LIBS and XRF: two techniques for the rapid measurement of nutritional elements in the soils

>>> The advent of portable analytical devices such as x-ray fluorescence spectrometry and laser induced breakdown spectrometry, allows for practical and rapid tools to effectuate element measurements directly on the soils without advance sample preparation. Their use can be envisaged to map out a plot, to deliver real-time indicators of the potentialities of the soil but equally to monitor its performance over time as a function of a context change. <<<

■ Introduction

The determination of the element composition of soils constitutes an obligatory step in agronomic and environmental studies. It is most often undertaken in a laboratory with the help of atomic spectrometry techniques and a preparation of samples in advance (drying, grinding, dissolution). These steps take a long time (several days) and severely limit the rapid detection of deficiency or contamination of a plot. Under these conditions, a technique of rapid analysis that can be used directly in the field would be an important advancement to address these needs. The current technologies that most effectively respond to this problem are the X-ray fluorescence spectrometry or XRF[1] and the laser induced breakdown spectrometry or LIBS[2]. Both cases represent multi-element analysis techniques that show little or no harm to the sample, and that are available in the form of portable instruments.

These techniques are capable of detecting all of the elements between sodium and uranium on rocks, metals, polymers, food products and in the concentration-ranges going from mg/kg to percent.
The applications, however, remain rare in an agricultural context due to a lack of specific calibrations adapted to the nature of the samples[3, 4, 5]. Considering the known concentrations in the soils, they represent, however, an opportunity to analyze major elements and even some trace elements. Within the framework of the presentation of tools for field measurement in the vineyard, we describe, here, the possibilities of these two techniques with respect to analytical performance. For this purpose, in the laboratory, we analyzed archived agricultural soil samples from RMT Quasaprove (www.quasaprove.org). Their element contents were determined beforehand by reference methods (ICP-AES, ICP-MS), then the samples were pressed into tablet form and analyzed by XRF and LIBS.
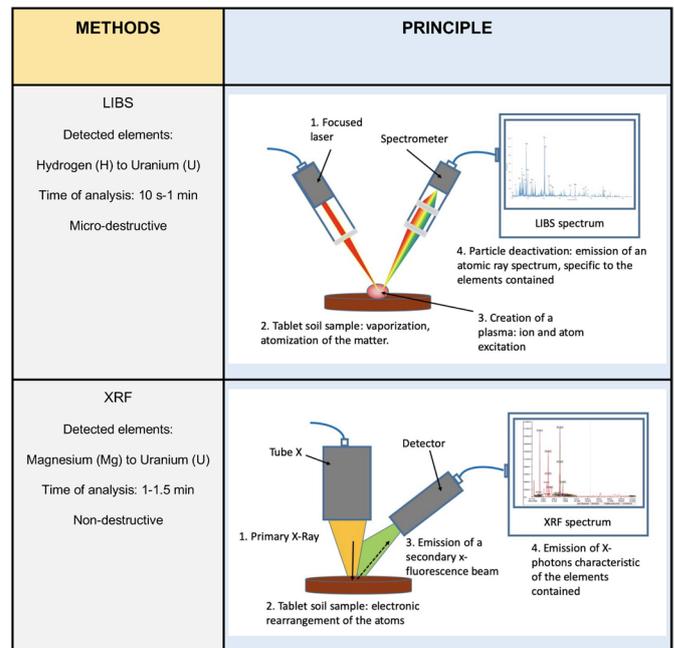

Figure 1. The principle characteristics of the two direct multi-element analysis methods LIBS and XRF.

■ XRF Spectrometry

The XRF is a secondary X-ray emission that is characteristic of chemical elements that make up the sample and that is produced following an external stimulus of sufficient energy (Fig. 1). The analytical signal is made up of intensities of this radiation which is normally proportional to the mass fraction of the elements contained in the sample. The device was directly used as a measurement instrument thanks to an internal calibration geared to the soils that include the identification of intensity peaks of each element and a mathematical correction based on the influence of other elements under measure (matrix effect).

The obtained results (Fig. 2) are in conformity with the expected results for elements in high concentrations (Al, Mg, Fe, K, Ca, P) or in moderate concentrations (Mn, Cu, Zn) with the exception of Na and S. The light elements are relatively insensitive. The correlations between the concentrations measured by XRF on the one hand and by the reference method on the other are good (R^2 > 0.92 and curve close to 1). However, the trace elements (Cd, As, Cr, Ni) are not detected except for Pb (Fig.3), a heavy element and hence sensitive to the XRF detection.

This study *ex situ* permits the conclusion that there is no specific "soil effect". To obtain an increased accuracy, it is possible to personalize the calibrations for same-nature samples taken from element data collection of the spectrometer.

■ LIBS Spectrometry

The LIBS is an atomic emission spectrometry technique. It is based on the interaction of a laser pulse with the matter to be analyzed. This pulse produces the vaporization of the matter (a few micrograms) on its surface. The atoms are brought to a high level of energy. With cooling, these excited species return to their original energy level by emitting photons of their own specific wavelengths. (Fig. 1). These photons are diffracted (creation of a spectrum) and recorded on a detector. The entire process lasts a few milliseconds. The intensity of the emitted rays is normally proportional to the mass fraction of the element contained in the sample. However, this relationship is rarely linear. A univariate calibration, taking only into account the emission ray of the element does not always permit the compensation of the physico-chemical factors that affect the analytical signal (matrix effect). The obtained regression for Mg taken from samples of known concentrations, is illustrated in Fig. 2. For the quantitative analyses, it is necessary to establish a multivariate calibration, that takes into account the concentrations of the other elements found and a certain number of physical properties. It allows for a more accurate estimation of the unknown sample concentrations. On the soils studied, it appears that the elements of high concentration are detected in the LIBS (Fig. 3) including Na and C that were not detected in XRF. The trace elements (As, Cd, Cr, Ni and Pb) and sulfur are not detected.
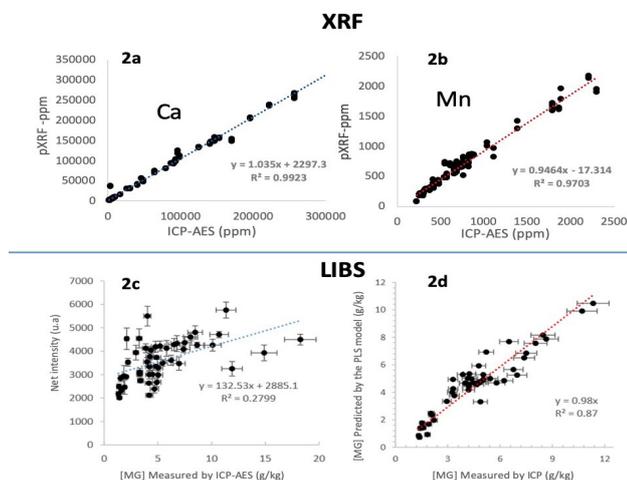
Detection and quantification Soils (Range of Concentrations)	Al 19-91 g/kg	Mg 1-15 g/kg	Fe 9-97 g/kg	K 5-27 g/kg	Ca 2-257 g/kg	P 379-3505 mg/kg	C 8-41 g/kg	N 1-4 g/kg	S 60-600 mg/kg
XRF	🙂	🙂	🙂	🙂	🙂	🙂	❌	❌	❌
LIBS	🙂	🙂	🙂	🙂	🙂	🙂	🙂	🙂	❌

Detection and quantification Soils (Range of Concentrations)	Na 1-16 g/kg	Mn 254-2290 mg/kg	Cu 5-124 mg/kg	Zn 28-238 mg/kg	Cd 0,1-0,7 mg/kg	Pb 14-372 mg/kg	As 4-52 mg/kg	Cr 8-182 mg/kg	Ni 4-46 mg/kg
XRF	❌	🙂	🙂	🙂	❌	🙂	❌	❌	❌
LIBS	🙂	🙂	🙂	🙂	❌	❌	❌	❌	❌

Figure 3. Detection of elements in the soils by LIBS and XRF and measurable by the calibrations obtained under laboratory conditions. Green smiley: Good detection, Orange smiley: detection to be confirmed, Red cross: not detected.

of XRF or LIBS signal intensities. There exist, however, compensation and signal normalization tools to diminish this matrix effect[6, 7].

These techniques are incapable of replacing the methods of traditional chemical analysis in terms of sensitivity, accuracy and precision. Be that as it may, the LIBS an XRF spectrometry methods currently represent the only field devices available that permit the rapid analysis of element composition variations of agrosystems and the diagnosis of the evolution of nutrient stocks of field crops and/or their contamination by micropollutants. ■

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XRF

2a — Ca
$y = 1.035x + 2297.3$
$R^2 = 0.9923$

2b — Mn
$y = 0.9464x - 17.314$
$R^2 = 0.9703$

LIBS

2c
$y = 132.53x + 2885.1$
$R^2 = 0.2799$

2d
$y = 0.98x$
$R^2 = 0.87$

Figure 2. Examples of calibrations obtained in the laboratory for the XRF (2a and 2b) and the LIBS (2c and 2d).

■ Sample humidity

The future challenge would be to reliably measure the composition of the soils in situ after core sampling. The measurements could be studied by the heterogeneity of the sample, its granulometry, its porosity and, above all by its water content. Humidity results in a reduction

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