



Near-infrared spectroscopy and X-ray fluorescence data fusion for olive leaf analysis and crop nutritional status determination

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ABSTRACT

Leaf analysis is a useful way of diagnosing the nutritional status of the plants and therefore fast methods of analysis are demanded to aid in fertilization management decisions. In this work, a strategy based on the combined use of near-infrared spectroscopy (NIR) and portable energy dispersive X-Ray Fluorescence (EDXRF) is proposed as a suitable cheap and rapid alternative to traditional wet analytical methodologies. The approach has the major benefit of minimal sample preparation since leaves need to be only dried and ground. The ability of both techniques individually and applying two strategies of data fusion for the prediction of the most important plant nutrients, namely N, P, K, Ca, Mg, Mn, Zn, and B was tested. Predictive models were constructed using Partial Least Squares (PLS) to correlate the spectra with the nutrient contents. Models of unequal prediction performance in terms of the ratio of predictive deviation (RPD) were obtained for the different parameters when considering both techniques separately. Low-level data fusion, which consists of a concatenation of the raw data from both techniques, showed little improvement and even decreased the predictive ability for some elements. Better results were obtained with mid-level data fusion, that is, merging data after a feature extraction step performed by means of Principal components analysis (PCA). The results show that a fair quantitative prediction is possible for Ca, K and Mn with RPDs ≥ 2 for external validation, whereas models for N and P allowed a semiquantitative estimation. Mg and B models were less satisfactory and can be used only for distinguish between low and high levels, while Zn content cannot be predicted. Finally, the potential of the fusion of FT-NIR and EDXRF spectroscopic data for the fast screening of olive crop nutritional status has been tested. Deficiencies in important elements like N and K has been successfully detected.

1. Introduction

Efficient nutrient management is a major concern for the future global crop production, particularly in areas of intensive production practices. This is the case of olive cultivation in many areas of the Mediterranean countries, especially south European Union countries. Suitable fertilization decisions require characterization of plant nutritional status. The leaf-nutrient analysis provides an indication of tree nutritional status that can reveal deficiencies and represents an important tool for determining fertilization requirements. The determination of macro and micronutrients normally include wet chemical methods including titrations, colorimetry and atomic techniques like atomic absorption spectroscopy (AA) or inductively coupled plasma (ICP) with optical or mass spectrometric detection [1,2]. All these methods have in common long and tedious sample preparation steps resulting in an expensive labor-intensive and time-consuming analysis.

In the context of sustainable precision agriculture, there is a demand for the introduction of more efficient analytical methods that can replace the traditional laboratory routine analysis allowing for effective crop nutrition monitoring [3].

The use of spectroscopic techniques is increasingly extended as an alternative for traditional laboratory wet methods because they could provide similar results with the benefits of being much faster and simpler. In addition, these techniques are more environmentally friendly, since no chemicals or disposables are needed. In the case of vegetable tissues study, one of the most promising techniques is near infrared spectroscopy (NIR) with several examples of application in different plant leaves. Most of the studies have focused on the determination of N, with good results for apple, cotton and cucumber leaves [4–6]. Other macronutrients, like P and K, have also been successfully predicted in sugarcane [7], and with more difficulties in other plants like tea, rice and fingered citron [8,9]. The determination of

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micronutrients using FT-NIR spectroscopy is less common and in general, calibrations are poorer than for macronutrients [10–13]. These previous studies indicated that the efficiency of FT-NIR spectroscopy in nutrition diagnosis differs among plant species [10]. In the case of olive leaves, few studies are available for characterization of the nutritional status using NIR spectroscopy, only one for determination of N content [14] and another for detection of N and K deficiencies without quantifying [15].

By another side, X-ray Fluorescence (XRF) is a technique that has been widely used for elemental analysis in very different fields [16], but its use in organic samples is much less extended. However, XRF, and particularly energy dispersive X-ray fluorescence (EDXRF) with portable instruments can be advantageous as a lower-cost alternative to ICP-OES and ICP-MS for direct analysis of leaf samples. In recent years, several studies of the application of this technique for element determination have been published for plants leaves [17–20]. Generally, for EDXRF, heavy trace metals such as Mn, Fe, Cu, Ni, and Zn can be detected even with limits of quantification down to a few ppm. Higher concentrations are needed to quantify S, P, K, Mg, and Ca, whereas light elements like B and N are generally not detectable. In most of these studies, the sample was prepared by grinding to a very fine particle size, mixing it with a binder and pressing to produce a homogeneous sample pellet. The use of EDXRF with olive leaves has been reduced to the determination of elevated iron levels in plants infected by “sooty mold” [21] and determination of some elements in olive residual biomass including leaves [22]. Up to our knowledge, no studies have been attempted to the determination of the nutrients in olive leaves using EDXRF.

In the context of leaf analysis for nutrient evaluation, it is clear that both spectroscopic techniques, FT-NIR and EDXRF spectroscopies, can provide complementary information, sharing the benefit of little sample preparation. Furthermore, since they are non-destructive techniques, the same sample can be easily analyzed by both instruments. However, it seems also clear that none of these techniques alone has the potential to provide complete nutrient status characterization, whereas their application in parallel is an interesting focus of research. In this work, we address the question of how to merge the information obtained from both techniques in the most efficient way. There are different strategies of data fusion [23], namely low-level data fusion, which consists in a fusion or concatenation of both raw data, mid-level data fusion, which consists in a previous variable selection or transformation using chemometrics, and to fuse these new variables to construct a new matrix and high level data fusion, a strategy better suited to gain qualitative information [24]. These fusion strategies have provided good results when working with spectroscopic data from different sources, including visible, NIR, and Raman spectra, as well as compositional data obtained by XRF [24–28]. However, no attempts have been made for the use of multiple spectra to characterize the chemical composition of plant leaves. In this work, we will evaluate for the first time the feasibility of combining the spectral information related to both molecular and elemental composition of olive leaves to determine the nutritional status by using different data fusion strategies.

2. Materials and methods

2.1. Leaf sampling and preparation

Leaves samples were obtained from foliar analysis laboratory Agronutrientes Jaén S.C.A. and correspond to more than 30 different municipalities of the provinces of Jaén, Granada, Córdoba, and Girona (Spain). The sampling procedure followed the *Specific regulations of integrated olive crop production, BOJA, 2008, Junta de Andalucía* [29]. Each sample was composed by at least eighty healthy leaves caught from no less than ten olive trees. These leaves were always picked from branches at eye level, and taking the third and fourth pair of leaves of every branch. From each tree, leaves were harvested from the five

orientations of the tree (Center, North, South, East, and West). Samples were collected from 2013 to 2016 years and include different olive cultivars (*Picual*, *Arbequina*, and *Koroneiki*). Leaf samples were washed with phosphate-free soap and distilled water to remove dust and any other contaminants. Samples were oven dried at 60 °C for 24 h and ground using an electric grinder. Samples were stored at 4 °C in the dark until use.

2.2. Spectroscopic techniques

Fourier transform NIR spectra were registered using an Antaris FT-NIR analyzer (Thermo Nicolet Corp.) equipped with an integrating sphere module for diffuse reflectance measurements. Spectra were collected between 4000 and 10,000 cm^{-1} , at 8 cm^{-1} resolution with 128 accumulations. Sampling cups of 30 mm were filled with ground leaf samples and placed on top of the integrating sphere window and rotated for measurement. The background was automatically recorded using the internal gold reference of the sphere.

X-ray fluorescence spectra collection was carried out with a handheld Niton XL3t GOLDD+ (Thermo Fisher Scientific Inc.) equipped with a Rh tube anode of 45 kV and 40 μA maximum and a Geometrically Optimized Large Drift Detector (GOLDD) and placed in the shielded SmartStand (Thermo Fisher Scientific Inc.) to avoid any scattered radiation. The instrument is provided with multiple programmable excitation filters that are optimized for specific ranges: main (40 kV), low (20 kV) and light ranges (10 kV). Approximately 3 g of sample were placed into XRF polyethylene sample cups of 32 mm (24 mm height and 26 mm inner diameter) and covered with a polypropylene film. Infinitely thick geometry is assumed and “soils and minerals” measuring mode was used with 45 s for main range and 30 s for low and light ranges.

2.3. Nutrients determination

The most important plant macro and micronutrients were determined in dry leaf samples [2]. N content was assessed by the Kjeldahl method which involves wet acid digestion. For the rest of the parameters, leaf samples calcination in a muffle furnace at 450 °C during at least 8 h was carried out. Phosphorous and B contents were then measured by colorimetry using the molybdovanadate and azomethine H methods, respectively. K was determined by flame atomic emission spectroscopy and Ca, Mg, Mn and Zn contents were determined by flame atomic absorption spectroscopy.

2.4. Chemometrics

All chemometric treatments were performed using MATLAB 2010a (MathWorks, Natick, USA) employing the PLS-toolbox from Eigenvector Research Inc. (Wenatchee, USA).

Hierarchical cluster analysis (HCA) was used to select representative samples to build the calibration dataset. To do this, four matrixes containing the analytical parameters of nutrients corresponding to each year were considered. The Ward's minimum variance method was used to create the dendrogram joining the existing clusters such that the resulting pooled within-cluster variance (with respect to each cluster's centroid) is minimized.

Different preprocessing methods were tested for FT-NIR and EDXRF spectra namely mean center, baseline correction, second derivative and detrend.

Partial least squares (PLS) regression method was used to build predictive models for nutrients from the spectra by calculating a small number of orthogonal factors (latent variables) that provide the maximum correlation with the dependent variable (concentration of the nutrients). Cross-validation by random subsets (5 groups and 5 iterations) was used to estimate the performance of the models when applied to new data. This involves that 27 samples are removed in each

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