Artificial neural network for Cu quantitative determination in soil using a portable Laser Induced Breakdown Spectroscopy system ☆

Edilene C. Ferreira [a,*], Débora M.B.P. Milori [a], Ednaldo J. Ferreira [a],
Robson M. Da Silva [a,b], Ladislau Martin-Neto [a]

[a] Embrapa Agricultural Instrumentation, Rua XV de Novembro, 1452, São Carlos, SP, CEP: 13560-970, Brazil
[b] University of São Paulo, São Carlos Chemistry Institute, Av. Trabalhador São-carlense, 400, São Carlos, SP, CEP: 13560-970, Brazil

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is an advanced analytical technique for elemental determination based on direct measurement of optical emission of excited species on a laser induced plasma. In the realm of elemental analysis, LIBS has great potential to accomplish direct analysis independently of physical sample state (solid, liquid or gas). Presently, LIBS has been easily employed for qualitative analysis, nevertheless, in order to perform quantitative analysis, some effort is still required since calibration represents a difficult issue. Artificial neural network (ANN) is a machine learning paradigm inspired on biological nervous systems. Recently, ANNs have been used in many applications and its classification and prediction capabilities are especially useful for spectral analysis. In this paper an ANN was used as calibration strategy for LIBS, aiming Cu determination in soil samples. Spectra of 59 samples from a heterogenic set of reference soil samples and their respective Cu concentration were used for calibration and validation. Simple linear regression (SLR) and wrapper approach were the two strategies employed to select a set of wavelengths for ANN learning. Cross validation was applied, following ANN training, for verification of prediction accuracy. The ANN showed good efficiency for Cu predictions although the features of portable instrumentation employed. The proposed method presented a limit of detection (LOD) of 2.3 mg dm^{-3} of Cu and a mean squared error (MSE) of 0.5 for the predictions.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopy which employs a highly energetic laser pulse to simultaneously prepare the sample and excite the species. Usually, excited species return to their fundamental states emitting characteristic radiation. The qualitative analysis of emission spectrum provides the "fingerprint" of sample with regard to its elemental composition [1].

Using LIBS for element identifications is advantageous in that it allows direct and fast analysis, besides being almost non-destructive, since the ablated sample mass for laser pulse is in the order of micrograms [2,3].

The main features of LIBS, as for instance, the requirement for a small amount of sample and minimal sample preparation, are partially responsible for unsatisfactory figures of merit. Given that a small amount of material is removed for analysis, the accuracy and precision can be dependent on the sample homogeneity. Other conditions that affect the figures of merit are physical parameters, atmospheric conditions and sample matrix composition [4]. Nevertheless, if experimental conditions can be well controlled, especially those dependent of sample and sampling procedure, the LIBS can reach good precisions. Like other analytical techniques, some inconvenient conditions of analysis can be minimized by using appropriate calibration standards, which match with the samples. In LIBS, under determined analysis conditions, the physical parameters and atmospheric conditions can be fixed variables, however matrix effects prove more difficult to be controlled, owing to the fact that the LIBS signals from the same element often depend on the matrix in which it is embedded [2]. Thus, calibration has been an important issue to be considered for LIBS methods.

The simplest and better known calibration technique is based on the use of standard calibration curves. It consists in plotting interest intensity line as a function of known concentration from a set of calibration standards. Ideally, there will be a linear relationship between the element response and the mass or concentration over the

* Corresponding author. Tel.: +55 16 3374 2477; fax: +55 16 3372 5958.
E-mail addresses: edilene@cnpdia.embrapa.br (E.C. Ferreira),
debora@cnpdia.embrapa.br (D.M.B.P. Milori), ednaldo@cnpdia.embrapa.br (E.J. Ferreira),
robson@cnpdia.embrapa.br (R.M. Da Silva), martin@cnpdia.embrapa.br (L. Martin-Neto).

entire range investigated, and a linear fit to the data should pass through the origin [5]. Nevertheless, calibration curves with a composition as close as possible to unknown samples are not feasible for most of the interest samples. In soil analysis, for instance, it is almost impossible to obtain matching standards calibration with samples. Moreover, soils from different regions present different chemical and physical compositions and, consequently, different matrices. Hence, it increases the difficulty in producing a set of calibration standards [5,6]. Moreover, the phenomenon of self-absorption may be considered as factor of linearity deviation in conventional calibration. This phenomenon is a consequence of loss of signal at high analite concentrations [5]. For this reason, linear models can be the most time unsatisfactory.

Methods employing calibration-free algorithm (without use of calibration curves) proposed by Ciucci et al. [7], have been applied to dribble matrix effects. Such approach is based on models proposed to account for the effect of relevant factors associated to the laser parameters, the sample and its environment [8]. However, this technique has not been widely considered as a method as it still needs to be better studied, since the quality of results has been sample dependent [5].

Chemometric methods have also been applied to different analytical methods. LIBS technique has increasingly been associated with these methods, in order to improve its analytical performance with respect to the standard calibration curve [6]. Chemometric techniques such as: principal component analysis (PCA), partial least-squares (PLS) and artificial neural network (ANN) have been applied to extract spectral information in different analytical techniques [9–13].

ANN is a massive parallel distributed processor that has a natural propensity for storing experimental knowledge, hence making it available for use. Due to its superior classification and prediction capabilities, ANNs have found their impact in spectral analysis [14–16].

This paper focuses on the use of ANN as a calibration strategy for Cu determination in soil samples using a portable LIBS system.

2. Theoretical

2.1. Laser Induced Breakdown Spectroscopy

LIBS is a simple analytical technique to determine the elemental composition, which utilizes a focused high energy laser pulse to create a plasma in a solid, liquid, or gaseous media. In analysis of solid or liquid samples, part of the energy in the plasma is used to ablate the material. After the ablation process, the plasma rapidly expands, sending a shock wave into the surrounding media. In the core of the plasma, effective temperatures can easily exceed 20,000 K. During this stage, material in the core of the plasma is vaporized, atomized and ionized, and the plasma is typically highly ionized. Usually after 0.5 to 1.0 μs, the neutral species in the plasma typically reach local thermodynamic equilibrium (LTE). From this time, upper electronic states of atoms and ions are populated in Boltzmann equilibrium [17,18].

As the plasma cools, continuum emission from the plasma (Bremsstrahlung emission) fades, typically much faster than emission lines from neutral and singly-ionized atomic lines. Thus, by adjusting an optimal temporal detector gating it is possible to collect elemental emission [19].

2.2. Artificial neural network

The ANN has been motivated right from its inception by recognizing that the human brain computes in an entirely different way from the conventional digital computer. The brain is a highly nonlinear information-processing system and parallel computer. It has the capacity to organize its structural constituents (neurons) to perform certain computations (e.g. pattern recognition, perception and motor control) many times faster than the fastest digital computer [20].

An ANN represents a computational paradigm that undertakes solving problems by imitating the structure of human brain. It involves a network of simple processing elements (artificial neurons), which can exhibit complex global behavior, determined by the connections (analogous to synapses in 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 [21].

In Fig. 1 is illustrated a useful scheme of an ANN structured in layers, like that used in this work. Each layer has a set of neurons and each neuron has a mathematical function responsible for its activation. Sigmoidal functions are commonly used for all the neurons. The first layer receives a set of values, i.e. an input vector containing the values for measured, 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 for representing 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 input for the next layer. As result, the output layer provides a value or a set of values, corresponding to propagation of a set of values from input layer to output layer (forward phase).

A task is learned for an ANN 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, whose function is to modify the weights of the network aiming to attain a desired goal [20]. During the training process, all the weights are changed to minimize the error between desired output and ANN output. The learning paradigm of ANNs involves developing mathematical models to extract important features from the training dataset [22].

After training process, a validating process should be performed to estimate the ANN performance on testing datasets. The ANN which yields good validation performance is an accurate model [22].

3. Experimental

Fifty nine Brazilian soil samples, provided by AIC (Agronomic Institute of Campinas), with reference values for Cu labile concentration, were used as calibration set. Each reference soil sample presents different composition with regard to sand, clay and silt amounts in their matrices. The use of different soil matrices for calibration was
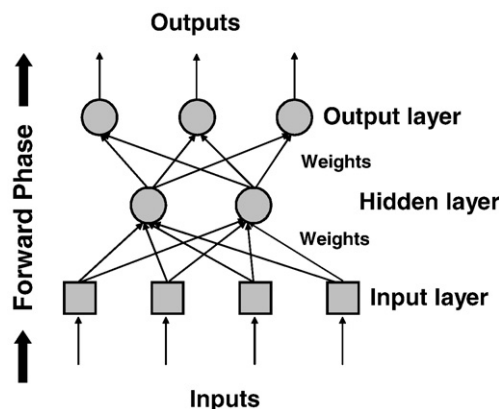

Fig. 1. A typical artificial neural network setup.