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Rapid Assessment of Extractability of Macronutrients from Yerba Mate (*Illex paraguariensis*) Leaves Based on Laser-Induced Breakdown Spectroscopy

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Abstract: Leaves of yerba mate plant (*Ilex paraguariensis*) have a wealth of nutrients, ingested by people who drink them in the hot water infusion popularly known as mate. In the present work, the laser-induced breakdown spectroscopy (LIBS) technique was applied for the first time to analysis of the extractability of macronutrients, including Mg, Ca, Na, and K, in commercial samples of yerba mate. Powdered samples from leaves' material were used to simulate the infusion process in the laboratory. To carry out LIBS analysis, the emission spectra were measured before and after the infusion from the samples prepared in pellets. The spectral data were processed and analyzed by a specially designed algorithm. A coefficient of extractability was calculated for each of the investigated macronutrients in the range 34–76%, showing a good correlation with the corresponding elemental concentrations leached into the water infusion, determined by Atomic Absorption Spectroscopy. The obtained results demonstrated the feasibility of our approach for the rapid analysis of extractable macronutrients present in yerba mate leaves.

Keywords: laser-induced breakdown spectroscopy; LIBS; yerba mate; macronutrients

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1. Introduction

Over recent years, research has shown that the leaves of yerba mate plant (*Illex paraguariensis*) are an important source of dietary minerals which are essential to the proper functioning of our body [1]. In South America, yerba mate is extensively cultivated in Argentina, Brazil, Uruguay, and Paraguay. Among them, Argentina is the major producer, consumer and exporting country worldwide, where it is consumed in the form of a hot water infusion traditionally known as mate [2]. Mate is prepared with the dried minced leaves of the plant and a given proportion of twigs, which is added as diluent. During the infusion process, the minerals contained in the leaves of yerba mate leach into the water which is directly ingested by consumers. According to their concentration level, these essential minerals are usually classified into macronutrients (i.e., P, Mg, Ca, Na, and K), and micronutrients (i.e., Mn, Cu, Mo, Cr, Fe, and Zn). While trace amounts of micronutrients are needed in the daily diet, major quantities of macronutrients are imperative to reach the body's nutritional and health requirements. The amounts of macronutrients contained in the crop yields of yerba mate can be affected by several issues along the supply chain, including soil characteristics, water irrigation, amendments, harvesting and processing practices, as well as the conditions under which the infusion is prepared, such as water temperature. In this scenario, the detection of macronutrients available in the final commercial products together with the evaluation of their extractability in the infusion, namely, the amount of the macronutrients that is effectively extracted into water, is of paramount importance for both yerba mate producers and consumers.

Nowadays, many scientific works have been reported dealing with the elemental analyses of yerba mate leaves and its infusion, as well as other plant stimulants, such as tea and coffee. In these studies, different analytical tools, such as ion beam and spectrometric techniques, were routinely employed. For instance, Wrobel et al. [3] determined total Al, Cr, Cu, Fe, Mn, and Ni in black tea, green tea, *Hibiscus sabdariffa*, and *Ilex paraguariensis* (mate) by electrothermal atomic absorption spectrometry (EAAS). Giulian et al. [4] analyzed dried powdered leaves of yerba mate of 20 different Brazilian trademarks. The elemental concentrations of several elements, including Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, and Rb in the commercialized samples and after the infusion were quantitatively determined by using a particle-induced X-ray emission (PIXE) technique. For calibration purposes, apple leaf standards were employed together with the assistance of two other techniques, Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA). The relative elemental percentages removed from the samples in the infusion were studied, as well as their dependence on water volume and temperature for one specific trademark. Malik et al. [5] carried out a quantitative analysis of nutritious and harmful elements for the human diet present in both the raw material and infusions from 31 samples of tea, coffee, rooibos, honeybush, chamomile, and 3 samples of mate, available in the market in Czech Republic. Inductively coupled plasma optical emission spectrometry (ICP-OES) was employed for determination of Al, B, Cu, Fe, Mn, P, and Zn, while atomic absorption spectrometry (AAS) was used for the analysis of Ca, K, and Mg. In addition, Pozebon et al. [6] investigated toxic and nutrient elements in 54 commercial brands of yerba mate from South America. The study was aimed at the determination of trace elements, contaminants, and the calculation of the percentage of extraction of the products produced in the different countries. ICP-OES was employed for the analysis of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, P, Sr, and Zn, and inductively coupled plasma mass spectrometry (ICP-MS) for the analysis of Li, Be, Ti, V, Cr, Ni, Co, As, Se, Rb, Mo, Ag, Cd, Sb, La, Ce, Pb, Bi, and U. Barbosa et al. [7] characterized the composition, the hot water solubility of the elements, including C, N, K, Ca, Mg, P, Al, Mn, Na, Fe, Zn, Ba, Cu, Ni, Pb, Cr, Mo, As, Co, Ag, V, and Cd, and the nutritional value of yerba mate (*Ilex paraguariensis St. Hill*) fruits and leaves collected from four yerba mate provenances of Brazil. Moreover, Vaccari Toppel et al. [8] determined the elemental composition of yerba mate leaves, including Ca, K, Mn, Mg, P, Al, Fe, B, Zn, Ba, Cu, Ni, Cr, V, and Co, from the Southern Region of the state of Paraná, Brazil, by means of ICP-OES. The concentrations of some key elements (i.e., Mn and Al) were found to be closely correlated to the chemical attributes of the cultivated soil of the sampled plants, such as pH. In a different research study, Urruchua et al. [9] investigated recycling of yerba mate waste as a raw material to produce biochar, a sorbent material with a magnetic response that can be potentially applied as a sustainable solution for water remediation processes. The main chemical composition of the material, including C, O, Na, Mg, P, S, K, and Ca, was determined by energy dispersive spectroscopy (EDS).

In spite of their high accuracy, the mentioned analyses often require wet chemistry procedures for sample preparation, e.g., acid digestion, or the use of ionizing radiation sources, e.g., X-rays. At the same time, laser spectroscopic techniques have gained great attention because of their advantageous analytical and practical conditions, namely, remote optical access, avoiding the use of ionizing radiations or chemical reagents and reduced preparation of the samples [10]. Among them, laser-induced breakdown spectroscopy (LIBS) is a useful atomic spectroscopic technique with distinctive advantages in terms of simplicity and versatility to accomplish rapid simultaneous multi-elemental analysis of the chemical composition of a wide variety of sample materials (gas, liquid, or solid) with a minimum of sample treatment [11,12]. LIBS is a very active field of research worldwide, with a widespread range of applications in many fields. Regarding LIBS applications for agricultural studies, the direct analysis of plant materials (leaves, roots, and fruits) has been reported due to its importance to monitoring nutrients and toxic metals [13]. From a review by Santos Jr. et al., it is noticed that Na has been noticeably less investigated than other major elements and only at a qualitative level (see Ref. [13], Table 1 (pp. 4–5)). This may be mainly attributed to the ease of Na contamination of liquid solutions in the laboratory and the high sensitivity for detection of this element for most analytical methods. Thus, the joint action of these issues usually hinders the achievement of accurate quantitative analysis of this element. In a previous study by our group, the suitability of the LIBS method was demonstrated for the analysis of Na in vegetable samples through a convenient liquid-to-solid matrix transformation [14].

To the best of the authors' knowledge, the application of the LIBS technique for the analysis of yerba mate plant has not yet been investigated. To fill the gap, in the present work, the LIBS technique was applied for the first time to the systematic study of yerba mate samples. The focus of the research was mainly on the determination of the extractability of the main macronutrients (Mg, Ca, Na, and K) contained in the final products bought by consumers. Moreover, bearing in mind that the commonly used method of constructing calibration curves to achieve quantitative results may be quite cumbersome and time consuming, with a lack of matrix-matched standards for plant materials, which would limit the applicability of the technique in real-life cases, a derived objective was to develop and test a LIBS-based analytical methodology relying on state-of-the-art insight into the emission and absorption of radiation by LIPs. To evaluate the analytical performance of our approach, the LIBS results were compared with the corresponding concentrations leached into water infusion determined by Atomic Absorption Spectroscopy (AAS). The obtained results demonstrated the feasibility of the LIBS technique for the direct rapid analysis of extractable macronutrients contained in yerba mate samples.

2. Materials and Methods

2.1. Samples

In this study, 10 samples of yerba mate (labelled from 1 to 10) of different trademarks produced in Argentina were employed. The first stage of sample preparation included the successive steps of grounding in a mortar, sieving to eliminate the twigs, and mixing to obtain a homogeneous powder of the leaves' material. Then, the powdered samples, representative of the different brands, were divided into 2 identical sets to be analyzed before and after the infusion process, respectively. The former set was preserved uncontaminated along the infusion process, whilst each powder belonging to the latter set was leached with hot water to simulate the infusion process in the laboratory, as explained in the following. Each powder was put in a small permeable bag which was immersed in 200 mL of ultrapure water at a temperature of 80 °C for 30 min. After infusion, the powders were dried at room temperature. Finally, all the pairs of samples (i.e., before and after the infusion) corresponding to a different brand were prepared in the form of solid pellets for LIBS analysis (Section 2.2). Each pellet was prepared by mixing 2 g of powder with a binder (2 g of polivinilic alcohol, Merck, $(C_2H_4O)_x$, diluted in 5 mL of hot ultrapure water) to improve cohesion. The mixture was stirred well to homogenize it, poured in a plastic die, and left dry at room temperature until hardening to get pellets of approximately 2 g of weight (diameter 3 cm, thickness 0.5 cm). It is worth mentioning that the water and the binder contained trace amounts of the analytes that did not significantly affect their concentrations in the samples. Moreover, the liquid solutions obtained from the individual infusions were frozen and saved to be analyzed using the AAS technique (Section 2.3).

2.2. LIBS Analysis

The employed LIBS equipment is shown in Figure 1. A Q-switched pulsed Nd:YAG laser (Big Sky Laser Technologies Inc., Naperville, IL, USA, wavelength 1064 nm, pulse width 5–7 ns, pulse energy 50 mJ) operated at 2 Hz was used as the excitation source to generate the plasmas in air at atmospheric pressure. The laser beam was directed through a reflective mirror and focused with a lens (200 mm focal length) on the samples. The estimated incident laser irradiance on the sample surface was about 0.5 GW/cm^2. The plasma emission was collected and focused with a quartz lens (100 mm focal length) onto the entrance slit (width 200 µm) of a Czerny–Turner spectrometer (Acton Research Corporation, Acton, MA, USA, focal length 0.39 m, grating of 1200 grooves/mm, spectral resolution 6 Å) coupled with a non-intensified, non-gated linear photodiode array detector (Princeton Instruments Inc., Trenton, NJ, USA, Model RY–1024) with spectral coverage in the 2000–10,000 Å range, over which all atomic and single-ionized elements have emission lines. The detector was triggered at the start of the laser pulse in such a way that it recorded the plasma emission during its entire life time. During the acquisition of the spectra, the samples were rotated at approximately 100 rpm to avoid the formation of a deep crater on their surface. The spectral lines of the elements of interest were measured in suitable spectral ranges (width 500 Å). The recorded spectrum on each spectral range was the result of the in-software accumulation of individual spectra generated from 50 consecutive laser shots to improve the signal-to-noise ratio, after discarding the first 5 cleaning shots delivered to avoid any possible superficial contamination due to handling of the samples.

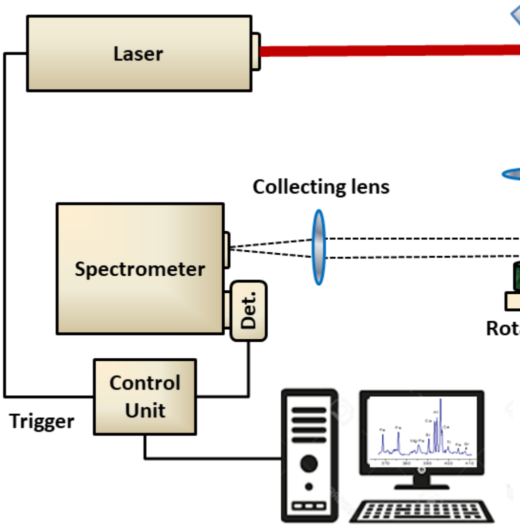

Figure 1. Experimental LIBS setup.

2.3. AAS Analysis

The determination of Mg, Ca, Na, and K in the liquid samples of the infusions was performed by a flame atomic absorption spectrometer (GBC 906, Keysborough, Australia) in air–acetylene flame under standard conditions [15]. The analyzer was calibrated by means of calibration solutions prepared by diluting standards solutions. Linear calibration curves ($R^2 \geq 0.997$) were obtained. The liquid samples were properly diluted and the corresponding absorbance values were measured to obtain the respective concentrations of the analytes. For each sample, two replicated measurements were carried out and further averaged to obtain its final concentration.

3. Results and Discussion

LIBS spectra from yerba mate samples were measured in four selected spectral regions: 2650–3100 Å, 3650–4100 Å, 5650–6100 Å, and 7450–7900 Å, where the main emission lines of the macronutrients investigated were detected. In each region, elemental identification was based on the NIST Atomic Spectra Database [16]. The spectra measured in the different spectral regions are shown in Figure 2 (for sample #1), where intense emission peaks of Mg, Ca, Na, and K are observed. In addition, O was observed because of contributions of both the surrounding ambient air excited by the plasma plume and the sample. Very weak spectral lines corresponding to traces of other minor elements, such as Si, Fe, Al, Ti, and Sr, were also detected. After acquisition, the spectral data (i.e., 1024 pixels vs. emission intensity) were processed by a specially designed algorithm implemented in the MATLAB®

environment which involved successive steps of (i) pre-processing, (ii) spectral analysis, and (iii) calculation of the extractability of the macronutrients, as explained in the following.

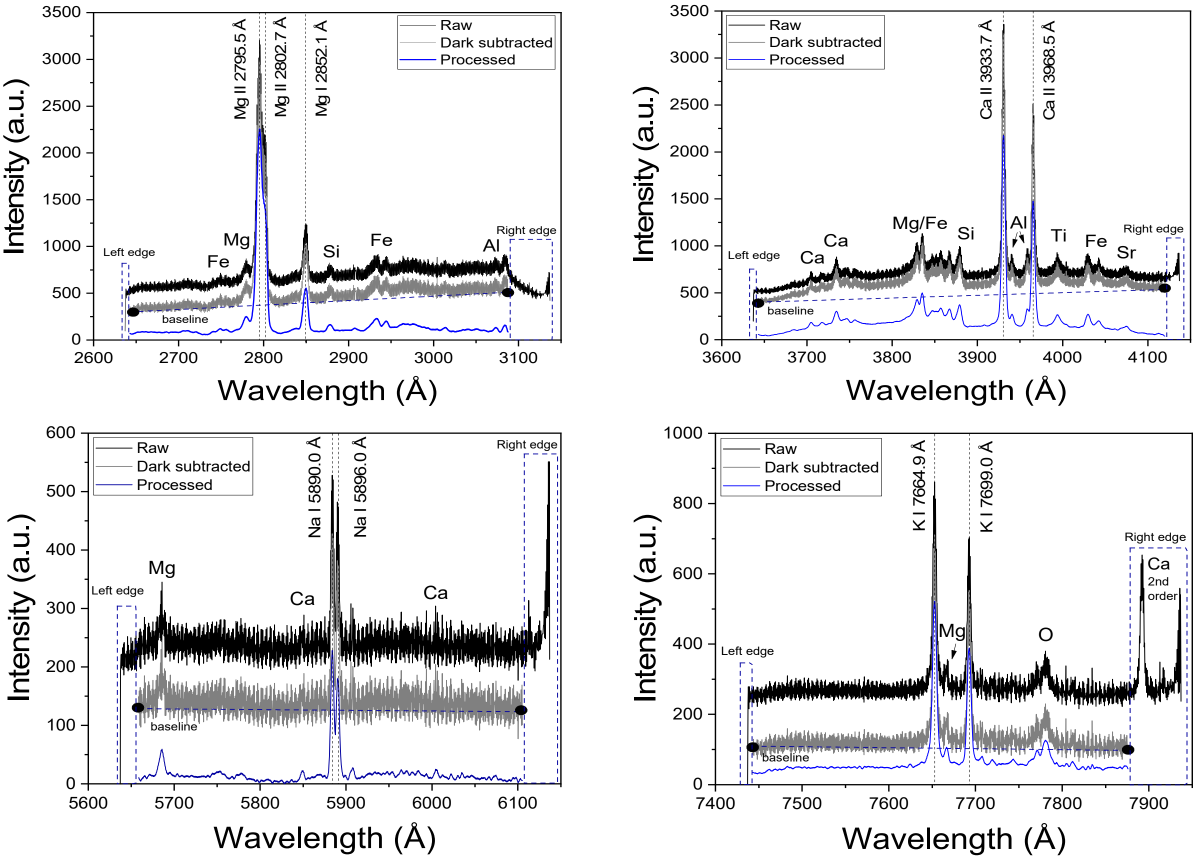

Figure 2. Measured and pre-processed LIBS spectra from yerba mate (sample #1).

3.1. Data Pre-Processing

Firstly, the measured spectra were pre-processed to prepare them for subsequent analysis. Specifically, pre-processing comprised automated routines for edge trimming to eliminate non-meaningful data recorded by the detector, wavelength calibration, removal of the dark current background, and subtraction of the continuous background mainly caused by bremsstrahlung radiation. Wavelength calibration was carried by recording a spectrum of a standard Hg pencil lamp to establish a pixel-to-wavelength relationship applied to the X-axis of all spectra. The background continuum was associated to a baseline under the discrete line spectra. This baseline, with the same number of points (i.e., wavelengths) as the spectra, was calculated by linear interpolation of two reference points located at both sides of each spectrum (after edge trimming), as indicated in Figure 2. For a given spectrum, the abscissas of the reference points corresponded to the left and right edges, whilst the ordinates were estimated by averaging 10 intensity values corresponding to the neighbor points adjacent to the first and last experimental values of each spectrum, respectively. Then, the baseline was subtracted for all wavelengths in the spectra. Pre-processing is illustrated in Figure 2 (for sample #1).

3.2. Spectral Analysis

After pre-processing, the spectra were analyzed to identify the detected spectral lines. Spectral lines with a suitable signal-to-background ratio and free of spectral interference from other elements were selected as analytical lines of the macronutrients (Figure 2). The analytical lines corresponded to transitions belonging to neutral atomic and singly ionized species with available atomic data from the NIST database, summarized in Table 1.

Table 1. Spectroscopic parameters of neutral (I) and single-ionized (II) analytical atomic lines for the studied macronutrients (data from NIST database [16]).

Element	Ionization State	λ_0 (Å)	A_{ji} (10^8 s^{-1})	E_i (eV)	E_j (eV)	g_i	g_j
Mg	I	2852.1	4.91	0.000	4.346	1	3
	II	2795.5	2.60	0.000	4.434	2	4
	II	2802.7	2.57	0.000	4.442	2	2
Ca	II	3933.7	1.47	0.000	3.151	2	4
	II	3968.5	1.40	0.000	3.123	2	2
Na	I	5889.9	0.61	0.000	2.104	2	4
	I	5895.9	0.61	0.000	2.102	2	2
K	I	7664.9	0.38	0.000	1.617	2	4
	I	7699.0	0.37	0.000	1.610	2	2

In Figure 3, the lines from Table 1 are plotted in detail for the pre-processed LIBS spectra measured before and after the infusion. The spectral lines were fit with a Gaussian function (mainly due to the instrumental profile) to get their net intensities, given by the integrated areas of the line profiles after subtracting the background baseline. Then, the net intensities of all the analytical lines corresponding to the same macronutrients were added to obtain their total intensity of emission.

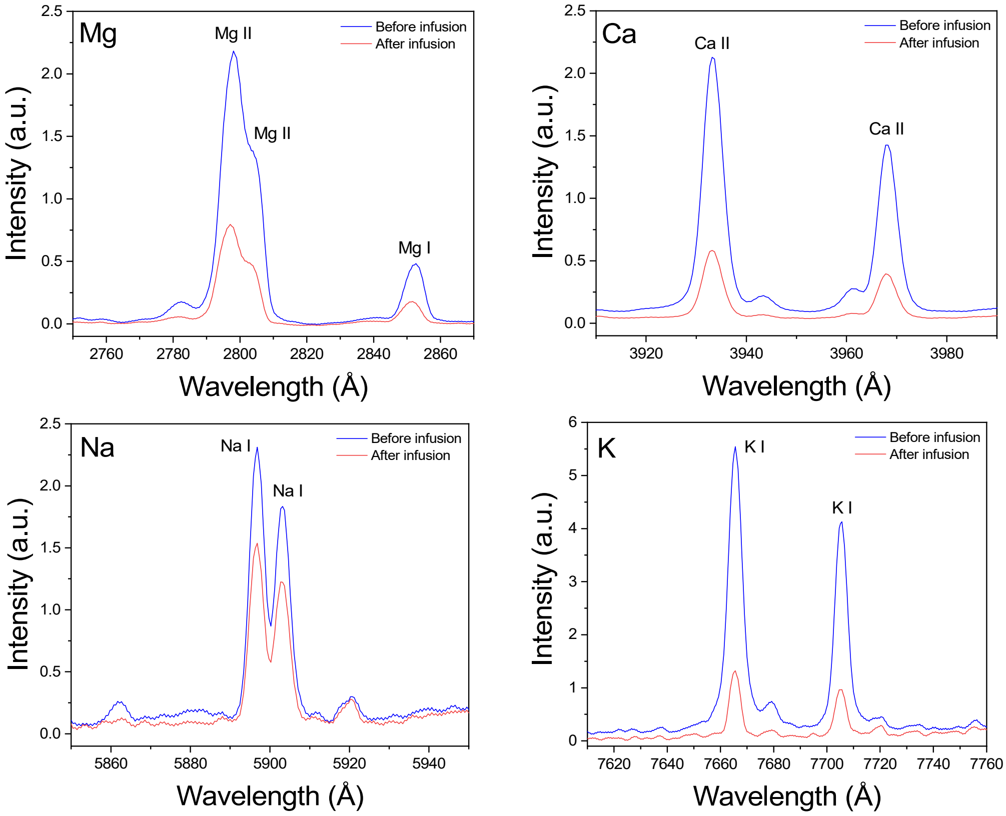

Figure 3. Analytical lines of Mg, Ca, Na, and K measured from yerba mate (sample #1) before and after the infusion process.

The capability of the proposed method to measure variations in the analyte concentrations before and after the mate infusion was assessed. In Figure 4, the total emission intensities calculated for the different macronutrients and samples are compared. It was observed that the intensities of emission measured after the infusion were lower than their corresponding initial values, measured prior to the infusion, thus indicating a significant decrease in their concentrations due to a leaching of those elements to water from yerba mate leaves in the infusion process.

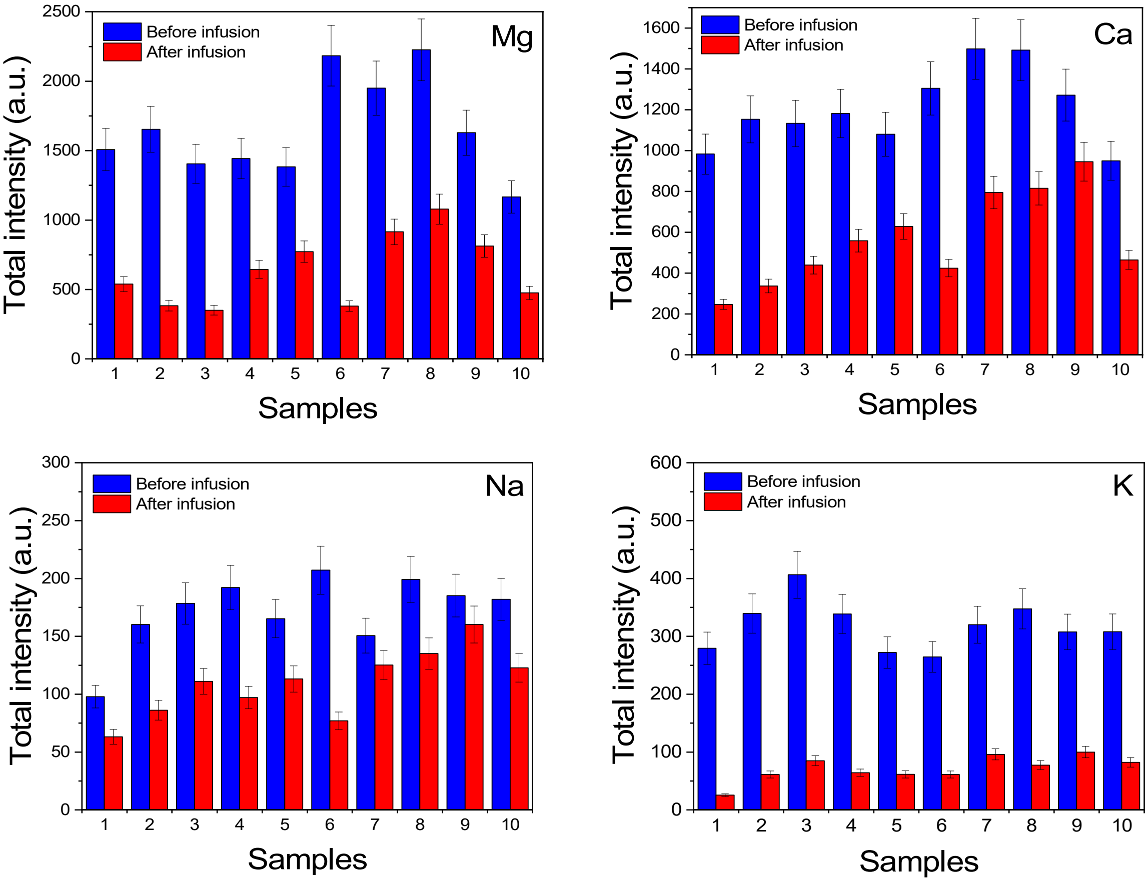

Figure 4. Total intensities of the macronutrients measured before and after the infusion for all yerba mate samples.

3.3. Extractability of Macronutrients

For element α, the measured integrated spectral line intensity I_{ji} (J s^{-1} m^{-1} sr^{-1} $Å^{-1}$) emitted along the line of sight in optically thin conditions from a homogeneous plasma in local thermodynamic equilibrium and assuming a stoichiometric ablation is given by solution to the equation of radiation transfer [17],

$$I_{\alpha}^{z} = F\frac{hc}{4\pi\lambda_0}A_{ji}\frac{10^{-2}Nr_iC_{\alpha}}{U_{\alpha}^{z}(T)}g_j e^{\frac{-E_j}{kT}} \tag{1}$$

where F is an experimental factor depending on the instrumental setup and accounting for the absolute efficiency and units, h (J s) is the Planck constant, c (m s^{-1}) is the speed of light in vacuum, λ_0 (Å) is the central wavelength of the transition, A_{ji} (s^{-1}) is the transition probability, N (m^{-3}) is the total density of all elements in the plasma, r_i is the ionization factor, C_{α} (at%) is the concentration of the element α in the sample, ${U_{\alpha}}^{z}(T)$ (dimensionless) is the partition function of the emitting species, g_j (dimensionless) is the degeneration of the upper level of the transition, E_j (eV) is the energy of the upper level, and kT (eV) is the plasma temperature [18]. According to Equation (1), the emission intensity of a spectral line is proportional to the concentration of the element in the sample, and it also depends on its spectroscopic parameters, the ionization degree, the total density of elements in the plasma, the temperature, and the electron density. The extractability E_{α} (%) of element α was defined as the relative percentage leached into water in the infusion. It was calculated by

$$E_\alpha = \frac{\Delta C_\alpha}{C_{\alpha,i}} * 100 = \left(1 - \frac{C_{\alpha,f}}{C_{\alpha,i}}\right) * 100 \tag{2}$$

where $\Delta C_\alpha \equiv C_{\alpha,f} - C_{\alpha,i}$ is the variation of its concentration between the final (f) and initial (i) stages of the infusion rationed over the initial concentration (i.e., $C_{\alpha,i}$). It is worth noting that all the spectroscopic parameters of Equation (1) cancel in Equation (2), except for the concentration. Hence, E_α can be determined by comparing the emission intensities of an analytical line measured for stages i and f. Namely,

$$E_\alpha = \left(1 - \frac{I^z_{\alpha,f}}{I^z_{\alpha,i}}\right) * 100 \tag{3}$$

where ${I_{\alpha,i}}^z$ and ${I_{\alpha,f}}^z$ are the corresponding net intensities (wavelength integrated and background subtracted), given by Equation (1).

It should be noted that Equation (3) was deduced based on the consideration that self-absorption effects on the measured line intensities were not strong. To evaluate the degree of self-absorption of the measured analytical lines, the experimental ratios of two lines belonging to the same multiplet were compared with the corresponding theoretical intensity ratios expected in an optically thin plasma. In this way, a reduction in the observed intensity of the stronger multiplet line relative to the weaker line would be indicative of self-absorption. On the other hand, if the line ratio remains approximately constant, then self-absorption is negligible [19]. The calculated experimental ratios were: 1.8 ± 0.2 for Mg; 1.7 ± 0.2 for Ca; 1.3 ± 0.2 for Na; and 1.4 ± 0.2 for K. Therefore, it was deduced that self-absorption was low to moderate. An alternative approach could be to select weaker lines affected by low self-absorption for analysis. Nevertheless, optically thin spectral lines are usually weak and hardly detected (e.g., due to spectral interference) at given conditions of measurement. Therefore, a tradeoff between self-absorption of the analytical lines and their emission intensities was addressed. For this reason, the resonant lines of Table 1 were selected because they featured a suitable sensitivity to variations in the analyte concentrations in the samples measured before and after the mate infusion. This is clearly evidenced in Figure 4. In addition, to improve the sensitivity of detection of the proposed method, the net intensities of all the corresponding analytical lines (Table 1) were added to calculate their extractabilities, as mentioned in Section 3.2, and demonstrated in our previous work [20].

The obtained E values for the studied macronutrients are exposed in Table 2, together with the concentrations of the macronutrients leached into the infusion, i.e., ΔC_α (ppm), determined with the reference analytical technique of Atomic Absorption Spectroscopy (AAS). Normal distributions were not assumed for the obtained results; therefore, the medians were considered as representative values for the different trademarks and the estimated errors corresponded to the corresponding interquartile ranges (IQR). The calculated extractabilities varied significantly for the different macronutrients analyzed. While K presented the highest extractability, intermediate values were obtained for Mg and Ca, and Na was the macronutrient with the lowest extractability in our experiment. In addition, higher scatterings (i.e., IQR) are observed in Table 2 for both the extractability values of Mg and Ca, and the amount of K leached to water, with respect to the other macronutrients. Although the study of these effects is beyond the scope of this work, it is interesting to highlight that the high variations mentioned can be linked to several factors taking place along the chain supply. In fact, a possible contamination of yerba mate with Mg and Ca may occur during growing, harvesting, and processing, as suggested by Pozebon et al. [6]. In turn, the large variation in K concentration could be related to a high variability of its initial content in the yerba mate leaves due to the particular soil characteristics of the crop.

Table 2. Extractability (E) of the macronutrients, calculated by LIBS, and concentrations (ΔC) leached into the water infusion, determined by AAS.

Element	E (%)	ΔC (ppm)
Mg	56 ± 23	30 ± 5
Ca	51 ± 21	18 ± 4
Na	34 ± 6	13 ± 1
K	76 ± 8	115 ± 29

From Equation (2), it is deduced that the concentration of a given analyte leached into the infusion is proportional to both the extractability and the initial concentration in the sample, i.e., the yerba mate leaves. In Figure 5, the values for E and ΔC determined by LIBS and AAS, respectively, are compared. It is observed that both parameters presented similar trends for the different macronutrients, denoting the consistency between LIBS and AAS results. A few outliers were obtained for the extractability of Na which were discarded since they were not representative of the final extractability value. Therefore, the experimental results evidenced the feasibility of the developed methodology for the analysis of the extractability of macronutrients in yerba mate.

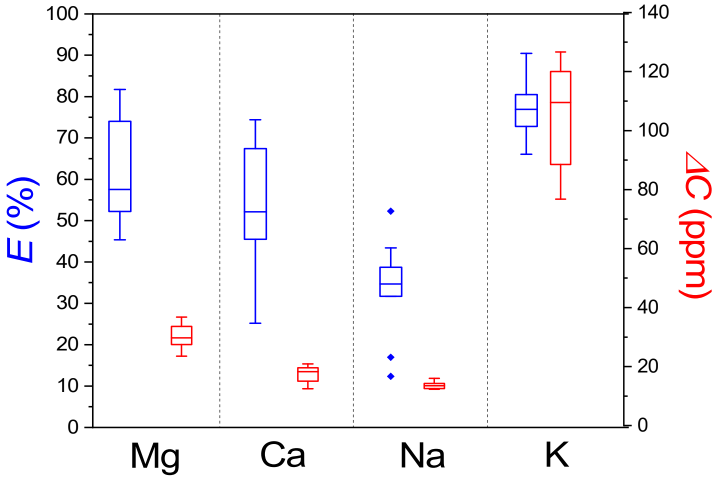

Figure 5. Comparison of the extractability values (E, in blue) and the corresponding concentrations (ΔC, in red) leached in the water infusion, determined for the studied macronutrients by LIBS and AAS, respectively. Box plot: whisker range: min–max; box: 25th percentile, median, 75th percentile; Outlier (τ).

4. Conclusions

In this work, the LIBS technique was successfully applied for the first time for the rapid analysis of the extractability of the main macronutrients present in leaves of yerba mate plant, i.e., Mg, Ca, Na, and K. The LIP properties regarding the emission and absorption of radiation were exploited to develop a straightforward analytical methodology assisted by a specially designed algorithm that does not require the use of calibration standards. The method was devised as a user-friendly analytical approach to be used with portable or benchtop LIBS equipment. The algorithm carried out a pre-treatment of the spectral data recorded from the different samples studied, i.e., LIBS spectra, a subsequent analysis of the detected emission peaks, and the calculus of the coefficient of extractability of the different macronutrients based on the comparison of their total emission intensities measured before and after the infusion process. In this approach, the obtained values for E (%), in decreasing order, were 76 ± 8 for K, 56 ± 23 for Mg, 51 ± 21 for Ca, and 34 ± 6 for Na, giving the relative percentage of each macronutrient that was leached into the water in the infusion process in laboratory conditions. These results were consistent with the concentrations of the macronutrients determined in the liquid solutions by the conventional

AAS technique. Overall, the analytical methodology and the results presented in this work demonstrated the feasibility of LIBS for the rapid analysis of extractable macronutrients in yerba mate plants aimed at agricultural studies. It is worth mentioning that information about the content of macronutrients in the yerba mate infusion is missing, or at least incomplete, in the commercial product. Thus, the novel approach developed in this work can potentially contribute to providing information regarding nutritional properties of yerba mate infusion as well as assessing the solubility of the main macronutrients for different forms of preparation of the beverage.

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