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Evaluation of grinding methods for pellets preparation aiming at the analysis of plant materials by laser induced breakdown spectrometry

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ABSTRACT

It has been demonstrated that laser induced breakdown spectrometry (LIBS) can be used as an alternative method for the determination of macro (P, K, Ca, Mg) and micronutrients (B, Fe, Cu, Mn, Zn) in pellets of plant materials. However, information is required regarding the sample preparation for plant analysis by LIBS. In this work, methods involving cryogenic grinding and planetary ball milling were evaluated for leaves comminution before pellets preparation. The particle sizes were associated to chemical sample properties such as fiber and cellulose contents, as well as to pellets porosity and density. The pellets were ablated at 30 different sites by applying 25 laser pulses per site (Nd:YAG@1064 nm, 5 ns, 10 Hz, 25 J cm^{-2}). The plasma emission collected by lenses was directed through an optical fiber towards a high resolution echelle spectrometer equipped with an ICCD. Delay time and integration time gate were fixed at 2.0 and 4.5 μs, respectively. Experiments carried out with pellets of sugarcane, orange tree and soy leaves showed a significant effect of the plant species for choosing the most appropriate grinding conditions. By using ball milling with agate materials, 20 min grinding for orange tree and soy, and 60 min for sugarcane leaves led to particle size distributions generally lower than 75 μm. Cryogenic grinding yielded similar particle size distributions after 10 min for orange tree, 20 min for soy and 30 min for sugarcane leaves. There was up to 50% emission signal enhancement on LIBS measurements for most elements by improving particle size distribution and consequently the pellet porosity.

1. Introduction

The determination of macro (P, K, Ca and Mg) and micronutrients (B, Fe, Cu, Mn and Zn) in plant leaves is of key importance to evaluate the nutritional status of crops of economic interest and is commonly used for the detection of nutritional deficiencies, that may limit the production and/or quality of e.g. fruits, vegetables and cereals [1].

In general, the direct determination of essential elements in plant materials is carried out in leaves properly collected, and requires, at least, three sample preparation steps, namely cleaning (washing), drying and homogenization [2]. Depending on the method chosen such as slurry sampling inductively coupled plasma optical emission spectrometry (ICP OES) [3], slurry sampling graphite furnace atomic absorption spectrometry [4], solid sampling graphite furnace atomic absorption spectrometry (SS-GFAAS) [5], X-ray fluorescence spectrometry [6], laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS) [7], instrumental neutron activation analysis (INAA) [8] as well as LIBS [9,10], a comminution step is also needed.

According to Markert [2], comminution of sample materials is one of the most important steps in the overall analytical procedure. Comminution usually refers to the grinding of solid samples made up of large particles into a powder consisting of small particles. If appropriate, it improves analyte microhomogeneity, and prevents segregation of the material as a result of wide particle size distribution within the sample. Plant materials are not homogeneous and the different concentrations of analytes in the leaves may impair quantitative direct microanalysis. Examples of such variability in plant leaves can be found in a comprehensive review [11].

Indeed, the choice of the grinding method generally depends on the following parameters [2]: (i) overall quantity and number of samples of the material to be homogenized; (ii) particle size of the original sample; (iii) fineness of the material when ground; (iv) physico-chemical properties of the sample to be comminuted and the grinding equipment (possibility of sample contamination and/or analyte volatilization); and (v) hardness of the material to be homogenized.

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Rossbach and Zeiller [12] pointed out that final particle-size distribution is critical for the preparation of natural matrix reference materials suitable for microanalytical techniques. The materials should exhibit a low maximum ($\leq$50 μm) and a narrow range. On the other hand, Kurfürst [13] and Zeisler [14] suggested that sample can be considered homogeneous when its particles are smaller than 10 μm. Thus, grinding procedures for sample comminution should be effective for obtaining smaller particle sizes, especially because the sample mass analyzed by microanalytical techniques usually varies from 0.1 to 10 mg [15].

Both cryogenic grinding [4,16–18] and ball milling [2,7] can be effective to reduce particle size aiming at microanalytical techniques. Sample preparation involving cryogenic grinding of plant materials for pellets presentation to LIBS is discussed elsewhere [10,19].

Arroyo et al. [7] investigated the soil comminution with a planetary ball milling prior to pellet preparation for further analysis by LA–ICP-MS, demonstrating that the particle size of ground material was generally smaller than 1 μm after 20 min grinding in tungsten carbide jars. This homogenization procedure improved cohesion of soil pellets without the addition of binding agents. Furthermore, a representative sampling at the micro-scale and appropriated reproducibility were observed.

LIBS analysis of pellets of plant materials aiming at the determination of macro and micronutrients have been recently described [9,10,20–22]. In LIBS, the laser/sample interaction depends strongly on the laser parameters and on the physical and chemical characteristics of the sample [23,24]. In the case of ground materials, large differences in particle size distribution and particle composition among samples may also produce differences in the laser/sample interaction thus affecting the quality of results [7,9,19]. For the sake of information, in some special applications LIBS can be used to investigate the elemental accumulation in different layers and/or parts of plant leaves without grinding (Galiová et al. [25,26] and Kaiser et al. [27,28]), but this is out of the scope of the present paper.

The aim of this work was to evaluated sample preparation procedures for the comminution of leaves prior to pellet preparation for the determination of macro (P, K, Ca and Mg) and micronutrients (Fe, Cu, Mn, Zn and B) by LIBS. Cryogenic grinding and ball milling were investigated for sugarcane (*Saccharum officinarum*), orange tree (*Citrus sinensis*), and soy (*Glycine max*) leaves comminution. The correlations of sample properties (e.g. fiber and cellulose contents), particle size distribution, pellet porosity, and LIBS results (i.e. emission signal intensity and repeatability) were investigated.

2. Experimental

2.1. 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 beam diameter with quality factor M^2 lower than 2, at 10 Hz repetition rate. The laser pulse was focused on the sample pellet by a plane-convex lens with 2.54 cm diameter and 20 cm focal length (Newport, USA). The lens-to-sample distance (LTSD) and the pulse energy were adjusted at 17.5 cm and 110 mJ, respectively, leading to 25 J cm^{-2} at the sample surface [20].

Individual test samples (i.e. 15 mm pellet diameter) were placed in a manually controlled two-axis translation stage that was moved in the plane orthogonal to the laser propagation direction. Argon flowing at 0.5 L min^{-1} was continuously fed into the ablation atmosphere by one entrance inlet positioned in the sample holder and the flow-rate was controlled by a rotameter. The plasma emitted radiation was collected by using a fused silica lens (i.e. 80 mm focal length) and collimated into a spectrometer optical fiber (1.5 m, 600 μm core) matching its numerical aperture by using a lens of 50 mm focal length (LLA Instruments GmbH, Germany). The optical axis of the collecting system was approximately 25° from the laser axis.

A model ESA 3000 spectrometer (LLA Instruments GmbH, Germany) equipped with echelle optics and focal length of 25 cm with numerical aperture of 1:10, and a 24.5 mm × 24.5 mm flat image plane was used. This was selected as a compromise between resolution in the wavelength range of 200–780 nm and resolving power ranging from 10 to 20 pm. The linear dispersion per pixel ranged from 5 pm at 200 nm to 19 pm at 780 nm. The detector is an ICCD camera, comprised of a Kodak KAF 1001 CCD array of 1024 × 1024 pixels full frame (24 μm × 24 μm) and a microchannel plate image intensifier of 25 mm diameter coupled to a UV-enhanced photocathode. The image signals were digitalized in dynamic range of 16 bits and further processed by an industrial computer. The dark current of the ICCD was automatically subtracted from the measured spectral data. The delay time, integration time gate and the number of accumulated pulses were fixed at 2.0 μs, 4.5 μs and 25, respectively [20].

2.2. Sample pre-treatment and grinding procedures

The collection of leaves was carried out taking into account the agricultural recommendation for plant diagnosis. Leaves of orange tree, soy and sugarcane were washed separately with running tap water and further rinsed twice with distilled water and three times with ultrapure water [29]. For sugarcane leaves the central vein was removed as recommended [29]. For soy and orange tree leaves, the whole dried leaves were used. After washing, samples were dried, chopped, and oven-dried to constant mass at 60 °C, and ground by using a knife mill (Marconi, Brazil) with outlet aperture of 600 μm. The knife ground sample was used in order to facilitate the grinding process in cryogenic or ball mill.

Cryogenic grinding was performed in a cryogenic mill (Spex model 6800, USA) with a self-container liquid nitrogen bath. The pre-cooling time was 5 min and grinding times were in the range from 10 to 50 min (5–25 cycles of 2 min grinding). After each grinding cycle, the magnetic field was turned off for 1 min to allow sample re-cooling. Four laboratory samples of 2 g can be independently and simultaneously ground and homogenized.

Planetary ball milling was carried out in a Retsch model PM 400 mill (Germany) which was furnished with four grinding agate jars (250 mL; Retsch, Germany) containing 10 or 20 g of sample (<600 μm) with 100 agate balls (10 mm diameter). Grinding was performed at 400 rpm, during 5 min clockwise/5 min counterclockwise with 10-s stop before changing the rotation direction. Grinding times from 20 to 60 min were tested for orange tree and soy leaves, and from 60 to 120 min for sugarcane leaves, based on preliminary experiments.

Pellets of ground leaves were prepared in a Spex model 3624B X-Press by transferring approximately 0.5 g of powdered material to a 15 mm die set and applying 8.0 ton cm^{-2} during 5 min. The resulting pellets were approximately 2 mm thick and 15 mm diameter. Thirty different sites on the pellet surface were analyzed. Each test portion was the mass removed from each site of the pellet after 25 laser shots at 25 J cm^{-2}. The background signal, in the surrounding of the selected emission line, was measured, averaged and subtracted from emission line intensity [30]. P I 213.618 nm, K I 404.414 nm, Ca I 442.544 nm, Mg I 277.669 nm, Fe II 261.187 nm, Cu I 324.754 nm, Mn II 257.610 nm, Zn II 206.200 nm and B I 249.772 nm emission lines were chosen taking into account spectral selectivity and sensitivity.

2.3. Particles size and pellets characterization

The determination of particle size distribution of the comminuted leaves was performed by low angle laser light scattering using an LS 13 320 Tornado Dry Powder System (Beckman Coulter, USA), according to the ISO guide 13320-1:1999. Pellets porosity was determined by using a mercury porosimeter (Aminco 5000 psi, USA). Pycnometric density of pellets was determined using a helium pycnometer (Accupyc 1330, Micromeritics Instrument).

The morphological characteristics of the analyzed pellets (i.e. craters) were evaluated using 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 applying an electron acceleration voltage of 10 kV using a secondary electrons detector.

The crater volume on the pellet surface after laser ablation was determined with a Taylor Hobson Precision perfilometer (Formtracer SV C525, United Kingdom).

2.4. Determination of lignin, cellulose and fiber contents

The fiber, lignin and cellulose contents of the orange tree, soy, and sugarcane ground leaves (<600 μm) were determined by using the AOAC official method [31]. The acid detergent fiber (ADF) was determined as the residue remaining after digestion with H_2SO_4 and 20 g L^{-1} cetyl trimethylammonium bromide. The fiber residues were predominantly cellulose and lignin. The ADF content was determined gravimetrically as the residue remaining after acid detergent extraction, and the lignin content was determined gravimetrically after the ADF residue extraction with 72% (v/v) H_2SO_4 and ashed. Cellulose contents were determined by subtracting the pre-ashed lignin value from the ADF values.

2.5. ICP OES analysis of digests

In order to verify the potential contamination occurrence during the comminution procedures with planetary ball mill (i.e. agate devices) or cryogenic mill (polycarbonate tubes and stainless steel devices), all ground materials were microwave-assisted acid digested in triplicate and analyzed by radially viewed ICP OES (Vista RL, Varian, Australia) with the operational conditions described elsewhere [9,10].

3. Results and discussion

It has been frequently mentioned that LIBS is a spectrochemical technique with a minimal or no sample preparation steps. However, in view of the inhomogeneous character of powdered materials, several drawbacks could be expected for quantitative analysis of plant materials [9]. Microanalytical methods based on direct solid sampling generally require grinding procedures for sample homogenization prior to the elements determination [30]. In the case of pellet analysis assisted by laser ablation, the small particles may increase the cohesion of sample pellets improving the reproducibility of measurements. The cohesion of aggregated particles affects precision because the more compact and mechanically resistant the pellet, the more reproducible the laser–sample interaction [7]. Indeed, it has been stressed that particle size distribution is the most important factor related to pellets presentation to LIBS that affects laser ablation efficiency and measurement precision [9].

The microheterogeneity of elements is an intrinsic characteristic of natural samples [32], and the direct analysis of plant materials by microanalytical methods can result in high coefficients of variation of measurements due to the inhomogeneous distribution of elements in the matrix. At our best knowledge, two strategies were evaluated for LIBS analysis of powdered plant materials. One was based on the fixation of the powdered material on a flat surface using a double-sided tape [33,34] and the other by pressing the ground leaves to form a pellet [10]. Although apparently simple, the first alternative requires careful manipulation for the uniform deposition of the comminuted sample onto the double-sided tape for getting reproducible layers.

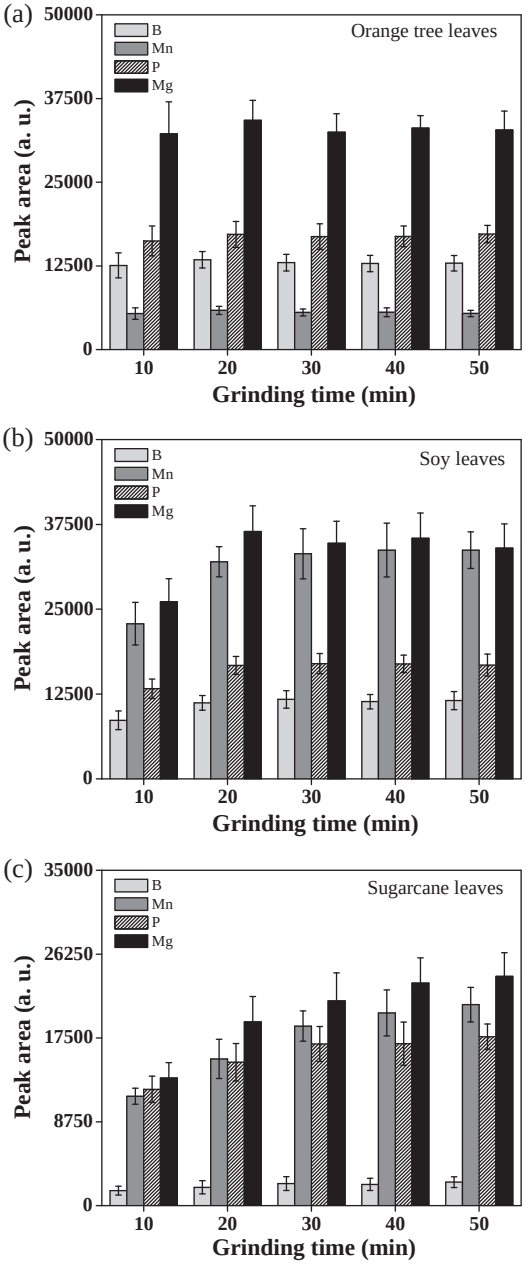

Fig. 1. B I 249.772 nm, Mn II 257.610 nm, P I 213.618 nm and Mg I 277.669 nm emission signal intensities (peak area) from pellets prepared with (a) orange tree, (b) soy and (c) sugarcane leaves after 10 to 50 min of cryogenic grinding. Error bars correspond to ± one estimated standard deviation ($n = 30$).

Pellets prepared with leaves after cryogenic grinding for 10, 20, 30, 40, and 50 min were analyzed by LIBS. A non-paired t-test (at 95% confidence level) was performed to check differences in emission signal intensities of analytes after each grinding time. Fig. 1a shows that 10 min grinding was enough to reach the maximum emission signal intensities of B, Mn, P and Mg in pellets prepared with particles of orange tree leaves (mean particle size 20 μm). In general, similar results were also observed for Cu, Zn, Fe, Ca

Table 1
Fiber, lignin and cellulose contents (% m/m) in orange tree, soy and sugarcane leaves. Uncertainties represented by ± one standard deviation ($n = 3$).

Plant leaf	Fiber	Lignin	Cellulose
Orange tree	26 ± 0.3	7 ± 0.2	19 ± 0.1
Sugarcane	41 ± 0.5	5 ± 0.3	35 ± 0.7
Soy	51 ± 0.9	11 ± 0.4	37 ± 0.5

and K. However, significant statistical differences in emission signal intensities were observed for soy and sugarcane samples after 10 min grinding. It was necessary 20 and 30 min grinding to reach the maximum emission signal intensities for pellets prepared with particles of soy (mean particle size 15 μm) and sugarcane leaves (mean particle size 18 μm), respectively (Fig. 1b and c).

The fiber, cellulose and lignin contents in plant leaves were determined in order to investigate the correlation between material composition and duration of the grinding step (Table 1). The data obtained indicate that the higher the fiber and cellulose contents in the samples the higher the grinding time necessary to reach the maximum emission signal intensities of analytes in pellets analyzed by LIBS (Fig. 1). However, it was not possible to establish correlations with the lignin content and grinding times because orange tree, soy and sugarcane leaves have a narrow range of lignin content (7–11%). According to Van Soest [35], wood tissues with a low lignin-to-cellulose ratio tend to bend rather than break, while with a high lignin-to-cellulose ratio tend to break rather than to bend. Consequently, the less lignified tissues tend to grind in long pieces while more lignified tissues tend to fragment into shorter pieces. During the grinding process the lignin becomes selectively distributed among the larger particles [35]. In the present work, the lignin-to-cellulose ratios were 0.37, 0.30 and 0.14 for orange tree, soy and sugarcane leaves, respectively, suggesting that sugarcane ground leaves samples are more difficult to comminuting than the orange tree and soy leaves.

Initially, the planetary ball milling experiments with 250 mL agate jars were carried out by using 50 grinding agate balls of 10 mm, as recommended by the manufacturer. In this condition, it was observed by visual inspection that comminution was effective only for orange tree and soy leaves. For sugarcane leaves, 100 grinding balls were necessary. In this way, 100 grinding balls were selected for the comminution of all samples.

Fig. 2a shows that at least 20 min grinding with ball mill were needed in order to reach the maximum emission signal intensities from the elements in the pellets prepared with particles of orange tree leaves (mean particle size 15 μm). For pellets of soy leaves (mean particle size 20 μm), no significant differences were observed in emission signal intensities for B, Mn, P and Mg by changing the grinding time from 20 to 60 min (Fig. 2b). In general, the remaining aforementioned elements did not present differences at 95% confidence level in emission signal intensities by increasing the grinding time. Significant differences on particle size distribution were observed for sugarcane leaves processed by different grinding times using ball mill. It must be mentioned that with 20 min grinding it was not possible to obtain pellets with adequate cohesion. Results indicated that at least 60 min were required for appropriate sugarcane leaves comminution (e.g. mean particle size in the order of 15 μm). It is important to point out that by increasing the grinding time from 60 to 120 min, the mean particle size was reduced from 15 to 8 μm. However, no significant differences were observed in emission signal intensities obtained by LIBS (Fig. 2c).

On the other hand, by taken into account the presence of some elements of interest in the components of the grinding materials, experiments were also carried to evaluate the possibility of systematic errors due to contamination. Agate material is composed

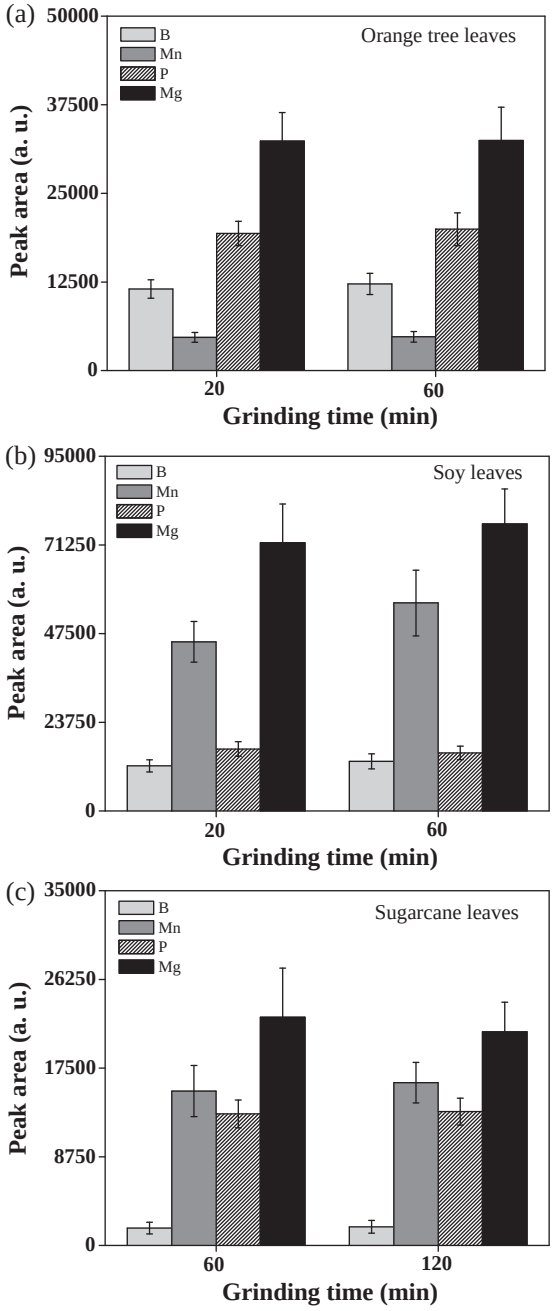

Fig. 2. B I 249.772 nm, Mn II 257.610 nm, P I 213.618 nm and Mg I 277.669 nm emission signal intensities (peak area) from pellets prepared with (a) orange tree, (b) soy and (c) sugarcane leaves after 20, 60, and 120 min of planetary ball grinding. Error bars correspond to ± one estimated standard deviation ($n = 30$).

mainly by Si (99.9%) and, according to the manufacturer, Al, Na, Fe, K, Mn, Mg and Ca are also present in relatively low concentrations (≤0.02% m/m). In case of cryogenic grinding, the magnetic bar and the end-plugs are composed by stainless steel 440 C (major components: 58–60% Fe, 16–18% Cr; minor components: C, P, S, Mo, Mn and Si). Before grinding procedures, the samples were microwave-assisted acid digested and the obtained solutions were analyzed by ICP OES. After each grinding procedure, a portion of comminuted material was also digested and analyzed by ICP OES. The overall results indicated that there were no significant contaminations during the comminution procedures. In addition, the possibility of contamination during the pellet preparation due to stainless steel

Table 2
Particle size parameters after comminution of orange tree, soy and sugarcane leaves by ball and cryogenic grindings.

Sample	Planetary ball milling			Cryogenic grinding		
	Grinding time (min)	Mean size (μm)	d_{95} (μm)	Grinding time (min)	Mean size (μm)	d_{95} (μm)
Orange tree	20	15	38	10	20	64
Soy	20	20	75	20	15	57
Sugarcane	60	15	54	30	18	62

d_{95} = 95% of cumulative particles smaller than 75 μm.

die set was investigated using high-purity cellulose. The results indicated that there was no perceptible contamination.

The reproducibility of laser–sample interaction and, consequently, the repeatability of measurements depend on particle size used for pellet preparation. Table 2 shows that the mean particle size diameter was smaller than 20 μm and 95% of cumulative particles (d_{95}) were smaller than 75 μm, after planetary ball and cryogenic comminution procedures. LIBS analysis of the pellets produced with these particles resulted in coefficients of variation of measurements in the range from 5 to 20% (site-to-site precision, n = 30 sites). Although the mean particle size could be smaller than 10 μm, by increasing the grinding time up to 120 min with ball mill, no significant improvements were observed in emission signal intensities from the investigated elements, as well as in measurement precision (site-to-site repeatability).

The particle size distribution and SEM images of craters produced by laser ablation in pellets prepared with particles of orange tree, soy and sugarcane leaves after ball milling and cryogenic grinding are shown in Figs. 3–5, respectively.

The SEM images and perfilometric analysis showed that pellets prepared with particles obtained by both grinding procedures presented similar crater morphologies, although slight differences were found among plant species. It was observed that leaves with lower fiber content such as from orange tree (Table 1) presented homogeneous craters with lower border deformities (Fig. 3). It must be mentioned that crater diameter and ablation depth per pulse depend primarily on laser irradiance [36], but this parameter was kept constant along this work. In general, laser ablation of pellets prepared with particle sizes lower than 75 μm did not present signs of crack and no binder addition was necessary. The mass ablated in each sampling site was estimated in view of pellet density and crater volume obtained by perfilometric analysis. Under this condition, approximately 100 μg were ablated per site (25 laser pulses per site, n = 30 sites).

Although not shown, the smaller the particles the smaller the pellet porosity, and this could be another factor contributing for better crater uniformity. In this work, it was observed that porosity varies by varying the plant species and the grinding method. In spite of similar particle size profiles after comminution, only soy leaves by both cryogenic grinding and ball milling as well as sugarcane leaves with ball milling, presented approximately the same pellet porosity (16%). On the other hand, up to 31% porosity was found in pellets of sugarcane leaves and orange tree leaves after cryogenic grinding. This shows why precaution is recommended

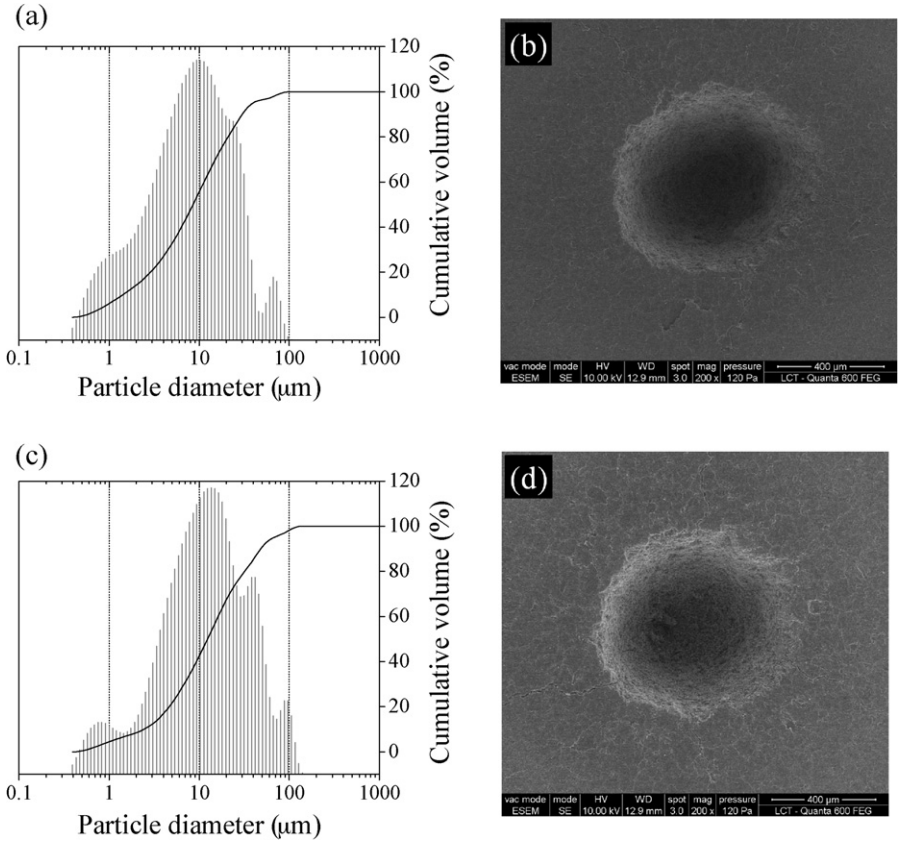

Fig. 3. Particle size distribution and scanning electron microscopic images of craters produced by laser ablation (25 J cm^{-2}, 25 pulses, 10 Hz) in pellets of orange tree leaves. Samples ground for 20 min by using the planetary ball mill (a and b) and 10 min by cryogenic grinding (c and d).

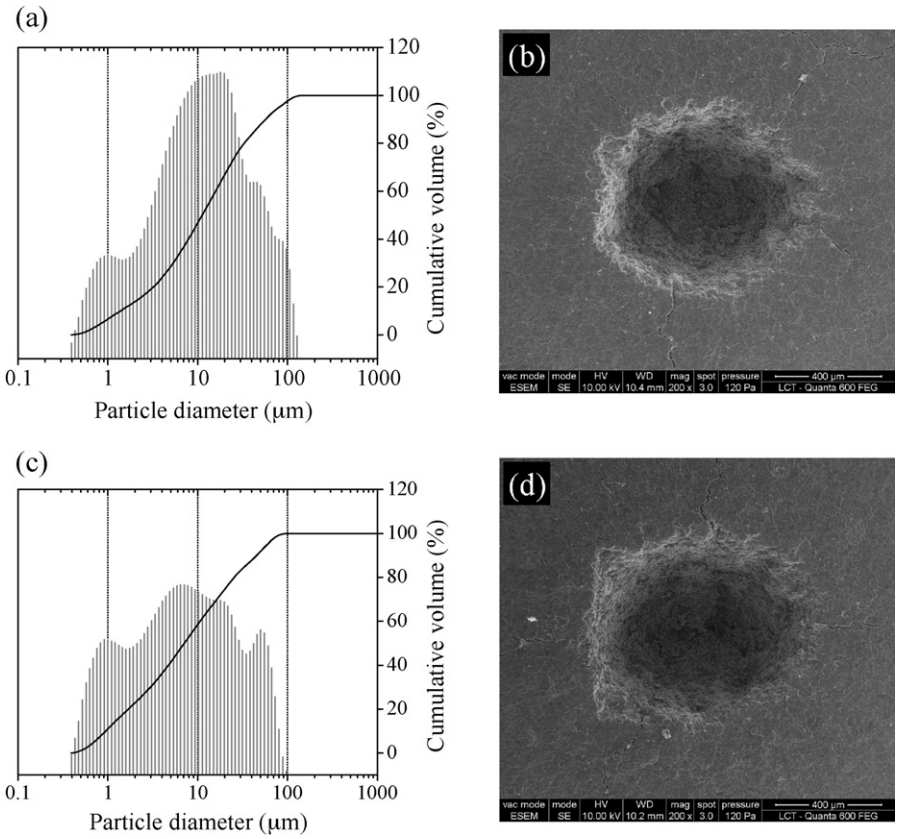

Fig. 4. Particle size distribution and scanning electron microscopic images of craters produced by laser ablation (25 J cm^{-2}, 25 pulses, 10 Hz) in pellets of soy leaves. Samples ground for 20 min by using the planetary ball mill (a and b) and 20 min by cryogenic grinding (c and d).

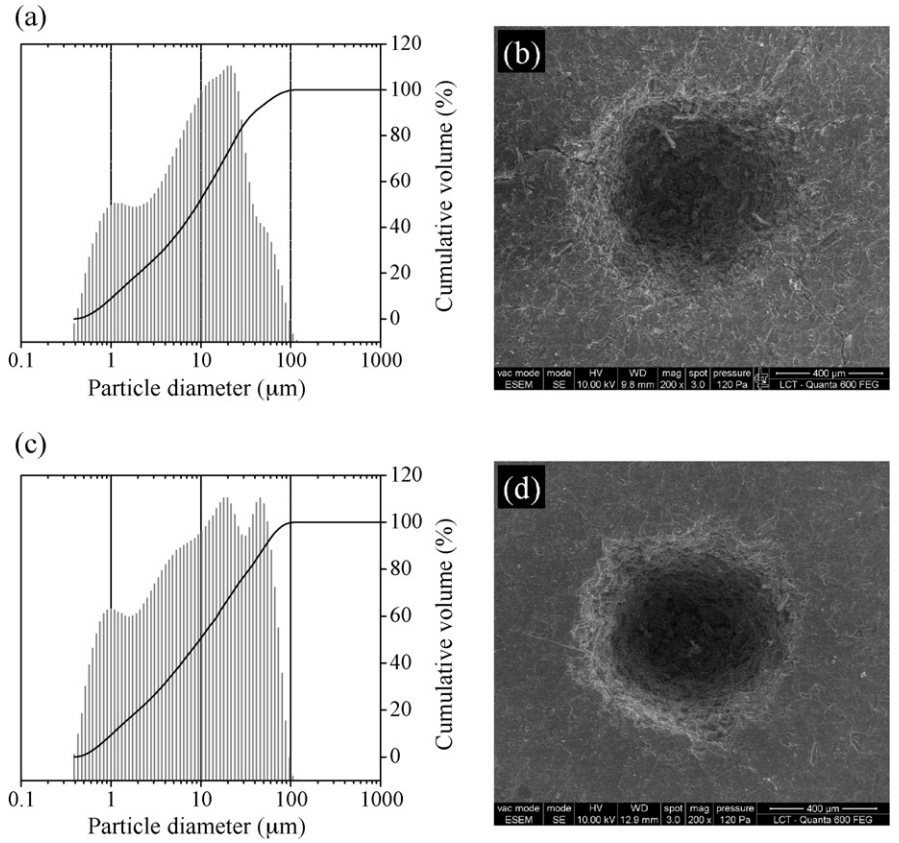

Fig. 5. Particle size distribution and scanning electron microscopic images of craters produced by laser ablation (25 J cm^{-2}, 25 pulses, 10 Hz) in pellets of sugarcane leaves. Samples ground for 60 min by using the planetary ball mill (a and b) and 30 min by cryogenic grinding (c and d).

for LIBS calibration with different plant species, under the experimental conditions outlined in this contribution.

4. Conclusions

Particle size is an intrinsic parameter that influences emission signal intensities in LIBS. Small particles reduce pellet porosity and may influence the ablation process and up to 50% emission signal enhancement on LIBS measurements were observed for most elements. Both planetary ball milling and cryogenic grinding presented good performances for comminuting knife mill ground leaves, allowing simultaneous grinding and homogenization of four independent samples, and can be recommended for pellets preparation for LIBS. The comminution time for getting similar and appropriate particle size distributions depends on the grinding process, on the plant specie and on fiber and cellulose contents. Data obtained herewith suggest that matrix effects can be minimized by using particles smaller than 75 μm, and both cryogenic grinding and planetary ball milling fit for this intended purpose.

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