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Influence of particle size distribution on the analysis of pellets of plant materials by laser-induced breakdown spectroscopy

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ABSTRACT

Pellets of sieved plant materials (150, 106, 75, 53 and 20 μm sieve apertures) were prepared and analyzed by laser-induced breakdown spectroscopy (LIBS), and the results for Ca, K, Mg, P, B and Mn were discussed as a function of particle size distribution. This parameter is of key importance for appropriate test sample presentation in the form of pressed pellets for quantitative analysis by LIBS. Experiments were carried out with a Q-switched Nd:YAG laser at 1064 nm, and a spectrometer with Echelle optics and an intensified charge-coupled device. Results indicated that smaller particles yielded up to 50% emission signal intensities' enhancement and attained better measurements' precision (site-to-site variation). Moreover, matrix effects were reduced by analyzing pellets prepared from <75 μm sieved fractions (mean particle size = 32 μm ; d_{95} = 102 μm) and by using a 50 J cm^{-2} laser fluence (220 mJ per pulse; 750 μm laser spot size). The preparation of pellets from laboratory samples with monomodal particle size distributions, where most particles were smaller than 100 μm , was decisive for improving analyte micro-homogeneity within the test samples and for attaining lower coefficients of variation of measurements, typically lower than 10% (n = 10 sites per pellet; 20 laser pulses per site).

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an attractive and powerful tool for direct solid analysis of agricultural, environmental and industrial samples due to its inherent analytical capabilities for fast and simultaneous multielemental determinations [1]. LIBS presents appropriate analytical figures of merit aiming at the quantitative determination of P, K, Ca, Mg, B, Cu, Fe, Mn, Zn [2] and Si [3] in pellets of plant materials. Although the use of matrix-matched standards has been recommended [4], the establishment of boundary conditions for quantitative analysis is still necessary, mainly to compensate the variations in laser–sample interactions in different matrices [2].

Particle size distribution of ground leaves is a key parameter for appropriate test sample presentation in the form of pressed pellets [2,5]. In fact, there are some indications that matrix effects can be reduced by analyzing pellets prepared from particles smaller than 75 μm [2,5]. The particle decomposition and vaporization, as well as the analyte atomization and excitation efficiencies within laser-induced plasmas, are generally favored when smaller particles are ablated. There is an inverse relationship between particle size and

sensitivity of the calibration curve, with the slope increasing as the particle size decreases [6,7].

The effect of particle size on the analysis of aerosol by LIBS has been exploited elsewhere [8]. While the analysis of aerosols dates back to some of the earliest LIBS contributions, the complex nature of the physical processes involved in the laser–particle interactions is not well understood [8,9]. In general, there is an upper particle size limit beyond which the particle is not completely vaporized, thus decreasing the relationship between the particle size and emission line intensity [6,10,11]. The upper size limit depends on the particle composition and on the experimental conditions (e.g., laser fluence and plasma volume), being often smaller than 10 μm [12] for attaining complete particle vaporization as well as quantitative analyte diffusion into laser-induced plasma.

Particle size distribution critically affects the performance of microanalytical methods [13] because the small mass of the test portion (e.g. 0.001–10 mg) may not represent the bulk sample composition, leading to imprecise and inaccurate results [13–15]. This holds true also for electrothermal vaporization inductively coupled plasma optical emission spectrometry (ETV-ICP OES) [16], laser ablation ICP OES (LA-ICP OES) [17], LA-ICP mass spectrometry (LA-ICP-MS) [18], solid sampling graphite atomic absorption spectrometry (SS-GFAAS) [19], and micro-energy dispersive X-ray fluorescence spectrometry (μ -EDXRF) [20,21].

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Plant materials usually contain particles of different compositions, which are intrinsically inhomogeneous at a microscopic scale [22,23]. Therefore, grinding procedures should be effective for obtaining finer comminution [5]. Laboratory samples presenting narrow particle size distribution with most of the particles smaller than 10 μm may fulfill the requirements for homogeneity at smaller sample sizes (e.g., 1.0 mg) [13]. Nevertheless, there was a recommendation that reference materials suitable for microanalysis may present a narrow particle size distribution, but with most particles smaller than 50 μm [15]. Therefore, the quality of LIBS results (i.e. trueness and measurement precision) depends on particle size distribution for pellet preparation and on the micro-homogeneity of the analytes within the test sample [2].

The aim of this work was to evaluate the influence of particle size distribution on the analysis of pellets of plant materials by LIBS. The variations in Ca, K, Mg, P, B and Mn emission signal intensities and measurement precision were evaluated by analyzing pellets prepared with different particle size distributions.

2. Materials and methods

2.1. Sample preparation

Boldo (*Peumus boldus* Molina) leaves were selected as laboratory sample. Leaves were ground in a Wiley type cutting mill MA-340 (Marconi, Brazil) with a 600 μm outlet aperture. Thereafter, this material was comminuted in a cryogenic mill (Spex 6800 Freezer Mill, USA) after a 5 min pre-cooling step, during 6, 10 and 30 min (3, 5 and 15 cycles of 2 min grinding, respectively), with 1 min re-cooling step between cycles [21]. The whole comminuted laboratory sample was sequentially sieved through stainless steel sieves of 150, 106, 75, 53 and 20 μm apertures (ASTM 100, 140, 200, 270, and 635 mesh), assisted by an electromagnetic vibratory shaker (Bertel, Brazil).

Pellets were prepared in a Spex model 3624B X-Press by transferring 0.5 g of each sieved fraction to a 15 mm internal diameter stainless steel die set and applying 8.0 t cm^{-2} for 5 min. The powdered materials and pellets were oven dried at 60 $^{\circ}\text{C}$ and kept in a desiccator containing anhydrous magnesium perchlorate.

2.2. LIBS instrumentation

Experiments were carried out with a Q-switched Nd:YAG laser (Brilliant, Quantel, France) at 1064 nm, generating 5 ns pulses up to (365 ± 3) mJ, in a 6 mm diameter beam with M^2 factor < 2 , at 10 Hz repetition rate. The laser pulse was focused on the pellet surface by a convergent lens with 25.4 mm diameter and 200 mm focal length (Newport, USA). Individual test samples (i.e. 15 mm diameter pellet) were placed into a plastic sample holder in a two-axis manually controlled translation stage that moved in the plane orthogonal to the laser direction [24]. Argon flowing at 5.0 L min^{-1} was continuously fed into the ablation atmosphere. The plasma emission was focused by a telescope, composed by 50 and 80 mm focal length fused silica lenses (LLA Instruments GmbH, Germany), into an optical fiber (1.5 m, 600 μm core) coupled to the entrance slit of a model ESA 3000 spectrometer with Echelle optics and an intensified charge-coupled device (LLA Instruments GmbH, Germany).

The lens-to-sample distance was adjusted at 175 mm for obtaining 750 μm laser spot sizes on the sample surface. The sampling strategy was based on site-to-site measurements, where 10 different sites on the pellet surface were assayed. Each test portion corresponded to the mass removed from each site after 20 laser pulses at 25 or 50 J cm^{-2} (110 and 220 mJ per pulse, respectively). The pulse energy was monitored with an energy meter equipped with a pyroelectric sensor (FieldMaxII-P Coherent, USA). Plasma emission was measured by using 2.0 μs delay time and 5.0 μs integration time gate [24]. The

following emission lines were used: Ca I 442.544, K I 404.414, P I 213.618, Mg I 277.983, B I 249.773 and Mn II 257.610 nm.

2.3. Acid digestion and ICP OES measurements

The sieved fractions were microwave-assisted acid digested and the resulting solutions were analyzed by ICP OES in order to investigate the possible occurrence of contamination and elemental fractionation through sieving (i.e. chemical segregation). A two-tailed Student's *t*-test was applied to compare the elemental concentrations in different sieved fractions prepared from Boldo leaves.

Microwave-assisted acid digestions were carried out in closed TFM® vessels (ETHOS 1600, Milestone, Italy) in triplicate. A 250 mg test portion was digested with 6.0 mL of 20% v/v HNO_3 and 2.0 mL of 30% m/m H_2O_2 up to 220 $^{\circ}\text{C}$. Details on the microwave heating program are described elsewhere [4]. The contents of Ca, K, Mg, P, B, Cu, Fe, Mn and Zn in the final digests were determined by a radially-viewed inductively coupled plasma optical emission spectrometer (Optima 3000 DV, PerkinElmer, Germany) [3].

Four certified reference materials (CRMs) from the National Institute of Standards and Technology (NIST, Gaithersburg, USA) were used to check the accuracy of the results related to the acid digests analyzed by ICP OES: Apple Leaves (NIST SRM 1515), Peach Leaves (NIST SRM 1547), Trace Elements in Spinach Leaves (NIST SRM 1570a) and Tomato Leaves (NIST SRM 1573a).

2.4. Particle size distributions

The particle size distributions were obtained by laser diffraction using a MicroTec Plus Analysette 22 (Fritsch, Germany) analyzer. The sieved fractions of the comminuted laboratory samples (50–100 mg) were ultrasound-assisted dispersed in water and transported towards the measuring cell, where the suspension flowing at 6 L min^{-1} across the laser beam was analyzed. Measurements were made in triplicate.

2.5. Scanning electron microscopy

The morphological characteristics of the pellet surface were investigated with a LEO scanning electron microscope (StereoScan 440, United Kingdom). Pellets were covered with a thin Pt layer during 80 s using a Bal-Tec equipment (MED 020, United Kingdom) and the micrographs were obtained by using an electron acceleration voltage of 10 kV and a secondary electron detector.

2.6. μ -EDXRF measurements

Among the elements selected in the present contribution, potassium was chosen for micro-energy dispersive X-ray fluorescence spectrometry (μ -EDXRF) mapping due to appropriate limit of quantification (ca. 0.9 g kg^{-1} K [20]), which provides accurate measurements for each 400 sites, even for the most heterogeneous fraction.

The spatial distribution of potassium in pellets of different fractions of Boldo leaves was assessed by μ -EDXRF. To this end, a benchtop instrument (μ EDX-1300, Shimadzu, Japan) furnished with a Rh X-ray tube and a Si(Li) semiconductor detector was used. A 1.0- mm^2 area was randomly selected on the surface of each pellet comprising 400 sampling sites of 50 μm X-ray spot size and a 50- μm step from each site. The μ -EDXRF instrumental parameters were 15 kV tube voltage, 100 μA tube current, and 10 s measurement time per site (with 25% dead time) [20].

Semi-quantitative data were estimated by dividing the potassium mass fraction in the bulk sample by the averaged K $\text{K}\alpha$ 3.31 keV characteristic X-ray intensities from 400 sites in the 1.0 mm^2 -sampling area. The resulting factor was used for converting intensity (cps μA^{-1}) into mass fraction (g kg^{-1}) units.

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