



Application of a series of artificial neural networks to on-site quantitative analysis of lead into real soil samples by laser induced breakdown spectroscopy



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ABSTRACT

Artificial neural networks were applied to process data from on-site LIBS analysis of soil samples. A first artificial neural network allowed retrieving the relative amounts of silicate, calcareous and ores matrices into soils. As a consequence, each soil sample was correctly located inside the ternary diagram characterized by these three matrices, as verified by ICP-AES. Then a series of artificial neural networks were applied to quantify lead into soil samples. More precisely, two models were designed for classification purpose according to both the type of matrix and the range of lead concentrations. Then, three quantitative models were locally applied to three data subsets. This complete approach allowed reaching a relative error of prediction close to 20%, considered as satisfying in the case of on-site analysis.

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1. Introduction

Laser-induced breakdown spectroscopy is recognized to have high potential for geochemical applications since this technique is able to achieve rapid and multi-elemental on-site analysis with very little sample preparation [1–5]. In the framework of a collaborative project, our objective was to quantify heavy metals in soil samples by LIBS analyses. In this paper, a special focus on the analysis of lead is presented. Generally speaking, when considering a series of samples related to a single matrix, the common normalization by an internal standard has been applied to the LIBS data [6–8]. Unfortunately, in the specific case of soil samples, the LIBS signal is known to be highly dependent of the matrix [9] and consequently different matrices must be taken into account. Thus, the basic univariate approach, which consists in building the so-called calibration curve [10] becomes inappropriate in this case, even after several attempts of normalization, and advanced data treatment is required.

Soils are natural samples that are not easy to simply describe. However, it was considered in this work that the two main matrices of soils are i) the silicate matrix ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) and ii) the calcareous matrix ($\text{CaO} + \text{MgO}$). Matrix effects have already been reported in the case of LIBS analyses of heavy metals in soil samples [9,11] but no major element was encountered under constant concentration, preventing

the application of normalization by internal standard [12]. To overcome this problem when dealing with quantitative analysis, two opposite strategies were proposed: i) the Calibration-Free method [13], not discussed in this paper, and ii) the use of multivariate approach known as chemometrics [14,15]. Multivariate analyses have already been successfully applied to the treatment of LIBS data from soil samples [16]. More precisely, several multivariate methods such as PCA, SIMCA, LDA and PLS-DA have been applied to classify soil or geo-material samples [16–21]. Regarding quantitative LIBS analysis, the most common technique of chemometrics is the partial least square (PLS) regression [22,23]. This method has been exploited for soil analysis by Essington et al. [24] who discussed the difficulty to achieve quantitative analysis with acceptable relative error of prediction. Moreover, PLS has been used to quantify both major and trace elements from the LIBS signals provided by the ChemCam instrument on Mars [25,26]. In this latter work, in order to obtain better prediction ability, the authors suggested to eliminate outliers. Moreover, they used independent component analysis (ICA) to efficiently identify the elements present in the samples. They finally demonstrated that despite the complexity of the samples, univariate analysis provided better results than PLS for trace elements. Then, in order to take into account potential nonlinearities contained into the LIBS spectra, the method of artificial neural networks – hereafter called ANN – has been efficiently applied [16,27,28]. More precisely, in a previous work of our group, we have used ANN to predict the concentrations of major elements such as calcium, aluminum and iron and also those of trace elements as copper. In this

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past work, we highlighted the importance of taking into account spectral lines from the matrix in addition to those of the analyte as input data of the ANN in order to improve the prediction ability of the model [28].

In the present work, we focus on the analysis of lead contained in soil samples from three different geological sites. In this case, the lead concentrations ranging between 250 and 147 000 ppm induced some difficulties for a direct treatment. As a consequence, we demonstrate in this paper that applying a series of ANN models for both classification and quantification purposes allowed to obtain satisfying results.

2. Experimental

The experimental setup, sample preparation and LIBS measurements have been already described in [28] so only a brief description is given in this section. The LIBS system dedicated to the on-site LIBS measurements of soils was the MobiLIBS III from IVEA SAS, including a Nd:YAG laser at 266 nm–20 Hz–5 ns, a focusing system providing 43 GW/cm² and an Echelle spectrometer coupled to an ICCD camera. The light emitted by the laser-induced plasma was collected with a patented achromatic telescope and injected in a 3-meter fused silica optical fiber of 550 μm diameter. The software AnaLIBS (IVEA SAS) was used to control the experimental parameters. The full system was integrated in a van, as a mobile laboratory, in order to allow on-site LIBS measurements.

Three geological sites located in France were analyzed. The first one – hereafter called SLM – was characterized by high concentrations of lead, zinc, barium and calcium. The two other sites – hereafter called ME and SEB – were characterized by the silicate matrix with much lower concentrations in ores and in calcium than the ones measured on the first site. Smart sampling of the sites was achieved in order to sample the most relevant soils from the ground, avoiding redundancy and taking advantage of the whole range of concentrations that one can observe on each site. This smart sampling was achieved by the use of a portable XRF device (Niton XL3t800, Thermo Scientific). Each soil sample extracted from the ground was sifted at 2 mm maximum grain size and split into two parts, one dedicated to direct LIBS analysis and the other one to later laboratory ICP-AES analysis in order to provide the reference values of concentration. It should be pointed out that in the case of environmental monitoring, sampling is of major importance and could strongly affect the analytical results. However, thorough considerations about sampling are out of the scope of the present paper and consequently, the analytical performances given hereafter may be criticized. The best example to illustrate this point is that, for a given soil sample, two separate amounts of matter were prepared, one for the LIBS analysis and the other for the ICP-AES analysis. They were assumed to be two perfect replicates but this point was not fully assessed. It should be emphasized that the values obtained after ICP-AES analysis were considered as reference values and consequently they had to be measured by reliable and robust method. The ICP-AES measurements were performed at BRGM and based on the international standardization ISO 14869-2:2002. Briefly, it consists in grinding the soil powder at 80 μm, then making the soil fusion by sodium peroxide in an oven at 450 °C and then achieving a dissolution with hydrochloric acid prior to the ICP-AES measurement. During this lab analysis, 10% of the samples were duplicated for the mineralization step in order to evaluate the analysis.

For LIBS analysis, the soil samples were finally dried with the use of a microwave oven since it has been reported that the higher the moisture level the lower the LIBS signal [5]. Finally the dried soils were prepared as pressed pellets of 13 mm diameter by applying 8 tons/cm² during 2 min with a manual press. To optimize to signal-to-noise ratio, it was decided that each LIBS spectrum would be the result of 25 laser shots accumulated at the same point of the sample, with a gate delay of 300 ns and a gate width of 3 μs. And to reduce the effects of heterogeneity, 25 spectra were acquired for each sample. One single average spectrum

was calculated for each sample and used for quantitative analysis. Indeed, side experiments allowed verifying that averaging over 25 locations of the laser spot at the sample surface was sufficient to correctly take into account the sample's heterogeneity.

Finally, statistics were calculated by running five times each ANN model. Each calculation starting with different initial random values of weights, the same input LIBS data generated five slightly different output values. Thus, the results of the ANN calculations are given by the average value and the RSD value over five repetitions.

3. Results

3.1. Description of the samples within a ternary diagram

Soil is considered to be amongst the most complex samples and consequently the most difficult to analyze by LIBS due to the high diversity of matrices. Thus, prior to quantitative analysis, it is highly recommended to have a strong understanding of the matrix related to the sample under study. Indeed, this could allow selecting the more efficient model of calibration.

As a first observation, let us have a look at the data provided by ICP-AES. From the values of concentrations, three values were calculated in order to highlight the type of matrix, namely to determine if the sample should be related to a silicate, calcareous or ore matrix. The three values calculated from ICP-AES data are given hereafter.

For the silicate matrix:

$$V1 = ([Si] + [Al]) / ([Si] + [Al] + [Ca] + [Mg] + [Ba] + [Zn] + [Pb]) \quad (1)$$

For the calcareous matrix:

$$V2 = ([Ca] + [Mg]) / ([Si] + [Al] + [Ca] + [Mg] + [Ba] + [Zn] + [Pb]) \quad (2)$$

For the ore matrix:

$$V3 = ([Ba] + [Zn] + [Pb]) / ([Si] + [Al] + [Ca] + [Mg] + [Ba] + [Zn] + [Pb]) \quad (3)$$

It should be emphasized that Si and Al are frequently strongly correlated in geological samples (more precisely SiO₂ and Al₂O₃), and thus, they were considered together to calculate the value V1 characterizing the silicate matrix. In the same way, Ca and Mg both contribute to the calcareous matrix (more precisely CaO and MgO) and consequently both were taken into account in the calculation of the value V2 characterizing the calcareous matrix. Finally, Ba, Zn and Pb were selected to represent the ore matrix (value V3) regarding the range of concentrations provided by the ICP-AES analysis. High values of concentration for Pb should be related to the natural ore of Galena (PbS) while the presence of Zn could be related to two types of natural ores, namely sphalerite (ZnS) and calamine (ZnCO). Finally, high concentrations in Ba should be associated to a soil rich in barite (BaSO₄).

Eqs. (1) to (3) illustrate that the values V1, V2 and V3 were normalized to 1 so that each of them expressed a percentage. Consequently, any soil sample could be described through these three values. As an example, a soil sample characterized by the values V1 = 0.8, V2 = 0.15 and V3 = 0.05 should be considered as a soil with a matrix 80% silicate, 15% calcareous and 5% ores.

Soil samples from three geological sites and thus potentially three different matrices were studied: 27 samples from the site SEB, 30 from the site ME, and 60 from the site SLM. Finally, Fig. 1 displays these 117 soil samples inside a ternary diagram based on the calculation of the three values V1, V2 and V3, namely based on the three types of matrices: silicate, calcareous and ore. It should be emphasized that the values reported in Fig. 1 were retrieved from the values of concentrations provided by ICP-AES.

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