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FOREWORD FROM THE PRESIDENTOF THE INTERNATIONAL HUMIC SUBSTANCES SOCIETY

In 2011 IHSS will reach 30 years since its creation! These have been years of important achievements and activities that fulfilled objectives stated at the beginning. For sure it is time to celebrate and to thank very much those pioneers that started the Society, as well as the many others who have contributed to the development of the Society. We need to thank those who worked to standardize chemical procedures to extract humic substances and produce the highly valued reference and standard collection of humic samples, and those who contributed to our Newsletters, to the organization and operation of National and Regional IHSS Chapters and to the organization of the bi-annual international conferences, which have been held on all continents. This legacy is very important but this effort must continue, to maintain and advance our Society. This is the commitment of IHSS Board Members, and all members are invited to join us in current and future efforts to strengthen IHSS, as well as to celebrate the 30 years of IHSS, at this 15th IHSS Meeting, in Tenerife.

It is very well accepted that natural organic matter (NOM) research is much more relevant than ever, being associated with global climate change, one of the more challenging issues for the future of the Planet. A new emphasis in research has emerged related to carbon compounds in different environments. We are involved in this research field, which offers many opportunities and we must be aware of the best ways to take advantage of the opportunities, and make a positive contribution to IHSS. We face much greater competition from several other groups of researchers, with different scientific backgrounds, and there has been a multiplication of the number of scientific meetings and organizations involved in NOM associated research. For IHSS it is crucial to develop a strategic plan to take advantage of the opportunities in the best way that we can.

In addition to good planning, for our Society to stay healthy we must invest in young researchers and motivate them in their activities. In this IHSS can be proud, because for many years we have sponsored the IHSS Travel Award, a worldwide competition that provides an outstanding opportunity for PhD students to participate in our bi-annual meetings. In 2008, for the meeting in Russia, IHSS Board members decided to support 17 students, the highest number until that meeting. For the 15th IHSS meeting the number is even higher, and 22 students from all continents were given awards to attend the meeting. These 22 were chosen from 47 applications, a record, which demonstrates growing interest in the IHSS Travel Award.

Finally I would like to recognize those who have contributed to the organization of this bi-annual international meeting, and so on behalf of IHSS I would like to thank very much all members of the Organizing and Scientific Committees of the 15th IHSS Meeting in Tenerife, Spain, and particularly Dr Jose A. GONZÁLEZ-PÉREZ and Dr Francisco J. GONZÁLEZ-VILA, Chair and Co-Chair, for their willingness to organize the meeting and their strong dedication and motivation. I am sure that we will have a very high level scientific conference that is productive and enjoyable, on the Island of Eternal Spring!

Thank you very much for your attendance.

Best regards.

Ladislau MARTIN-NETO
President of IHSS

Photonics Technologies for Analysis of Organic Matter and Metal in Soils

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1. Introduction

Soil tillage intensity and crop residue management affect soil organic matter (SOM) and, are considered to be the key factors in regulating soil carbon (C) balance. Thereby, agricultural and degraded soils have significant potential sinks for atmospheric carbon. However, soil C accumulation is not linear with increasing of C inputs. Depending on the situation, soil C may until decrease despite of residues addition. Continued research on chemical and biological mechanisms in soil is needed if soils are to be relied upon for food and fiber production and for the mitigation of climate change. The scenario makes clear that in order to advance in this scientific area, more research about low cost and quick methods, which make possible a high number of analyses, is immensely coveted. On the other hand, information obtained in conditions near of field soil conditions, without chemical or physical treatments, also are a demand of soil scientists. Photonic techniques have high potential of miniaturization and frequently are applied in equipments on the several areas of knowledge, such medicine and odontology. Usually, they show high potential to perform analysis *in situ*. This study consists in to apply two photonic techniques to assess carbon and metals in whole soil samples.

Laser-induced breakdown spectroscopy (LIBS) is an emerging technique for simultaneous multi-elemental analysis of solids, liquids and gases with minute or no sample preparation and thus revolutionized the area of on-line analysis technologies. During the LIBS analytical process the sample is irradiated by a highly energetic laser pulse and absorbs this energy. The high temperature of ablated material generates a small plasma plume. During the plasma cooling, the excited species return to their ground state emitting electromagnetic radiation in characteristic wavelengths. In this sense, analysis of sample emission spectra gives a qualitative view of sample elemental composition. Nevertheless, to accomplish LIBS quantitative analysis is not so simple, because elements emission lines in LIBS spectrum are closely related with the matrix in which they are embedded. This feature of the signal becomes very difficult to find appropriate calibration standards for LIBS methods. In some

cases, the appearance of so-called matrix effects could be reduced by a multivariate calibration. However, many efforts have been dispended to adapt univariate calibration models.[2] Artificial Neural Network (ANN) is a kind of multivariate technique which due to its superior classification and prediction capabilities, has found their impact in spectral analysis and has gained space in LIBS spectroscopy.[3,4]

Fluorescence of soils is originated mainly from organic matter (OM), since it has several functional groups containing unsaturated bondings in rigid systems. Such groups are present mainly in more humified OM, such as aromatic rings, phenolics, quinone structures and carboxylic groups.[5] In general, the more complex molecular structure of humic substances, the higher their stage of humification. For this reason, when soil samples are illuminated with near-ultraviolet or blue laser, mainly the more complex structures are excited, and the area under the fluorescence emission, normalized by C content, provides a parameter proportional to humification degree of SOM.[6] This method is interesting because allows analysis without chemical treatment in a very precise and quick way.

The goal of this work is to evaluate LIBS and LIFS portable systems for non-destructive analysis of organic matter and metal in whole soils.

2. Materials and Methods

The total carbon content in the samples was determined by the method of dry combustion using a Total Organic Carbon (TOC) (Shimadzu TOC - V).

Before LIBS and LIFS analyses, around 0.5 g of grinded soil was pressed into a pellet during 10 min using a force of 14 tons. For each soil sample two pellets were done.

The spectra the samples were obtained using a portable LIBS system from StellarNet (model PORTA-LIBS-2000) fitted with Nd:YAG laser of 25 mJ with pulse duration of 4 ns, repetition rate of 1Hz; spectrometric range of 190-1000 nm and optical resolution of 0.2 nm, with the fixed delay time of 2 μs. To improve the relation signal/noise, 60 spectra were obtained from each sample, each corresponding to one shot in different areas of the pellet. The final spectrum of each sample was the average of 60 spectra. Calibration models using ANN for LIBS quantitative measurements were evaluated for determination of C and some metals, such as Ba, Co, Cu, Cr, Mn, Ni, V and Zn.

Also it was assessed a portable LIFS system, built by Embrapa Agricultural Instrumentation, to estimate humification degree of soil organic matter. The bench system, described by Milori and co-workers[6], was used as reference technique.

3. Results and Discussion

The results show that concentration values determined by LIBS proposed method presented good agreement with reference values obtained by ICP OES. The correlation coefficient for the comparisons between LIBS values and reference values were all above 98%.

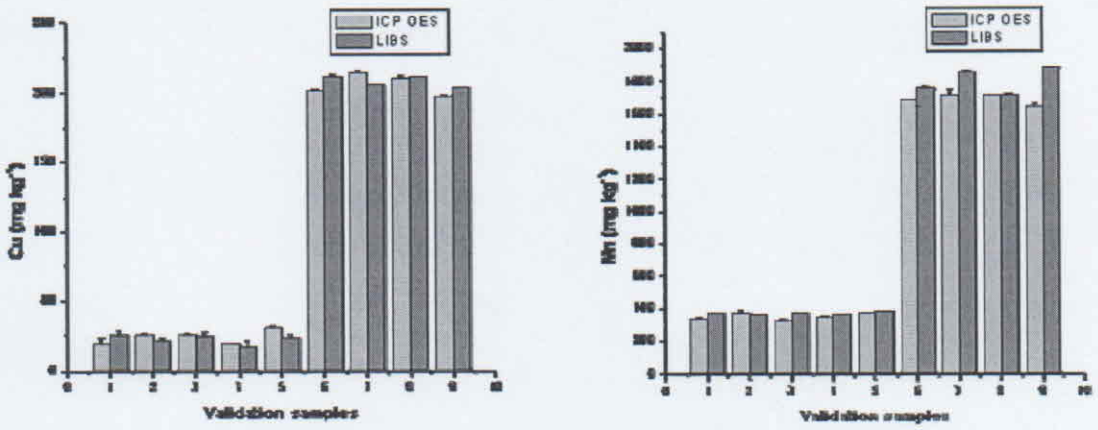

Figure 1: Correlation among ICP OES reference concentrations and LIBS determined concentrations for Cu and Mn, two important plant micronutrients

Although the LIBS proposed method presented higher limit of detection (LOD) when compared to ICP OES reference method, the obtained results were considered satisfactory for direct evaluation of soil fertility or contamination. Moreover the proposed method practically avoid sample preparation step, taking only 3 minutes to prepare a pellet.

The results for C determination were similar to metals. The calibration model obtained presented a correlation coefficient of 0.94. By using this model, the predicted values presented 93% of correlation with reference values determined by TOC. The absolute medium error was 0.08% for almost all samples in the validation set and the LOD was around 0.3%.

Table 1: Validation results of LIBS using calibration method based on ANN

C reference concentration (%)	C predicted concentration (%)	Absolute Error
0.51	0.43 (±0.04)	-0.08
0.79	0.94 (±0.08)	0.15
0.62	0.78 (±0.15)	0.16
0.48	0.56 (±0.09)	0.08
0.65	0.76 (±0.10)	0.11
0.36	0.44 (±0.07)	0.08
0.45	0.51 (±0.07)	0.06
0.72	0.76 (±0.07)	0.04

The portable LIFS system to evaluate chemical properties of SOM related to more humified structures also presented interesting results. The correlation obtained between the portable and bench equipments was around 94%, with P <0.0001. This high value shows that the prototype reached the expectations and reduced the measurement time from 1 min. to 5 sec. per sample.

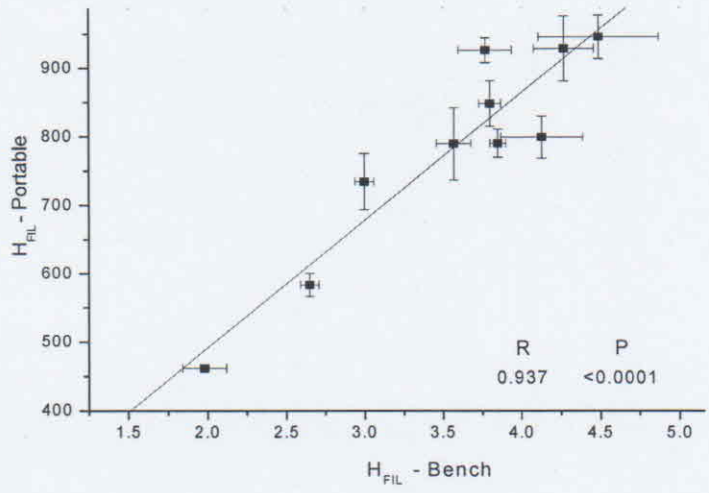

Figure 2 Correlation between humification degree determined by LIFS portable and bench systems

4. Conclusions

These results highlight the high potential for future applications as field sensor oriented for precision agriculture and studies directed to soil carbon sequestration in projects about climate changes. Also many others opportunities to more detailed studies on soil organic matter dynamics and reactivity, without risks of artificial laboratory or chemical preparations, could be addressed with important impact in this research area.

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