Analytica Chimica Acta 876 (2015) 26–38

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Direct determination of the nutrient profile in plant materials by femtosecond laser-induced breakdown spectroscopy

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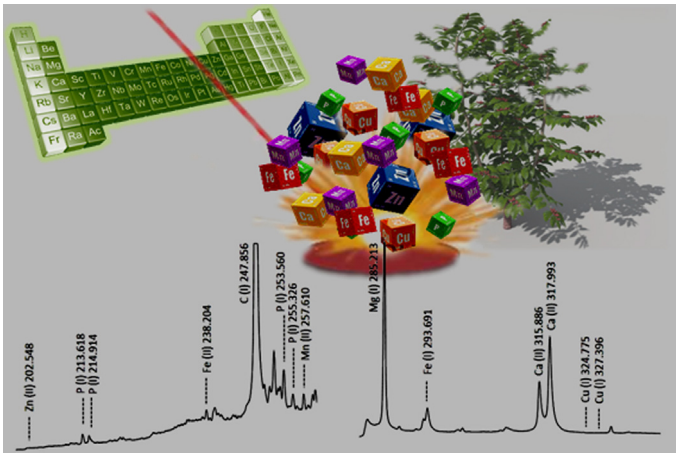
HIGHLIGHTS

- Mass fractions of nutrients in plant materials are quantified by fs- and ns-LIBS.
- Performance of univariate and multivariate modeling approaches has been compared.
- PLS models solve the non-linear relations between emissions and mass fractions.
- fs-LIBS-PLS accurately quantifies nutrient contents whatever the material matrix.
- Accuracy errors below 20% for predictions on future unknown samples are expected.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form 6 March 2015
Accepted 12 March 2015
Available online 18 March 2015

Keywords:
Femtosecond laser-induced breakdown spectroscopy
Nanosecond laser-induced breakdown spectroscopy
Laser wavelength
Plant materials
Nutrients
Multivariate calibration

ABSTRACT

Femtosecond laser-induced breakdown spectroscopy (fs-LIBS) has been used for the first time for quantitative determination of nutrients in plant materials from different crops. A highly heterogeneous population of 31 samples, previously analyzed by inductively coupled plasma optical emission spectroscopy, covering a wide range of matrices was interrogated. To tackle the analysis, laser-induced plasmas under argon atmosphere of pellets prepared from sieved cryogenically ground leaves were studied. Predictive functions based on univariate and multivariate modeling of optical emissions associated to macro- (Ca, Mg, and P) and micronutrients (Cu, Fe, Mn and Zn) were designed. Hierarchical cluster analysis was performed to select representative calibration (n_{cal} = 17) and validation (n_{val} = 14) datasets. The predictive performance of calibration functions over fs-LIBS data was compared with that attained on spectral information from nanosecond LIBS (ns-LIBS) operating at different wavelengths (1064 nm, 532 nm, and 266 nm). Findings established higher accuracy and less uncertainty on mass fractions quantification from fs-LIBS, whatever the modeling approach. Quality coefficients below 20% for the accuracy error on mass fractions' prediction in unknown samples, and residual predictive deviations in general above 5, were obtained. In contrast, only multivariate modeling satisfactorily handled the

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http://dx.doi.org/10.1016/j.aca.2015.03.018

non-linear variations of emissions in ns-LIBS, leading to 2-fold decrease in the root mean square error of prediction (RMSEP) of Ca, Mg, P, Cu, Fe, Mn and Zn in comparison with the univariate approach. But still, an averaged quality coefficient about 35% and residual predictive deviations below 3 were found. Similar predictive capabilities were observed when changing the laser wavelength. Although predicted values by ns-LIBS multivariate modeling exhibit better agreement with reference mass fractions as compared to univariate functions, fs-LIBS conducts better quantification of nutrients in plant materials since it is less dependent on the chemical composition of the matrices.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a powerful tool for direct solid analysis of agricultural and environmental samples owing to its inherent analytical capabilities for fast and simultaneous multielemental determinations. The ability of LIBS to interrogate solid samples has been recently demonstrated for the direct analysis of plant materials (*e.g.*, leaves, roots, and fruits) in the widespread scenario of agricultural and environmental sciences [1–4]. The validation of quantitative methods will contribute to the applications of LIBS in the assessment of nutritional status of plants and the composition of foods, environmental monitoring processes and the development of certified reference materials.

Most recently, it has been demonstrated that LIBS presents appropriate features for the quantitative determination of P, K, Ca, Mg, Fe, Cu, Mn, Zn, B [1] and Si [5] in pellets of plant materials by using matrix-matched calibration samples [6,7]. In spite of the advantages of LIBS, difficulties have been noted for quantitative analysis, which are mainly attributed to variations in laser-sample interactions involving different matrices [8,9], even when multivariate calibration approaches based on partial least squares (PLS) are employed [10].

In general, the analytical performance of LIBS depends primarily on the laser properties (*e.g.*, wavelength, pulse duration and energy) and the sample characteristics (*e.g.*, chemical composition, conductivity and reflectivity). These aspects determine the mechanisms of energy absorption, plasma generation and furthermore the analytical response (*i.e.*, plasma emission) [11]. Recent findings obtained with Nd:YAG lasers at 1064 nm demonstrate that the use of appropriate laser fluence and spot size can improve the analytical performance of LIBS in the quantitative analysis of pellets of sugarcane leaves [5,12], and also diminish matrix effects caused by differences in particle size distributions within pellets [13].

In the case of nanosecond (ns) laser pulses, the laser wavelength affects the processes of plasma generation and the laser–plasma interaction. The formation and growth of free electrons as well as plasma initiation occur mainly by multiphoton ionization when using active medium operating in the ultraviolet (UV) regime, whereas cascade ionization is the prevalent mechanism in the case of infrared (IR) lasers [14]. After plasma formation, the interaction of the later part of the incoming ns laser with the plasma occurs mainly by inverse *bremsstrahlung* absorption. The importance of this process grows as the laser wavelength increases [14]. In general, UV laser pulses provide larger ablation rates, better measurement precision, lower fractioning effects and lower continuum emission [15–18]. To the best of our knowledge, there is only one contribution dealing with the influence of laser wavelength in the analysis of plant materials by LIBS. Zhang et al. [19] analyzed fresh holly leaves by using Nd:YAG laser operating at 266 nm and 1064 nm, and concluded that IR irradiation resulted in stronger plasma emission whereas better measurement precision was attained by UV irradiation. However, the lack of information regarding the main operational parameters impaired appropriate data interpretation.

On the other hand, among the aforementioned parameters, the pulse duration is the most relevant variable affecting the laser ablation process. Interaction of ns pulses with materials differs substantially from those of femtosecond (fs) pulses since the rate of energy deposition is significantly shorter in the fs regime. For ns pulses, the material undergoes transient changes in the thermodynamic states from solid into a plasma state. Furthermore, the leading edge of the laser pulse generates plasma, and the remaining part of the pulse heats the plasma instead of interacting with the target material [11]. In the case of ultrashort laser pulses (*i.e.*, <1.0 ps), the pulse energy is delivered on the target before the occurrence of thermodynamic changes and, at the end of the laser pulse, only a hot electron gas plume and a practically undisturbed lattice are found [11]. This phenomenon provides ablation processes less-dependent on the physical and chemical matrix properties, and lower continuum emission since there is no plasma–laser interaction [20,21]. Recent findings have demonstrated that emission spectra from fs laser-induced plasmas do not necessarily reflect the average depth composition, presenting major contribution from the surface layer of the ablated region [22]. In general terms, contributions dealing with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) have shown that ultrashort laser pulses can provide better analytical figures-of-merit in terms of measurement precision and trueness than ns pulses [20,23–25]. However, it should be emphasized that appropriate results can also be obtained by using ns pulses, mainly when matrix-matched standards are available [6,20]. Most recently, Ohata et al. [26] have demonstrated that fs-LA did not offer substantial improvements on accuracy over ns-LA in the analysis of glasses by LA-ICP-MS. Authors concluded that the fact that fs-LA is superior than ns-LA should be reconsidered in some instances, although fs-LA is still recommended when a high degree of flexibility with respect to the range of material is desired.

To the best of our knowledge, to date, there is no contribution dealing with the quantitative analysis of plant materials by fs-LIBS. At moment, the use of fs lasers in plant analysis is restricted for chemical mapping of vegetal structures due to lower thermal effects on the sample surface and lower lateral damage [1,2,27]. fs-LA provide higher lateral and axial precision with resolution in the order of *ca.* 100 nm [28], thereby allowing the analysis of individual plant cells without collateral damage [29].

In the present study, the performance of fs-LIBS for the quantification of mass fractions of distinct macro- and micronutrients in a wide range of plant materials have been appraised from univariate and multivariate modeling. A critical comparison between worthiness of both ultrashort (fs) and short (ns) laser pulses, these last also when operating under a different wavelength regimes (1064, 532 and 266 nm), has been tackled. The strengths and weaknesses of each approach has been discussed on the basis of accuracy, precision and sensitivity of predictions of Ca, Mg, P, Cu, Fe, Mn, and Zn mass fractions in pellets prepared with leaves from different crops.