



ESPECTROSCOPIA DE EMISSÃO ÓPTICA COM PLASMA INDUZIDO POR LASER: UM NOVO E VERSÁTIL CAMINHO PARA ANÁLISE E MONITORAMENTO DE SOLOS, PLANTAS E ADUBOS

G.S. Senesi¹, G. Nicolodelli², C.H. dos Santos², C. Montes³, P.R. Villas-Boas², D.M.B.P. Milori²

- (1) Institute of Inorganic Methodologies and Plasmas, IMIP/CNR, Via Amendola 122/D, 70126 Bari, Italia, giorgio.senesi@ba.imip.cnr.it
- (2) Embrapa Instrumentação, Rua XV de Novembro, 13560-970, São Carlos, SP, gunicolodelli@hotmail.com, cleberhilario@gmail.com, paulino.villas-boas@embrapa.br, debora.milori@embrapa.br
- (3) Centro de Energia Nuclear na Agricultura, CENA/USP, Avenida Centenário, 303, 13400-970 Piracicaba, SP, crmlauar@usp.br

Resumo: Ao longo das últimas duas décadas uma intensa atividade foi realizada no estudo e desenvolvimento da técnica analítica de espectroscopia de emissão óptica com plasma induzido por laser, do inglês, (LIBS) em diversas áreas de pesquisa acadêmica e aplicada, incluindo a agricultura. LIBS é uma técnica rápida e confiável adequada para a análise simultânea qualitativa e quantitativa de elementos em amostras de diferentes naturezas e origens. Este trabalho revisa e discute alguns artigos sobre aplicações de LIBS e sua viabilidade para o estudo na agricultura, com foco em solos, plantas e adubos. Os resultados obtidos na detecção e quantificação dos elementos, identificação e discriminação são brevemente revisados e discutidos. Em particular, gostaríamos de chamar a atenção sobre como LIBS poderia ser adotado no meio-ambiente brasileiro, com resultados promissores. Por exemplo, novos métodos que permitem medições de C orgânico *in situ* são cruciais para solos da Amazônia e um encorajador método para quantificar C em solos brasileiros será apresentado baseado em linhas de emissão atômica obtidos por um sistema LIBS de bancada. Além disso, medições de campo também são possíveis utilizando um aparelho portátil compacto LIBS e realmente útil em ambiente hostil, por exemplo, a região da Amazônia.

Palavras-chave: Espectroscopia, Análise elementar, Solos, Plantas, Carbono Total.

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): A NEW VERSATILE WAY TO ANALYZE AND MONITOR SOILS, PLANTS AND COMPOSTS

Abstract: Over the past two decades an intense activity has been conducted in the study and development of the analytical technique of laser-induced breakdown spectroscopy (LIBS) in several fields of academic and applicative research, including agriculture. LIBS is a fast and reliable technique suitable for the simultaneous qualitative and quantitative analysis of major and trace elements in samples of various nature and origin. This review reports and discusses some works on LIBS applications and his feasibility to agriculture studies with focus on soils, plants and composts. Results obtained on element detection and quantification, identification and discrimination are reviewed and briefly discussed. In particular, we would focus the attention on how LIBS could be adopted in the Brazilian environment with promising results. For example, new methods that allow soil C measurements *in-situ* are crucial for Amazonian soils and an encouraging resolution method to quantify C in Brazilian soils will be provided by means of atomic emission lines obtained by a portable LIBS system. Furthermore, field measurements are also possible by using compact portable LIBS apparatus really helpful in hostile environment, e.g., Amazonia region.

Keywords: LIBS, elemental analysis, soil, plant, Total Carbon.

1. Introduction

Soil testing and plant analyses have been proven to be invaluable tools in the diagnosis of nutritional deficiencies and problems related to plant growth. Each advance in the basic understanding of plant physiology and soil chemistry, and each advance in instrumentation leads to improvements in methodology and interpretation (GARDNER, 1990). Soil analysis has always been used to distinguish different functions and land-use activity over a site, and to aid the identification and interpretation of settlement features. Considering the diversity of soil types and properties, quality, usability, unrestrained human intervention and pollution, the scientific study of the elemental and chemical composition, quality and usability of soils is very important. Further, in the last decades, the use of metal accumulator plants, in combination with compost, has become a cheap and sustainable alternative technique to lower soil contamination by toxic heavy metals. The elemental concentrations of soils and plants are typically obtained following digestion by strong mineral acids, typically nitric, or *aqua regia* (nitric and hydrochloric) acids.

The elemental concentrations in the digested solutions obtained are then analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). These techniques usually provide good Limits of Detection (LOD) but are time-consuming, need consistent sample manipulation prior to analysis, and require specific soil sampling procedures and accurate specimen selection. Alternatively, and especially for the detection of contaminants in soils, the use of a real-time, *in-situ* analytical technique such as laser-induced breakdown spectroscopy (LIBS) would allow the assessment of the degree and kind of soil contamination, followed by immediate application of tailored remediation strategies, in order to avoid irreversible damages to environment, human and animal health.

LIBS is an adaptable and total multi-elemental analytical spectroscopic technique based on atomic emission spectroscopy. LIBS is largely free of sample preparation, which is a great benefit especially in conditions where sample preparation is very difficult or impossible to perform with regard to needed results, and requires a small sample amount.

The simplicity of LIBS apparatus represents a great advantage in comparison to other analytical methods. LIBS is especially sensitive to light elements such as B, C, H, Li, N, and O, which are difficult to determine by many other analytical techniques. Due to its inherent advantages, LIBS developed very fast since its introduction in '60s, and during the last decade has undoubtedly achieved tremendous popularity in several fields of applications including environmental analyses, cultural heritage, combustion, forensics, and food, pharmaceutical, biomedical, nuclear and industrial analyses (HAHN and OMENETTO, 2012). However, LIBS has also a number of drawbacks, e.g. the quality, accuracy and precision provided where a quantitative analysis is needed. In some cases the technique may not meet the analytical requirements requested because quantitative LIBS is subject to a number of operating parameters that may or may not be controllable. For example, the so-called "matrix effect" and "self-absorption phenomena" are great challenges in the LIBS experiment. Although sampling by laser ablation involves highly complex and not entirely understood physical and chemical phenomena, LIBS has been successfully implemented for both elemental detection and quantitative chemical analysis.

Since the late '90s many papers appeared in the LIBS literature on the laboratory analysis of soils (CIUC-CI et al., 1996; DA SILVA et al., 2008;) and, successively, plants (SANTOS et al., 2012). Research in this domain is still very active and is mainly aimed at refining the technique and evaluating its capabilities in comparison with other well established techniques. The purpose of this article is to present a review focusing on some recent achievements obtained by the authors and other researchers in the field of elemental analysis of soils, plants and composts. The potential of LIBS will be illustrated, and its capabilities at the present state of development will be highlighted.

2. Material and Methods

Two different instruments have been used in the experiments. A traditional laboratory bench-top LIBS apparatus was employed by Senesi et al. (2009; 2014), which consisted of a ns-pulsed laser, Nd:YAG, with a repetition rate of 10 Hz and a laser pulse duration of 6 ns. The laser was focused on a rotating target by using a 10 cm focal quartz lens for $\lambda = 532$ nm and a 30 cm focal quartz lens for $\lambda = 355$ nm. A 7.5 cm focal quartz biconvex lens was used to collect the plasma emission and to obtain the 1:1 image that was focused directly towards the spectroscopic system with a monochromator coupled with an intensified charge coupled device (ICCD) and a pulse generator that controlled the triggering scheme for the emission spectra acquisition. Six soil samples were analyzed by Senesi et al. (2009): a silty loam soil collected in the Murgia hills, in the province of Bari, Italy, with a typical natural concentration of heavy metals (S_0); two polluted loam soils from the same area (S_1 and S_2); two polluted soils from other two different sites, i.e. a clay loam soil from Milano, Lombardia, Northern Italy and a sandy clay loam soil from Fano, Marche, Central Italy (S_3 and S_4).

A depurated sewage sludge (SS) of known Cr concentration was also studied to evaluate the possible matrix effects. Further, two commercial composts of different origin and nature and four plant species typically used for soil remediation processes (i.e. *A. halimus*, *B. alba*, *B. napus*, and *E. vesicaria*) were studied by Senesi et al. (2014). In the Nicolodelli et al. (2014) paper, soil samples were collected from two Brazilian forests, a spodosol and an oxisol. The spodosol samples were collected from the dense Amazonian rainforest close to the city of São Gabriel da Cachoeira, Amazon State. Red oxisol samples were collected from a remnant of the Atlantic Forest close to the city of Sao Carlos, Sao Paulo State. These authors performed the LIBS measurements by using a portable LIBS2500 spectrometer equipped with a Q-switched 1064 nm Nd:YAG laser operating at a 75 mJ maximum power energy and a 10 Hz frame rate. The laser beam was focused over the sample inside an ablation chamber. Plasma emission was collected by an optical fiber bundle connected to seven spectrometers, each one providing a 2048 element linear silicon CCD array. The distance from the sample to the collecting optical fiber bundle was approximately 7 mm. The spectra were acquired from 189 to 966 nm with an approximate optical resolution of 0.1 nm. 60 measurements were performed on each soil sample, each one corresponding to two accumulated shots.

3. Results and Discussion

Senesi et al. (2009) and Dell'Aglio et al. (2011) measured the contents of Cr, Cu, Pb, V, Zn, in a number of soil and sludge samples, finely grained and pressed in pellets, and LIBS performance was compared to that of ICP-OES. Calibration lines were drawn on the basis of ICP-OES measurements. For these lines the emission intensity of analytes was normalized to that of the spectral background, because no suitable internal standard was found for the analyzed set of samples. The good linearity of calibration lines was a clear confirmation of the fe-

asibility of the adopted LIBS method, and showed that limited matrix effect occurred. In order to compare LIBS performance with that of ICP-OES, the following procedure was followed for each element: one sample, chosen from the central part of the concentration range covered, was excluded from the calibration curve of the considered element and treated as an unknown sample; then a new calibration line was drawn without the excluded sample, and the concentration was determined. The results of such comparisons are reported in Table 1 and show a good agreement between the two techniques.

Table 1. Comparison between concentrations of heavy metals in soil samples (S₁ and S₂: two polluted loam soils from undefined area; S₃ and S₄: respectively, a clay loam soil from Milano, Lombardia, Northern Italy and a sandy clay loam soil from Fano, Marche, Central Italy) determined by ICP-OES and by LIBS.

Element	Unknown sample	ICP-OES (mg kg ⁻¹)	LIBS (mg kg ⁻¹)
Cr	S3	550 ± 82	698 ± 144
Cu	S4	100 ± 15	88 ± 21
Zn	S2	897 ± 135	846 ± 37
Pb	S1	180 ± 27	168 ± 18
V	S1	84 ± 12	80 ± 7

In analogy to other enrichment factors used in the agrochemical literature, an anthropogenic index (A.I.) was introduced to rapidly evaluate the degree of heavy metal pollution of soils. Recently, Senesi et al. (2014) have determined the concentrations of selected elements, including Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Sr, and Zn, in two composts of different origin and nature and four accumulator plant species, commonly used in combination for soil remediation processes. The plant samples were analyzed either as bulk plant material or as specific organs (i.e. shoots and roots). The concentrations measured by LIBS were assessed by complementary ICP-OES. The significant correlation found between the data obtained by the two techniques ($R=0.732-0.999$) supports the feasibility of LIBS for fast screening of major, trace and toxic elements in plant and compost samples. Although the accuracy for the LIBS-detected elements is sometimes lower than that obtained by ICP-OES, data reported in Senesi et al. (2014) clearly indicate the appropriateness of LIBS for metal monitoring in plants and composts. Further, thanks to the acceptable LOD values obtained, it was possible to follow the migration of these elements from the soil to the different plant organs.

The feasibility of LIBS to measure the concentration of C in forest spodosols and oxisols has been investigated by Nicolodelli et al. (2014), using well-established elemental analysis methods as reference. Carbon has a few emission lines the main at 193.03 and 247.86 nm, which show strong interference by Fe, Si, and other lines (Figure 1). In particular, Al lines interfere with the C line at 193.03 nm. However, a method was developed in this study which was able to correct the Al interference on the C I (193.03 nm) LIBS emission line, and a strong correlation ($R > 0.91$) was found between the C content measured by LIBS and elemental analysis in a set of forest soils. In conclusion, the results of Nicolodelli et al. (2014) confirm the promising potential of LIBS for *in-situ* quantitative analysis of C using a portable, low-resolution apparatus. Further, the model developed has the potential to correct other interfering emission lines.

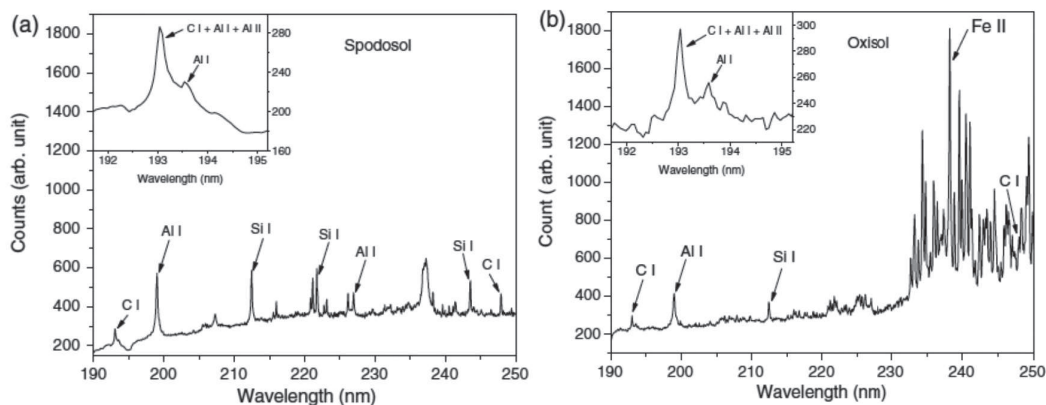


Figure 1. LIBS spectra of (a) spodosol and (b) oxisol samples. Copyright 2014, with permission from OSA.

4. Conclusion

The LIBS technique applied to agriculture studies has been demonstrated to yield an acceptable elemental profiling and identification of eco-toxic elements in soil, and as a new way to analyze plant ecology and provide real-time measurement of plant nutrition status useful for precision application of fertilizer. If the developments of LIBS will be confirmed to be successful, the resulting technology will generate a relevant step change in the prac-

tice of precision agriculture with potential returns to Brazilian manufacturers of precision agriculture equipments and will offer abundant opportunities to landscape manufacturing.

Acknowledgment

The authors thank CNPq, EMBRAPA and CNR (Italy), for their financial support to these studies.

Reference

- CIUCCI, A.; PALLESCHI, V.; RASTRELLI, S.; BARBINI, R.; COLAO, F.; FANTONI, R.; PALUCCI, A.; RIBREZZO, S.; VAN DER STEEN, H. J. L. Trace pollutants in soil by a time-resolved laser induced breakdown spectroscopy technique. *Appl. Phys. B* 63, 1996, p. 185–190.
- DA SILVA, R. M.; MILORI, D. M. B. P.; FERREIRA, E. C.; FERREIRA, E. J.; KRUG, F. J.; MARTIN-NETO, L. Total carbon measurement in whole tropical soil sample, *Spectrochim. Acta, Part B* 63, 2008, p. 1221–1224.
- DELL'AGLIO, M.; GAUDIUSO, R.; SENESI, G. S.; DE GIACOMO, A.; ZACCONE, C.; MIANO T. M.; DE PASCALE, O. Monitoring of Cr, Cu, Pb, V and Zn in polluted soils by laser induced breakdown spectroscopy (LIBS), *J. Environ. Monit.* 13, 2011, p. 1422–1426.
- GARDNER, W. R. in: *Soil testing and plant analysis*, Third Edition, Ed.: Westerman R. L. Soil Science Society of America, Inc., USA, 1990, p. 17.
- HAHN, D. W.; OMENETTO, N. *Laser-Induced Breakdown Spectroscopy (LIBS), Part II: Review of instrumental and methodological approaches to material analysis and applications to different fields.* *Appl. Spectrosc.* 66, 2012, p. 347–419.
- NICOLODELLI, G.; MARANGONI, B. S.; CABRAL, J. S.; VILLAS-BOAS, P. R.; SENESI, G. S.; DOS SANTOS, C. H.; ROMANO, R. A.; SEGNINI, A.; LUCAS, Y.; MONTES, C. R.; MILORI D. M. B. P. Quantification of total carbon in soil using laser-induced breakdown spectroscopy: a method to correct interference lines. *Appl. Opt.* 53, 2014, p. 2170–2176.
- SENESE, G. S.; DELL'AGLIO, M.; GAUDIUSO, R.; DE GIACOMO, A.; ZACCONE, C.; DE PASCALE O.; MIANO, T. M.; CAPITELLI, M. Heavy metal concentrations in soils as determined by Laser-Induced Breakdown Spectroscopy (LIBS), with special emphasis on chromium, *Environ. Res.* 109, 2009, p. 413–420.
- SENESE, G. S.; DELL'AGLIO, M.; DE GIACOMO A.; DE PASCALE O.; AL CHAMI, Z.; MIANO, T. M.; ZACCONE C. Elemental composition analysis of plants and composts used for soil remediation by laser-induced breakdown spectroscopy. *Clean – Soil, Air, Water*, 42, 2014, p. 791–798.
- SANTOS, JR., D.; NUNES, L. C.; CARVALHO, G. G. A.; DA SILVA, G. A.; SOUZA, P. F.; LEME, F. O.; DOS SANTOS, L. G. C.; KRUG, F. J. Laser-induced breakdown spectroscopy for analysis of plant materials: A review, *Spectrochim. Acta, Part B* 71–72, 2012, p. 3–13.