Spectrochimica Acta Part B 94–95 (2014) 27–33

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Laser ablation inductively coupled plasma optical emission spectrometry for analysis of pellets of plant materials

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ARTICLE INFO

Article history:
Received 30 January 2014
Accepted 7 March 2014
Available online 18 March 2014

Keywords:
LA-ICP OES
Laser ablation
Optical emission spectroscopy
Plant material
Macronutrient
Micronutrient

ABSTRACT

An evaluation of laser ablation inductively coupled plasma optical emission spectroscopy (LAICP OES) for the direct analysis of pelleted plant material is reported. Ground leaves of orange citrus, soy and sugarcane were comminuted using a high-speed ball mill, pressed into pellets and sampled directly with laser ablation and analyzed by ICP OES. The limits of detection (LODs) for the method ranged from as low as 0.1 mg kg^{-1} for Zn to as high as 94 mg kg^{-1} for K but were generally below 6 mg kg^{-1} for most of the elements of interest. A certified reference material consisting of a similar matrix (NIST SRM 1547 peach leaves) was used to check the accuracy of the calibration and the reported method resulted in an average bias of ~5% for all the elements of interest. The precision for the reported method ranged from as low as 4% relative standard deviation (RSD) for Mn to as high as 17% RSD for Zn but averaged ~6.5% RSD for all the elements ($n = 10$). The proposed method was tested for the determination of Ca, Mg, P, K, Fe, Mn, Zn and B, and the results were in good agreement with those obtained for the corresponding acid digests by ICP-OES, no differences being observed by applying a paired *t*-test at the 95% confidence level. The reported direct solid sampling method provides a fast alternative to acid digestion that results in similar and appropriate analytical figures of merit with regard to sensitivity, accuracy and precision for plant material analysis.

1. Introduction

Essential elements are classified as macronutrients (N, P, K, Ca, Mg, S) and micronutrients (Fe, Cu, Mn, Zn, B, Mo, Ni and Cl) and the classification is based on the relative abundance in plants. From the knowledge of the concentration of the most important nutrients, it is possible to define a strategy to correct for deficiencies, if present, that will limit the production and/or the quality of plant materials. Under limited conditions, the plant may exhibit visual symptom(s) indicating the deficiency for a specific nutrient, which normally can be corrected or prevented by supplying the most appropriate fertilizer.

Foliar nutrient analysis is a useful diagnostic tool to complement soil testing as a best-management practice with plants [1]. In general, the determination of nutrients in plant materials is carried out in leaves properly collected, washed, dried and homogenized [2]. The homogenized samples are frequently acid digested [3] for further analysis by inductively coupled plasma optical emission spectroscopy (ICP OES), flame atomic absorption spectrometry (FAAS), inductively coupled plasma mass spectrometry (ICP-MS) [4–7] or by using other analytical methods [8].

The procedures utilized for the acid digestion of plant material are relatively simple, but can be time-consuming compared to the procedures for analysis of solids using atomic spectrometry techniques. Direct solid sampling analysis of plant material offers a practical advantage over wet digestion methods, including time-saving, lower risks of contamination, improved laboratory safety (no reagent manipulation, no chemical residues), and minimal number of uncertainty sources. Solid sampling analysis of plant materials by different analytical techniques have been reported [9], such as micro-energy dispersive X-ray fluorescence spectrometry (μEDX) [4], laser ablation ICP-MS (LA-ICP-MS) [10,11], electrothermal vaporization inductively coupled plasma optical emission spectrometry (ETV-ICP OES) [12,13], secondary ion mass spectrometry (SIMS) [9], proton/particle induced X-ray emission (PIXE) [9], X-ray and synchrotron techniques [9,14] and laser-induced breakdown spectroscopy (LIBS) [15,16].

In the case of plant leaves, a grinding step, usually referred to as comminution [2], is necessary prior to the micro-analysis due to the inherent heterogeneity of the elemental concentration distribution within the leaf. In general, pellets of plant materials have been prepared prior

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http://dx.doi.org/10.1016/j.sab.2014.03.005
0584-8547/

to analyte determination [15,17]. The test portion usually analyzed by microanalytical techniques varies from 0.1 to 10 mg [18], and thus the comminution procedure should be effective for obtaining appropriate homogeneity. The cohesion of the resulting pellet has also been reported to improve the measurement precision [19], and enhances the analyte emission line intensity by reducing the particle size distribution and pellet porosity [20].

The first attempt for coupling a laser ablation (LA) unit to the inductively coupled plasma of an optical emission spectrometer was made by Thompson et al. [21] for the analysis of steel and silicate rocks. To obtain good results, authors recommended that analytes should be homogeneously distributed in the matrix and that calibration curves should be linear.

There are many contributions in the literature dealing with laser-based microsampling coupled to ICP-MS which have been successfully employed in spatially-resolved spectrochemical analysis of biological samples [9,11,22]. Regarding LA-ICP OES, to our knowledge, this method has not yet been used for quantitative analyses of plant material. The reader will find very useful information on fundamentals of laser–sample interactions, including the laser parameters, plasma conditions and sample surface [23–25], and applications such as shell analysis in geochemistry [26,27], analysis of heterogeneous catalysts in industry [28] and analysis of glass in forensic chemistry [29]. More information on laser ablation in analytical chemistry can be found in excellent reviews from Russo et al. [30,31], and in contributions from Gooijer and Mank [32] and Smith [33].

The main objective of this work is to demonstrate that LA-ICP OES can be used for quantitative analysis of pelleted plant materials. In the present study, the evaluation was based on Ca, Mg, P, K, B, Fe, Mn and Zn measurements in test samples of citrus, soy and sugarcane leaves. Sample preparation was also evaluated with particular attention to the optimization of solid sampling by laser ablation, including the use of Sc as an internal standard for the correction of possible variations in the ablated mass. LA-ICP OES can also be viewed as an analogous technique to the previously reported LIBS [15] method and compared within the same context with regard to the analytical figures of merits.

2. Experimental

2.1. Description of samples and sample pre-treatment

Leaves of orange citrus (*Citrus sinensis*), soy (*Glycine max*) and sugarcane (*Saccharum officinarum*) were used in this work. The leaf samples were collected from plants and washed with tap water, rinsed twice with distilled water and three times with high purity water to remove contaminants [20]. For sugarcane leaves, the central vein was removed as recommended [34]. For soy and orange citrus leaves, whole leaves were used. After washing, samples were dried, chopped, and oven-dried to constant mass at 60 °C.

2.1.1. Grinding procedures and pellet preparation

Samples were initially ground using a cutting mill (Marconi LTDA, model MA680, Piracicaba, SP, Brazil) with an outlet aperture of 600 μm. Thereafter, samples were comminuted in a mixer mill (Retsch, model MM 200, Haan, NW, Germany), with a tungsten carbide (WC) container and one 9 mm WC ball. Each sample was homogenized for 5–120 min, with a frequency of 25 Hz, in order to investigate the influence of particle size distributions on the quality of pellet formation for appropriate sampling in the test samples.

Pellets were prepared by using a manual press (Carver Bench top Pellet Press, model 4350L, Wabash, IN, USA) by transferring approximately 0.4 g of comminuted material to a 15 mm die set under vacuum at 8.0 t cm^{-2} for 5 min. Resulting pellets were approximately 2 mm thick and 15 mm diameter.

2.1.2. Internal standard

Scandium (Ricca Chemical Company, Arlington, TX, USA) was used as an internal standard by pipetting 160 μL of a solution containing 400 mg kg^{-1} Sc over the comminuted material prior to pressing into a pellet as described elsewhere [35]. Thereafter, the resulting mixture was homogenized, and dried at 55 °C for 24 h.

2.2. Instrumentation

An ICP OES (PerkinElmer, model Optima 7300 DV, Waltham, MA, USA) equipped with an Echelle-based polychromator and two segmented-array charge-coupled device detectors for ultraviolet (UV) and visible (VIS) range was used. Laser ablation analyses were performed using a 266 nm Nd:YAG laser ablation system (CETAC Technologies, model LSX-500, Omaha, NE, USA). The LSX-500 sample cell was mounted on an X–Y–Z translation stage, with a step size increment of 0.25 mm. To achieve optimal reproducibility, highest signal-to-noise ratio (SNR), precision and accuracy, the effect of laser energy per pulse at 10 Hz was also evaluated. The laser pulse was focused on the surface of the test sample using a depth profiling ablation mode and a 200 μm spot size as previously reported for elemental analysis of cotton and glass [29,36]. In addition, the signal integration was accomplished in transient mode [29] with a 20 s argon blank followed by a 50 s ablation of the test sample. As the initial laser coupling can cause signal instability [37], the first 20 s of the ablation signal was ignored for analytical signal integration. The cell was swept for an additional 30 s post-ablation to remove material from the cell and tubing to avoid carryover between replicates. Argon has been utilized as plasma and auxiliary gas as well as the entire makeup gas (0.5 L min^{-1}) for transport of ablated particles [29]. All analyses were conducted with ten replicates for every pellet with distances between spots of at least 1.5 mm. The laser fluence for all studies was approximately 9.2 J cm^{-2}.

2.2.1. Limits of detection

The limits of detection for LA-ICP OES analyses were estimated using CRMs with the lowest mass fraction of the analyte in the calibration curve [38]. The standard deviation of the background (s) was measured during the first 20 s gas blank. The LODs were calculated as $3.3\ s / b$ [39,40], where b is the slope of the calibration curve and s is the estimated standard deviation of the blank signal measurements.

2.2.2. Certified reference materials

Calibrations were carried out with the following CRMs from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA): apple leaves (SRM 1515), peach leaves (SRM 1547), spinach leaves (SRM 1570a), tomato leaves (SRM 1573a), and pine needles (SRM 1575a).

2.2.3. Acid digestion and ICP OES

The CRMs and plant materials were microwave-assisted acid digested in triplicate. A closed vessel microwave oven (ETHOS 1600, Milestone, Italy) was used according to the following procedure: 250 mg of ground material was accurately weighed in the TFM® vessels and then 6.0 mL of 65% v v^{-1} HNO_3 and 1.0 mL of 30% v v^{-1} H_2O_2 were added. Thereafter, the residual solutions were transferred to 25 mL volumetric flasks and the volume was made up with high purity deionized water (resistivity 18.2 MΩ cm). The final solutions were analyzed by a radially viewed ICP OES (Vista RL, Varian, Australia) [41].

2.2.4. Sample characterization

A digital microscope (Keyence, model VHX-1000, Osaka, Japan) was used for particle size inspection and imaging of the morphology and volume of the resulting craters. A small portion of milled sample was fixed onto a double-sided carbon conductive tape and observed with 200× magnification. The density of pelleted material was determined taking into account the width and thickness of the pellet.