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Evaluation of laser induced breakdown spectroscopy for multielemental determination in soils under sewage sludge application

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique for simple, direct and clean analysis, with great application potential in environmental sustainability studies. In a single LIBS spectrum it is possible to obtain qualitative information on the sample composition. However, quantitative analysis requires a reliable model for analytical calibration. Multilayer perceptron (MLP), an artificial neural network, is a multivariate technique that is capable of learning to recognize features from examples. Therefore MLP can be used as a calibration model for analytical determinations. Accordingly, the present study proposes to evaluate the traditional linear fit and MLP models for LIBS calibration, in order to attain a quantitative multielemental method for contaminant determination in soil under sewage sludge application. Two sets of samples, both composed of two kinds of soils were used for calibration and validation, respectively. The analyte concentrations in these samples, used as reference, were determined by a reference analytical method using inductively coupled plasma optical emission spectrometry (ICP OES). The LIBS–MLP was compared to a LIBS–linear fit method. The values determined by LIBS–MLP showed lower prediction errors, correlation above 98% with values determined by ICP OES, higher accuracy and precision, lower limits of detection and great application potential in the analysis of different kinds of soils.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) is an emerging analytical technique based on atomic and ionic emission of elemental sample constituents. Due to its instrumental features, LIBS is able to perform multielemental direct analysis, dispensing the pre-treatment of samples, in addition to showing the potential to perform *in situ* analysis [1]. During the LIBS analytical process the sample is irradiated by a high-energy laser pulse, which then absorbs this energy. This absorption causes a local heating of the material, resulting in its evaporation or sublimation. The high temperature of the ablated material generates a small plasma plume. As a result of the plasma temperature, the ablated material breaks down into excited atomic and ionic species [2]. During the plasma cooling, the excited species return to their ground state, emitting electromagnetic radiation in characteristic wavelengths. Therefore, the emission spectra analysis gives a qualitative view of the sample's elemental composition. Notwithstanding, it is not a simple task to perform LIBS quantitative analysis, because the elements emission lines in LIBS spectrum are closely related with the matrix in which they are embedded. The chemical matrix effects in LIBS spectra occur due to several reasons: all of the elements in the plasma may not be equally ionizable, creating variations in the equilibrium between neutral and ionized atoms; the mass of different ablated elements changes due to differences in the heat capacity and vaporization temperatures [3,4]. Some, other drawbacks of LIBS include its strict dependence on the fulfillment of equilibrium conditions in the plasma, the possible saturation of the signal for high concentration elements due to self-absorption effects, even for high-energy lines, hence making their quantification difficult or impossible with LIBS and the large number of complex physical–chemical phenomena involved in the processes of ablation and plasma formation, evolution and interaction with the background ambient [5]. Due to this feature of LIBS emission signal, it is very difficult to find appropriate calibration standards for LIBS methods. In some cases the appearance of the so-called matrix effects could be reduced by using multivariate calibration techniques [6,7]. However, some authors have found a way

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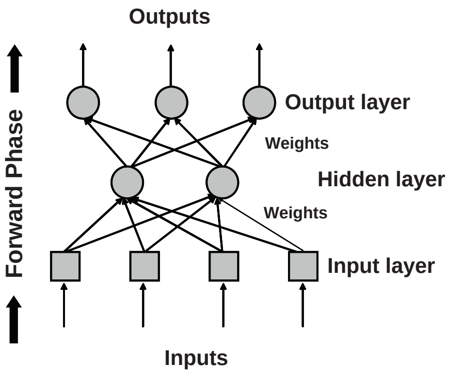

Fig. 1. A typical artificial neural network setup.

to adapt univariate calibration models, constructed with classical least-squares regression for specific LIBS application [8,9].

Artificial neural network (ANN) is a multivariate technique which due to its superior classification and prediction capabilities, has impacted spectral analysis and has gained ground in LIBS spectroscopy [10–12]. An ANN represents a computational paradigm that solves problems by imitating the structure of a human brain. It involves a network of simple processing elements (artificial neurons) that can exhibit a complex global behavior determined by the connections (analogous to synapses in the human brain) between the processing elements and element parameters. In other words, ANNs are nonlinear statistical models or decision making tools, whose practical use comes with algorithms designed to alter the strength (weights) of the connections in the network to produce a desired signal flow [13].

The multilayer perceptron (MLP) is a type of ANN based on supervised learning. An MLP maps the sets of input data onto a set of appropriate output. It is an extension of the standard linear perceptron in which three or more layers of nonlinear neurons are fully linked. This arrangement is more powerful than the linear perceptron as it can distinguish the data that are not linearly separable, or separable by a hyperplane [14].

Fig. 1 illustrates a useful scheme of a layer-structured MLP like that used in this work. Each layer has a set of neurons and each neuron has a mathematical function responsible for its activation. The first layer receives a set of values, i.e. an input vector containing the values measured for the variables. The dimensionality of the vector corresponds to the number of neurons in the input layer. The weights are a set of numerical values (weight vector) associated with each neuron to represent its synaptic connections. The knowledge is codified in weights by means of an algorithm. The inner product between input vector and weight vector is applied to the activation function to produce the neuron output. The outputs of a layer are used as inputs for the next layer. As a result, the output layer provides a value or a set of values, corresponding to the propagation of a set of values from the input layer to the output layer (forward phase).

A task is learned by an MLP from a training dataset, which is a set of input vectors with their respective desired outputs. The procedure applied to perform the training process is called learning algorithm and its function is to modify the weights of the network in order to attain a desired goal [15].

During the training process, all the weights are changed to minimize the error between the desired output and MLP output. The learning paradigm of MLPs entails developing mathematical models to extract important features from the training dataset. After the training process, a validating process should be conducted to estimate the MLP performance on the testing datasets.

Thus, the use of LIBS and MLP can result in a fast, direct and clean method for multielemental determinations with great application potential in environmental sustainability studies. Therefore, this study evaluates a LIBS–MLP method for determination of Ba, Co, Cu, Mn, Ni, V and Zn in two kinds of soils for sustainability studies, in which sewage sludge was applied to agricultural soil as fertilizer.

2. Experimental

2.1. Samples

A set of samples was constituted of 28 samples from two tropical soils, classified as Typic Eutrorthox and Typic Haplorthox, exhibiting different textures. The samples were collected from an experimental field which was previously submitted to the application of different amounts of sewage sludge.

After the sample collection was performed, the samples were dried at room temperature and passed through a 5 mm sieve.

2.2. Reference concentration determinations

To obtain the reference values for LIBS calibration and validation, the soil samples were submitted to elemental determination by inductively coupled plasma optical emission spectrometry (ICP OES). Before ICP OES measurements, a sample preparation step was carried out to obtain samples in liquid form. For this, a digestion step was performed by means of a modified procedure based on the use of high pressure microwave heating, previously proposed by Vieira et al. [16]. A mass of 0.1 g of soil samples was directly weighed in the modified polyethylene (TFM) microwave vials, then 2.0 mL of decomposition solution was added, prepared by mixing 3 parts of nitric acid (14 mol L^{-1}) with one part of hydrochloric acid (6 mol L^{-1}). These mixing solutions were kept in contact for 1 h, to enable a pre-decomposition. Afterwards, 1.0 mL of hydrogen peroxide (30%, w w^{-1}) was added, and after 30 min the samples were submitted to microwave irradiation, in a cavity-microwave oven, model Multiwave Sample Preparation System (Anton Paar, Austria).

At the end of the heating program and cooling of the vials, the samples were transferred to graduated polypropylene vials, and the volumes were adjusted to 10 mL with ultra pure water. The silicate compounds, which remained after the decomposition procedure, were separated from the solution by centrifugation. These compounds were dissolved at room temperature by adding 1.0 mL of concentrated hydrofluoric acid and 48 h of mixing. After dissolution of the silicates, 0.5 g of boric acid was added to the sample in order to complex the remaining fluorides to prevent reactions with the quartz ICP torch. The silicates from the resulting solution were merged with the supernatant collected earlier, with the volume made up to 15 mL with water. Each sample was prepared in duplicate.

The ICP OES elemental determinations were carried out in a radial view spectrometer model VISTA PRO-CCD from Varian (Australia).

2.3. LIBS determinations

The set of 28 samples was divided into calibration and validation sets. The calibration set comprised 19 samples, 11 samples from Haplorthox typic soil and eight from Eutrorthox soil. The validation set was composed of nine samples with five samples (referred as 1–5) from Haplorthox soil and four samples (referred as 6–9) from Eutrorthox soil.

The samples were submitted to 10 ton of pressure for 2 min to form pellets. Three pellets were prepared with the samples from the calibration set and two from the validation set. Twenty LIBS spectra were captured from different regions of each pellet, with

Table 1
Spectral variables used for ANN training and validation.

Analyte	Selected emission lines (nm)
Ba	(I) 307.16; (II) 413.06; (II) 455.40; (I) 553.55
Co	(II) 234.74; (I) 241.16; (I) 242.49; (I) 344.36; (I) 347.40; (I) 356.94
Cu	(I) 217.89; (II) 219.23; (I) 223.01; (I) 324.75; (I) 327.40
Mn	(II) 257.61; (II) 259.37; (I) 279.48; (II) 344.20; (I) 403.31
Ni	(II) 217.51; (II) 221.65; (I) 234.55; (I) 300.25; (I) 341.35; (I) 346.17; (I) 352.45; (I) 356.64; (I) 361.94
V	(II) 311.07; (II) 311.84; (I) 318.54; (II) 319.07; (I) 385.58; (I) 412.81; (I) 413.20; (I) 437.92; (I) 439.52; (I) 609.02
Zn	(II) 202.55; (I) 213.86; (II) 250.20; (I) 307.59; (I) 328.23; (I) 468.01; (I) 472.22; (II) 491.16; (I) 636.23

(I) and (II) atomic and ionic lines, respectively.

each spectrum corresponding to two accumulated laser pulses. A previous laser pulse was always used to clean the surface of the pellets, before capturing a spectrum. The average of the twenty spectra (40 pulses) in a pellet was considered a single measurement. Thus, the final average and deviation was calculated using the mean spectrum obtained in all three pellets of the same sample.

The LIBS spectra of the pellets were captured using a system model LIBS2500, from Ocean Optics (USA). This system comprises seven spectrometers, which allows a resolution of ~0.1 nm (FWHM) for the spectral analysis ranging from 188 to 980 nm, a Q-switched Nd:YAG laser at 1064 nm, manufactured by Quantel (Big Sky Laser Ultra50), an ablation chamber, a lens for laser focalization and an optical system to collect plasma emission and to conduct plasma emission to the spectrometers made up of a lens and an fiber optic bundle. All measurements used pulse energy of 50 mJ with 8 ns duration and the fixed system instrumental conditions of delay time (relative to a Q-switch delay) and 2.1 ms of integration time.

Before the calibration study, the spectra were corrected for the offset, discounting from all spectra the average of a pure noise region, at the beginning of the spectrum.

2.4. Linear fit: assessment strategy for calibration of LIBS

Emission lines free of spectral interferences were chosen to correlate their intensities with the reference concentration, in the linear fit calibration procedure. The lines chosen were: Ba (II) 455.40 nm, Co (I) 242.49 nm, Cu (I) 324.75 nm, Mn (I) 403.08 nm, Ni (I) 341.48 nm, V (I) 438.47 nm and Zn (I) 328.23 nm.

A single linear model obtained for each analyte was applied to predict the concentration in the samples of the validation set.

2.5. MLP: assessment strategy for calibration of LIBS

The average spectrum, obtained after the individual offset correction and the reference analyte concentrations, previously determined by ICP OES, were used as inputs for MLP.

A MLP was trained for each single analyte. Table 1 describes the set of emission lines selected for each MLP training and validation.

The Weka system (Waikato Environment for Knowledge Analysis) version 3.5.7 was used for the training and for the validation of the calibration methods [17]. The activation function used for the neurons was the hyperbolic tangent. The number of neurons in the hidden layer was in accordance with the number of input variables plus one divided by two, considering only the numbers referent to the entire term. Thus, for instance, a MLP with 5 inputs has $(5 + 1)/2$ neurons in the hidden layer.

Table 2
“Back-Propagation” parameters and MLP topology defined for different analytes.

Analyte	Training time (N)	Momentum (M)	Learning rate (L)	No. of neurons in the intermediate layer
Ba	1100	0.6	0.5157	2
Co	4600	0.5579	0.4314	3
Cu	2150	0.01	0.2629	3
Mn	2500	0.01	0.6	3
Ni	400	0.4314	0.0521	5
V	1450	0.305	0.5157	5
Zn	50	0.4736	0.5157	5

The MLP was trained by Back-Propagation algorithm and the better combinations among Back-Propagation parameters were previously obtained by using a cross validation method in 10 folds [18]. Each parameter was varied in 15 levels, in agreement with the following rate values: training time, from 50 to 5000, momentum, from 0.01 to 0.6 and learning rate, from 0.01 to 0.6. The best set of parameters and the MLP configuration for each analyte are detailed in Table 2.

The performance of the MLPs was evaluated in the validation set by Pearson’s correlation coefficient and the absolute error of prediction.

3. Results and discussions

Currently, sustainability studies that involve soil elemental determinations require fast, clean and reliable analysis methods. The traditional methods used to determine elements in soil are developed by using techniques such as atomic absorption spectroscopy (AAS) or ICP OES. For these techniques, the soil samples should be converted into liquid samples by acid decomposition, high-temperature and, sometimes high pressures [19]. Considering the interesting features of LIBS analysis, especially regarding the possibility of direct analysis that dispenses chemical treatments for sample preparation, a multielemental determination method in soil under sewage sludge application was studied.

For quantitative analysis in LIBS it is important to generate plasmas in local thermodynamic equilibrium (LTE). However, to determine LTE is not an easy task in an inhomogeneous and time-varying multi-element plasma. A detailed description of the plasma requires careful knowledge of the distribution of the population of the different atomic and ionic electronic levels as well as of the free electrons.

In accordance with Cremers and Radziemski [20] the properties, such as the relative populations of energy levels and the distributions of the speed of the particles, can be described if LTE exists. However LTE is rarely complete, so physicists have settled for a useful approximation. For this reason, many analytical purposes assume LTE in laser induced plasmas [21]. In this paper the LTE occurrence was also assumed.

Table 3
LODs calculated for LIBS–MLP and LIBS–linear fit.

Analyte	LOD (mg kg^{-1})	
	LIBS–linear fit	LIBS–MLP
Ba	37.6	8.01
Co	9.32	9.33
Cu	28.5	9.94
Mn	416	114
Ni	8.87	7.86
V	260	46.9
Zn	42.3	30.7

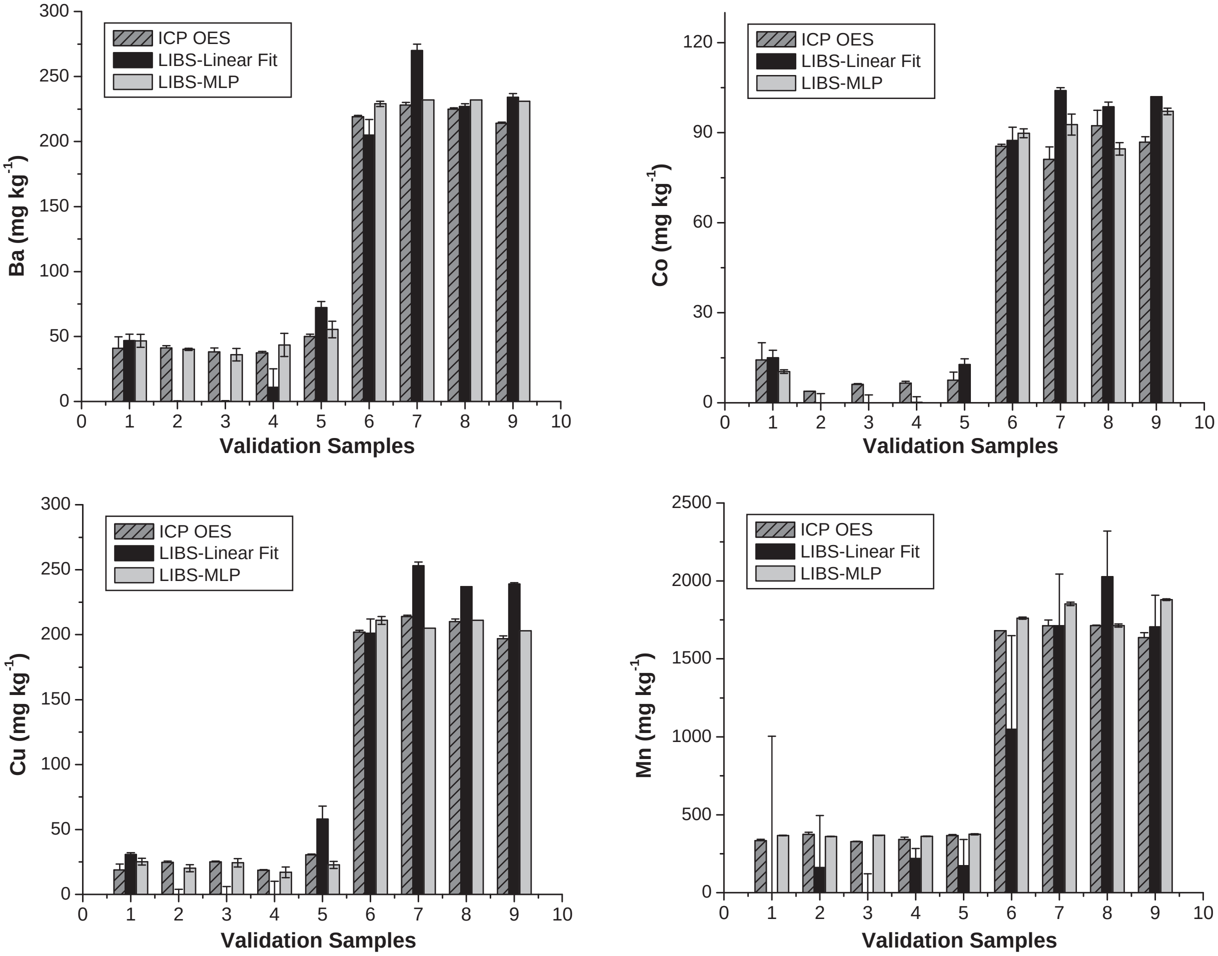

Fig. 2. Validation results for Ba, Co, Cu, Mn, Ni, V and Zn for LIBS–linear fit and LIBS–MLP.

Firstly, a conventional unvaried calibration involving the linear fit of samples from a calibration set was experimented. The linear models obtained for each element were applied to predict the analyte concentrations in the samples from the validation set. Next, an MLP was trained with samples from the calibration set and the mathematical models obtained after training were applied to the concentration predictions in the samples of the validation set. Fig. 2 shows the detailed plots for the concentration results of seven elements determined in the samples from the validation set using the linear fit and MLP as strategy for LIBS calibration. The concentrations predicted by the two evaluated calibration models are compared to ICP OES determinations, which were considered as the reference values.

For Co the LIBS–MLP determinations were not possible for samples 2–5, because the concentration of these samples was lower than the limit of detection. With the exception of Co, a slightly better correlation was observed between the reference values and the concentrations determined by LIBS–MLP. The correlation coefficients for comparisons between the concentration determined by this strategy and the reference concentrations were all above 98%, while the linear models show *R* ranging from 95 to 99%.

In the bar plots, the difference between the bar heights of the studied prediction methods and the ICP OES reference method represent the prediction errors. As can be observed, the prediction errors of LIBS–MLP do not vary so drastically from all the validation samples when compared to those obtained by LIBS–linear fit. It is also interesting to notice that the high errors from the linear model were obtained in the predictions of the 1–5 samples, while the errors obtained for 6–9 samples were similar to that obtained by MLP. Two hypotheses could explain these error differences: the limit of detection (LOD), since the high linear model errors are concentrated in the samples of lower analyte concentrations (samples 1–5), and/or the applicability of the linear model for different kinds of soils simultaneously. To check these hypotheses, the LODs were calculated for the two evaluated models. The methods, the LODs for LIBS–linear fit and LIBS–MLP were estimated in the same manner, according to Sirven et al. [10], by fitting the predicted concentrations of the validation set versus the reference concentrations by a straight line $a + bc$, so that the LOD is given by:

$$\mathrm{LOD}(\mathrm{mg\ \ kg^{-1}}) = \frac{3\sigma_a}{b}$$

where σ_a is the standard deviation of *a*, given by the regression. Although this method has been proposed to calculate the LODs from calibrations performed with artificial neural networks, in the present work it was also applied to the linear calibration for the comparison of methodologies. Table 3 shows the calculated LODs for the two calibration models.

The results show that higher LODs were obtained by the LIBS–linear fit method, when compared to those obtained by LIBS–MLP. These results suggest the inability of LIBS–linear fit for low concentration predictions. This limitation can also be due to the difficulty demonstrated by unvaried calibration methods applied to LIBS in overcome matrix effects. The advantage of using MLP as a calibration strategy is to explore its ability to learn from the characteristic standards. Moreover the multivariate feature provided by

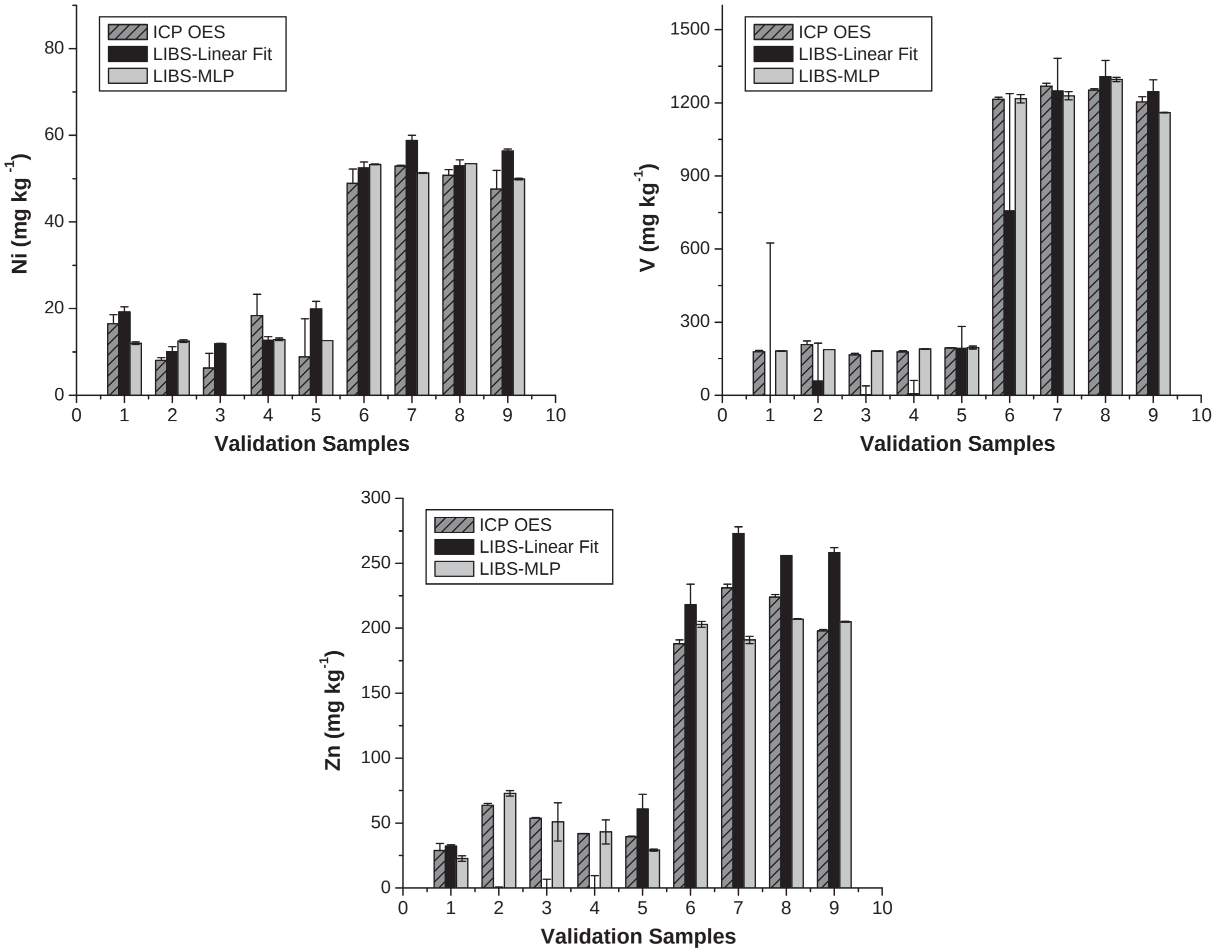

Fig. 2. *(Continued).*

the MLP rendered possible to overcome some drawbacks from the LIBS signal.

The LODs obtained by LIBS–MLP were considered satisfactory for predictions of the evaluated analytes as contaminants, since the calculated LODs are well below the safe limit established by USEPA (2010) and by the CETESB regulations (1999) [22,23].

The high precision of determinations, represented by lower standard deviation (bars errors at the top of the bar plots in Fig. 2) were also obtained in the LIBS–MLP predictions.

The results indicate that LIBS–MLP is a suitable method for soil contamination evaluation, exhibiting interesting features for sustainability studies, especially to provide fast and reliable results without generating chemical residues.

4. Conclusions

The evaluation of LIBS calibration alternatives, in order to propose a method for soil contaminants determination, shows that the use of MLP is an interesting alternative when compared to the conventional linear fit calibration. LIBS–MLP shows accurate and precise elemental predictions for the two different types of soil evaluated. The results suggested the ability of MLP to overcome the matrix effects, which is very common in LIBS spectra. Even though the proposed method used ICP OES data to calibrate and validate LIBS method, given that a calibration set was constructed based on this reference technique, the LIBS analysis can be carried out independently, providing fast and reliable results without generating chemical residues. Therefore, LIBS–MLP proved to be useful in environmental studies, particularly those concerning sustainability.

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