), normally used in Baghdad city in Iraq, were collected from local specialized markets. Each sample was coded for performing the laboratory analysis, as shown in Table 1. Atomic absorption spectrometry(AAS)was employed to determine the quantity of toxic metals in all the fertilizers samples. One gram of dried sample was taken for analysis in each experiment.

Table 1- Types and codes of fertilizer samples analyzed in this work

Fertilizer	Type	Code
Smart Fert	Organic	F_1
Beat Moos	Organic	F_2
G. GANA	Organic	F_3
NPK	Chemical	F_4
DAP	Chemical	F_5
TSP	Chemical	F_6
Urea	Chemical	F_7
Rock Phosphate	Chemical	F_8

Calibration curves were established using lab-made standard reference samples containing various weights per cent of lead (Pb). Accordingly, an accurate amount of pure lead dinitrate, Pb(NO3)2, was weighed and thoroughly mixed with the ground fertilizer. Nine standard reference samples comprised different Pb concentrations ranging from 200 to 12000 mg/kg. Finally, these samples were pressed, with a hydraulic press, with a 7 tons pressure for 2 min, into tablets of 12.0 mm diameter and 3.0 mm thickness. Ten LIBS spectra of these samples of fertilizers gathered from three different locations were recorded. The calibration curves were determined by drawing LIBS signal against Pb content.

2.2 Sample preparation for AAS analysis

For the AAS analysis, fertilizer samples were grinded in a blender and homogenized. 1.0 g of each sample was digested using the Aqua regia method, by mixing three volumes of 37% concentrated HCL acid with one volume of 69% concentrated HNO_3 acid and then placed in a shaker for 24 hours. Filtration process was done using Whitman type filter No.1 and centrifuged at 2000 revolutions per minute (RPM) for 5 minutes. The clear solution was moved into a 50 ml volumetric glass flask and then diluted with deionized water to 50 ml volume. The samples were analysed using the atomic absorption spectrometer (Model: Shimadzu).

2.3 LIBS System

Figure 1 represents a schematic diagram of a typical LIBS system. Most LIBS systems contain two main components: the laser excitation source and the optical collection system. In this work, laser pulses were generated by a Q-switched Nd:YAG laser of (250 mJ energy, 1.064 nm wavelength, and 9 ns pulse duration). The collection system that collects and transports the light emitted by the plasma to the detection system is equipped with an optical fiber of 600 mm diameter, 1 meter long, and a spectrometer (Model:Ocean Optics : USB4000) combined with charge coupled device (CCD) camera.

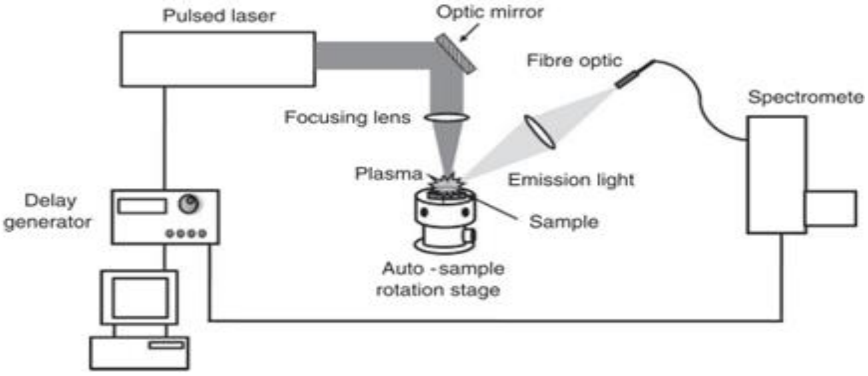

Figure 1- LIBS experimental setup

3. Results and discussion

3.1 The measured concentrations of four toxic metals: lead, chromium, cadmium and cobalt, in the fertilizer samples using the AAS varied greatly according to the analyzed element, as shown in Table 2. The toxic metal contents varied as (Pb: 12.6–47.1; Cr: 22.3–66.2; Cd: 30.2–82.3; Co: 4.9–44.3 mg•kg−1). Significant lead levels were found in all fertilizers compared with other elements. The highest lead concentration of 47.1 mg/kg was detected in sample F2. , whereas the lowest concentration of 12.6 mg/kg was found in sample F8. On the other side, cobalt concentration was the lowest for all studied samples. From these results, it can be noted that the concentrations of the fertilizer samples in the current study were within the permissible values indicating there is no pollution problem at present. However, increased use of chemical fertilizers, in particular, the types that contain high concentrations of heavy metal elements may result in an increase in environmental pollution as a result of their accumulation in the soil over time. (AAS) Analysis Results

Table 2- Toxic metals concentrations in different fertilizer.

Sample Code	**Concentration of metals (mg/kg)**			
	Pb	**Cr**	**Cd**	**Co**
F_1	19.2	22.3	30.2	6.6
F_2	47.1	29.4	82.3	10.3
F_3	39.6	51.2	76.5	9.2
F_4	13.2	66.2	26.4	44.3
F_5	16.3	34.4	38.4	17.7
F_6	23.1	62.2	47.2	11.8
F_7	25.8	46.4	54.1	4.9
F_8	12.6	30.2	33.2	7.0
Max.	**47.1**	**66.2**	**82.3**	**44.3**
Min.	**12.6**	**22.3**	**26.4**	**4.9**

3.2 LIBS Spectral characteristic and qualitative analysis

The surface of the samples were ablated by the focused Nd: YAG laser beam. The plasma emissions were collected to be analysed with the spectrometer. Figure 2 shows the LIBS spectrum of the F1 sample recorded at a spectral window of (250-850) nm. The integration and delay times of the spectrometer were fixed at 20 ms and 8μs, respectively. The recorded spectrum reflects an average of 10 laser shots. All spectra were assigned and analyzed with the information provided by the National Institute of Standards and Technology database (NIST) [18]. It can be observed that there are strong and clear signals for the abundant elements such as phosphor (P), potassium (K) and calcium (Ca), while the emission lines intensities corresponding to magnesium (Mg), manganese (Mn), copper (Cu), iron (Fe) and titanium (Ti) were relatively low. Furthermore, the characteristic lines of lead (Pb), chromium (Cr), cadmium (Cd), and cobalt (Co) were also determined, as listed in Table 3. The attributed spectral lines of Pb element identified by LIBS were (PbI 280.45 and PbI 296.64) nm, the signal to noise ratio of the spectral line PbI 296.64 nm was stronger than that of PbI 280.45, and can be detected with minimum interference of other spectral lines.

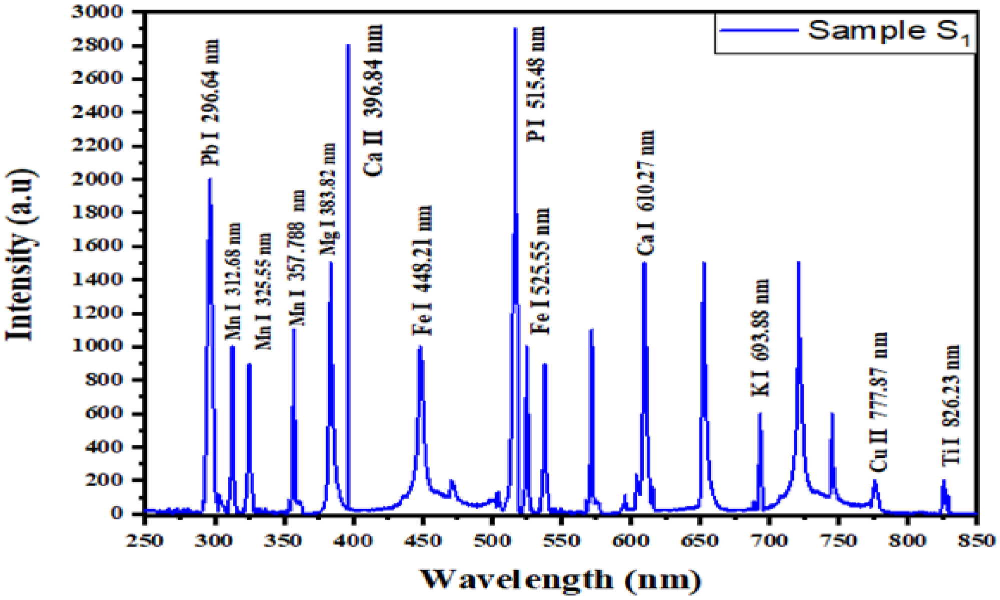

Figure 2- LIBS spectrum of F1fertilizer sample at 250–850 nm wavelength.

Table 3- Spectroscopic data of assigned elements in the fertilizes

Element (λ/nm)	**$(E_i - E_k)$ eV**	**Terms**
Pb I (296.94 nm)	0.8589- 5.0330	$3d^7(^4F)4s$ -$3d^6(^5D)4s4p(^1P°)$
Cr I (470.80 nm)	3.1676- 5.8003	$3d^4(^5D)4s4p(^3P°)$ - $3d^44s5s$
Cd II (537.80 nm)	11.139- 13.443	$4d^{10}5f$ - $4d^{10}4f$
Co II (502.98nm)	11.365 - 13.829	$3d^7(^4F)4d$ - $3d^7(^4F_{5/2})4f$

3.3 External and Internal Standard Calibration

In order to evaluate the unknown concentrations of the considered elements, the simple relation between the observed intensity of PbI 296.64 nm in LIBS and the actual Pb content in lab-made standard samples was regulated and plotted, as shown in Figure 3. It can be observed that there is a well-defined linear correlation between LIBS intensity and the actual content of Pb in the standard samples with a regression coefficient R^2 of 0.942.

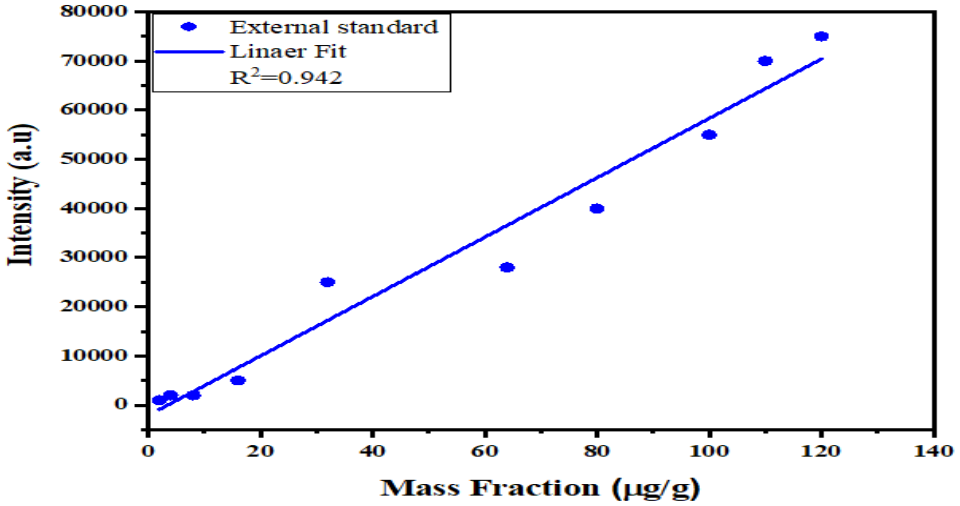

Figure 3-Calibration curve for Pb in fertilizers by external standard having correlation coefficients R^2 of 0.942.

It is noted that only the objective variable was considered by simple linear interpolation ignoring variations in the LIBS signal due to the sample composition. However, ignoring the rest matrix ingredients can fluctuate the calibration curves and result in the loss of effective information [19]. To cancel out these fluctuations of the observed line intensities and get better calibration curve, the MgI 383.82 nm emission lines were selected as the internal standard of the Pb element. The ratio intensity (I_{pb}/I_{Mg}) was measured and plotted as a function of the known concentration ratios of the reference samples, as shown in Figure 4. The fitted line was with a regression coefficient of R^2 of 0.974; the R^2 value has improved.

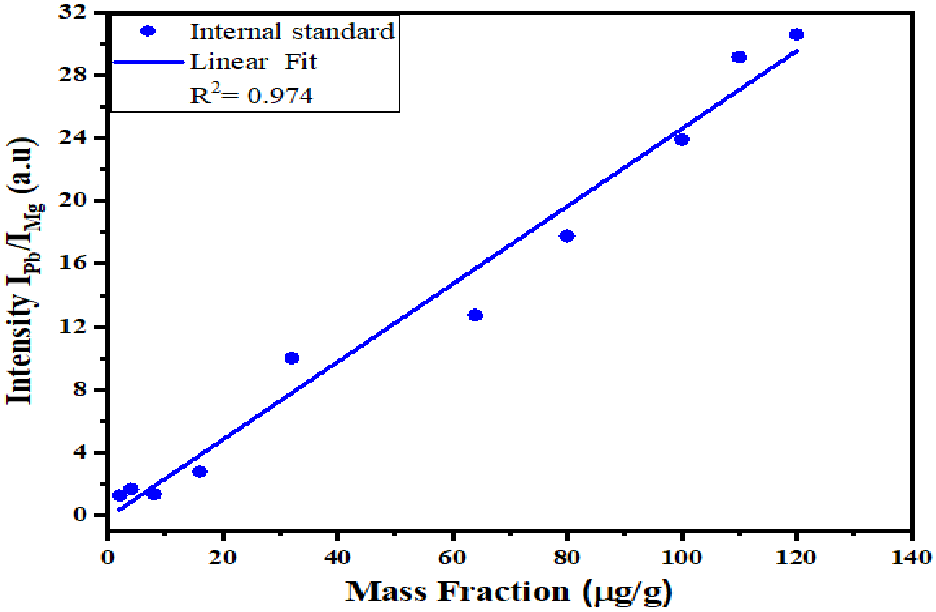

Figure 4-Calibration curve using MgI as an internal standard, with correlation coefficient R^2 of 0.974.

3.4 Multiple linear regression calibration

A technique used to enhance the efficiency of quantitative analysis is the multiple linear regression(MLR) model [20], in which the concentration (C_i) has a relationship with the intensity of the element of interest and/or the other corresponding elements. For LIBS, the considered signal may be affected not only by the mass fraction of the element of interest, but other elements could also play an important role. The mathematical equation used to obtain concentration by the multiple linear regression model is [21, 22]:

$$C_{MLR} = a_0 + a_1 \times I_1 + a_2 \times I_2 + ... + a_m \times I_m + e \quad (1)$$

C_{MLR} is the predicted concentration obtained by the multiple linear regression, a_0, $a_2 \ldots a_m$ are constants, I_1, I_2,..., I_m are multiple characteristics of a certain element of line intensity of the peak, and e is the error.

The Mn characteristic lines were chosen as an internal standard, as it was already presented in the spectral region from 310 to 360 nm. The mass fraction of Mn is relatively stable in various fertilizers. Because of this, the determination of Pb concentration was performed by taking into account the effect of Mn in the matrix. Thus, the sum of intensities of the Mn lines (MnI at 312.68 nm, Mn I at 325.55 nm, and MnI at 357.78 nm) and the PbI line at 296.64 nm was used as independent variables for the determination of Pb content. Then Equation (1) can be rewritten as:

$$C_{Pb} = a_0 + a_1 \times I_{Pb} + a_2 \times I_{\sum Mn} \quad (2)$$

Multiple linear regression was performed utilizing built-in function in the Origin software, the results are shown in Table 4. The coefficients are a_0 to a_2 as in Equaion (2), the t- start is t-test value while the P-value represents the significance level of regression variables.

Table 4- Summary of the results of multiple linear regression model..

Variable	Coefficient	t start	P value
Intercept (Pb)	36.18	2.2	0.063
I_{Pb}	0.0013	8.14	8.1E-5
$I_{\sum mg}$	-0.01	-1.89	0.1

These results indicate that all variables have an important impact on the determination of Pb, and the developed regression model is practical. On the basis of the above results, the regression equation used to predict the mass fractions of Pb may be expressed as:

$$C_{Pb} = 36.18 + 0.0013 \times I_{Pb} - 0.01 \times I_{\sum Mn} \quad (3)$$

From the results drawn, as shown in Figure 5, there is a direct relationship between the predicted and the actual mass fractions of Pb with a correlation coefficients of 0.992.

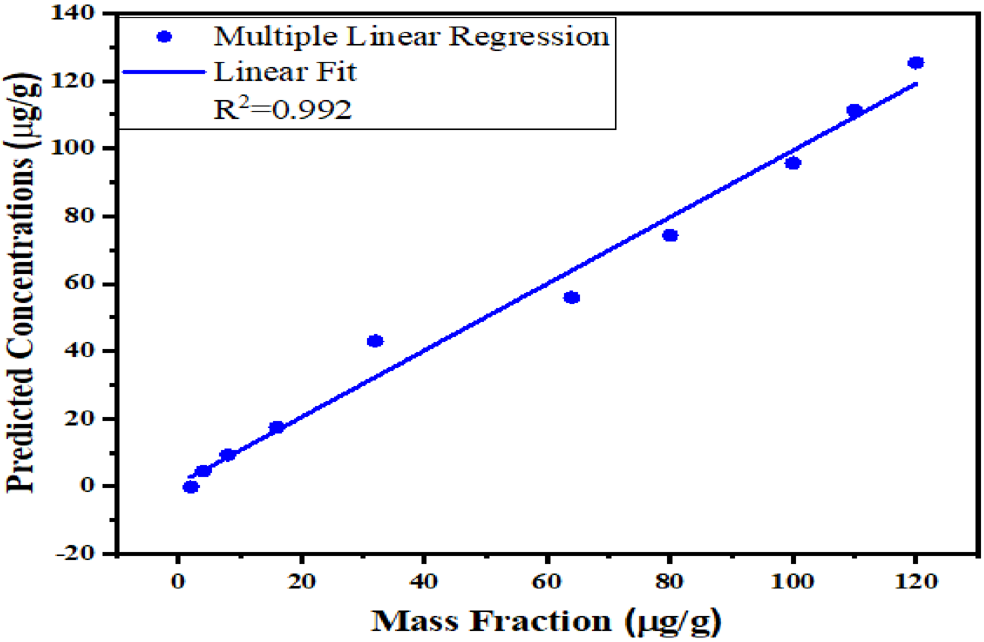

Figure 5-Multiple linear regression and the actual values for Pb, with a correlation coefficients R^2 of 0.992

Adopting the calibration line of the multiple linear regression (MLR) model, Pb concentrations in the fertilizer samples were calculated, as given in Table 5. The lead content was the highest in the F_2 fertilizer(Beat Moos organic fertilizer), while the lowest was observed in the F_8 fertilizer (Rock Phosphate fertilizer). The results for the Pb contents measured by LIBS were close to those measured by the AAS. The relative errors ranged from 2.16% to 5.3 %, indicating a good correlation between the two methods. The encouraging results demonstrate the capability of quantitative analysis using LIBS based on the MLR calibration method for the different fertilizers.

Table 5- Pb concentrations in fertilizers as determined by both LIBS and AAS techniques.

Sample Code	Pb Concentration AAS (μg g^{-1})	Pb Concentration LIBS (μg g^{-1})	Relative Error (%)
F_1	19.2	18.4	4.16
F_2	47.1	45.8	2.76
F_3	39.6	40.5	2.27
F_4	13.2	12.5	5.30
F_5	16.3	17.2	5.52
F_6	23.1	22.6	2.16
F_7	25.8	27.1	5.03
F_8	12.6	13.2	4.47

4. Conclusion

An accurate LIBS approach was used for the quantitative analysis of lead in organic and chemical fertilizers. The 296.62 nm wavelength PbI was selected as the analytical line. This work revealed and demonstrated the efficiency of the quantitative analysis of Pb in the fertilizer with the external standard, the internal standard and the multiple linear regression methods. Calibration models were developed using ten lab-made reference samples. The estimated Pb concentrations in the eight understudy fertilizers were calculated by LIBS using the MLR method with a correlation coefficient of 0.992. Pb concentrations, as evaluated by LIBS, were in an acceptable agreement with those obtained by AAS and the maximum error was less than 6%. It is concluded that the LIBS, in conjunction with the MLR method, is a favorable procedure for the straight analysis of the Pb content in fertilizers.

References

[1] L. R. Alves, A. R. Reis, and P. L. Gratão, "Heavy metals in agricultural soils : from plants to our daily life (a review)," *Científica,* vol. 44, no. 3, pp. 346–361, 2016.

[2] P. K. Rai, S. S. Lee, M. Zhang, Y. F. Tsang, and K. H. Kim, "Heavy metals in food crops: Health risks, fate, mechanisms, and management," *Environ. Int.*, vol. 125, pp. 365–385, 2019.

[3] K. Shirisha, K. L. Sahrawat, B. P. Devi, and S. P. Wani, "A Simple and Accurate Method for Routine Analysis," *Commun. Soil Sci. Plant Anal.*, vol. 45, no. 16, pp. 2201–2206, 2014.

[4] V. Azzi, V. Kazpard, B. Lartiges, A. Kobeissi, A. Kanso, and A. G. El Samrani, "Trace Metals in Phosphate Fertilizers Used in Eastern Mediterranean Countries," *Clean - Soil, Air, Water*, vol. 45, no. 1, pp. 1–30, 2017.

[5] M. Cheraghi, B. Lorestani, and H. Merrikhpour, "Investigation of the effects of phosphate fertilizer application on the heavy metal content in agricultural soils with different cultivation patterns," *Biol. Trace Elem. Res.*, vol. 145, no. 1, pp. 87–92, 2011.

[6] Q. Gong, P. Chen, R. Shi, Y. Gao, Sh. Zheng, Y. Xu, Ch. Shao, X. Zheng, "Health assessment of trace metal concentrations in organic fertilizer in Northern China," *Int. J. Environ. Res. Public Health*, vol. 16, no. 6, p. 1031, 2019.

[7] B. Hu, X. Jia, J. Hu, D. Xu, F. Xia, and Y. Li, "Assessment of heavy metal pollution and health risks in the soil-plant-human system in the Yangtze river delta, China," *Int. J. Environ. Res. Public Health*, vol. 14, no. 9, p. 1042, 2017.

[8] M. Ahmadi, S. Jorfi, and A. Azarmansuri, "Zoning of heavy metal concentrations including Cd , Pb and As in agricultural soils of Aghili plain , Khuzestan province , Iran," *Data Br.*, vol. 14, pp. 20–27, 2017.

[9] A. A.-K. Hussain and F. J. Moaen, “Diagnostics of Magnesium-Aluminum alloy plasmas produced by laser induced breakdown spectroscopy,” *Iraqi Journal of Science,* vol. 59, no. 1A, pp. 75-85, 2018.

[10] T. K. Hamad, A. S. Jasim, H. T. Salloom, A. J. Ghazai, “Multivariate Analysis of Toxic Heavy Metals Contents in Soil Detected by Laser Induced Breakdown Spectroscopy,” *Indian J. of Public Health Res. & Develop.* , vol. 9, no. 12, pp. 933-936, 2018.

[11] A. H. Khidhir and M. A. Hameed, “Using Laser - induced breakdown spectroscopy system to determine the fertility of middle Iraqi soil,” *Iraqi Journal of Science,* vol. 59, no. 4B, pp. 2012-2019, 2018.

[12] H. T. Salloom, T. K. Hamad, A. H. Mohammed, “Detection of Harmful Metal Elements in Rice Using Laser Induced Breakdown Spectroscopy,” *Journal of Physics: Conference Series.*, vol. 1818, no. 1, p. 012178, 2021. doi:10.1088/1742-6596/1818/1/012178

[13] D. F. Andrade and E. R. Pereira-Filho, “Direct Determination of Contaminants and Major and Minor Nutrients in Solid Fertilizers Using Laser-Induced Breakdown Spectroscopy (LIBS),” *J. Agric. Food Chem.*, vol. 64, no. 41, pp. 7890–7898, 2016.

[14] A. Farooq, N. Al-Mutairi, A. Khater, A. Al-Dwayyan, M. AlSalhi, and M. Atif, “Elemental analysis of fertilizer using laser induced breakdown spectroscopy,” *Opt. Spectrosc. (English Transl. Opt. i Spektrosk.*, vol. 112, no. 6, pp. 874–880, 2012.

[15] X. Fu, G. Li, and D. Dong, “Improving the Detection Sensitivity for Laser-Induced Breakdown Spectroscopy: A Review,” *Front. Phys.*, vol. 8, no. 3, pp. 1–11, 2020.

[16] J. Wang, M. Shi, P. Zheng, and S. Xue, “Quantitative Analysis of Lead in Tea Samples by Laser-Induced Breakdown Spectroscopy,” *J. Appl. Spectrosc.*, vol. 84, no. 1, pp. 188–193, 2017.

[17] B. Zhang, P. Ling, W. Sha, Y. Jiang, and Z. Cui, “Univariate and multivariate analysis of phosphorus element in fertilizers using laser-induced breakdown spectroscopy,” *Sensors (Basel),* vol. 19, no. 7, p. 1727, 2019.

[18] A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, “NIST Atomic Spectra Database Lines Form,” *NIST Atomic Spectra Database (ver. 5.2) [Online]*, 2014. [Online]. Available: http://physics.nist.gov/asd.

[19] B. Sezer, G. Bilge, and I. H. Boyaci, “Capabilities and limitations of LIBS in food analysis,” *TrAC - Trends Anal. Chem.*, vol. 97, pp. 345–353, 2017.

[20] V. L. Vesnin and V. G. Muradov, “Analysis of Aromatic Constituents in Multicomponent Hydrocarbon Mixtures by Infrared Spectroscopy Using Multiple Linear Regression,” *J. Appl. Spectrosc.*, vol. 79, no. 4, pp. 515–520, 2012.

[21] M. I. Yao, H. Yang, L. Huang, T. Chen, and G. Rao, and M. Liu, “Detection of heavy metal Cd in polluted fresh leafy vegetables by laser-induced breakdown spectroscopy,” vol. 56, no. 14, pp. 4070–4075, 2017.

[22] T. Chen, L. Huang, M. Yao, H. Hu, C. Wang, and M. Liu, “Quantitative analysis of chromium in potatoes by laser-induced breakdown spectroscopy coupled with linear multivariate calibration,” *Appl. Opt.*, vol. 54, no. 25, pp. 7807-7812, 2015.