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Article

Acid Decomposition of Yerba Mate (*Ilex paraguariensis*) Using a Reflux System for the Evaluation of Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn Contents by Atomic Spectrometric Techniques

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In the first part of this paper, two acid decomposition procedures for the determination of Al, Ca, Fe, Mg, Mn and Zn contents in yerba mate samples by inductively coupled plasma optical emission spectrometry (ICP OES) were compared. Using a reflux system, the samples were treated with a mixture of HNO_3 and H_2O_2 for 3 hours at 220 °C in the digester block. The results from five commercial yerba mate samples were compared with the results obtained from microwave digestion. Good agreement between the procedures at a 95% confidence level was obtained with relative standard deviation (RSD) values lower than 10.0%. The accuracy was evaluated using addition and recovery experiments (80.5 to 112.8%). In the second part, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb and Zn concentrations were evaluated in the yerba mate infusion. The results showed that elements such as Na, K, Mg and Zn are easily transferred to the hot water used for the infusion. For Pb and Cd, the concentrations found in the analyzed samples were lower than the values established by Brazilian legislation.

Keywords: acid decomposition, reflux system, yerba mate, spectrometric techniques

Introduction

Yerba mate (*Ilex paraguariensis*) is widely consumed in Southern Brazil (Rio Grande do Sul, Santa Catarina and Paraná states) and also in parts of Uruguay, Paraguay and Argentina, mainly in the form of mate (called "chimarrão"), which is obtained through the continuous addition of hot water to ground yerba mate. Another method of consumption is as tea via the simple addition of hot water to the dried leaves of this plant.[1-3] Yerba mate has certain defining characteristics, such as a bitter taste. It also has therapeutic properties, acting as an antioxidant, an antirheumatic, a diuretic, a glycogenolytic and a lipolytic.[4]

The Union of Industry Mate in the State of Rio Grande do Sul (RS-Sindimate) collates statistical data on the yerba mate market and reported that more than 82 thousand hectares were planted in 2012, leading to a production of over 513,000 tons of yerba mate. In that same year, over 62 million tons were exported. The data from 2013 show an increase of approximately 26% in exportation with Rio Grande do Sul exporting more than any other Brazilian state (approximately 74% of the value for 2013). It produces the most yerba mate as well.[5]

Due to the high consumption of yerba mate in the country, the need for quality control is important, primarily in the form of evaluating the chemical composition of the products that reach the marketplace. This evaluation is particularly relevant because mate consists of leaves and twigs that are regularly removed, causing the producers to replace some of the lost nutrients to ensure quality and productivity.[6] To determine the content of inorganic elements in yerba mate, it is necessary to apply a suitable sample preparation method with adequate sensitivity and accuracy.[7,8] A method widely employed for the preparation of organic samples is acid decomposition, which involves the use of strong oxidizing mineral acids and can be performed using both open and closed systems. There are certain disadvantages of open systems, including analyte losses and/or reagent

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volatilization caused by the high temperatures used in the decomposition process.[8] Moreover, the literature reports some studies using perchloric acid ($HClO_4$) for the decomposition of yerba mate samples, but these procedures require careful handling because perchloric acid is a strong oxidizer and can cause explosions.[1,9-11] Thus, alternative methods have been developed to avoid the use of this acid, especially in Brazil, where its acquisition is controlled by the government. Closed systems are an alternative that can address the disadvantages of open systems. Digestion assisted by microwave radiation has been widely used for various sample types.[8,12-14]

In addition to conventional methods, reflux systems for acid decomposition have recently been applied, providing satisfactory results for the determination of metal and volatile elements in different samples.[15-18] This reflux system is efficient due to the condensation of the generated vapors inside the flask, which minimizes analyte/acid loss due to volatilization when a high temperature is used in the digester block.

For the determination of metals in different types of samples, the literature reports various analytical techniques based on atomic spectrometry.[12] Techniques based on inductively coupled plasma are advantageous due to their applicability to multiple elements and their sensitivity, and they have previously been applied for the determination of metals in yerba mate samples.[6,13,19] This work aims to evaluate the decomposition products of yerba mate samples using a reflux system as well as a closed system assisted by microwave radiation for the subsequent determination of Al, Ca, Fe, Mg, Mn, Na and Zn contents by inductively coupled plasma optical emission spectrometry (ICP OES) and their concentrations in the yerba mate infusion. Calcium and Mg are important for the formation of bones, teeth and tissue elements and also help to maintain the growth and functions of the body.[20] Manganese has additional important functions in humans, in that it can act as an enzyme activator and is a component of many enzymes. The recommended daily intake of Mn is approximately 2 to 5 mg.[21,22] Iron is an essential element because it is a component in hemoglobin and myoglobin and plays a key role in transporting oxygen to cells. Zinc acts as a cofactor in over 200 metalloenzymes, which reflects its importance for growth.[20,22]

Experimental

Instrumentation

ICP OES

Analytical measurements of the Al, Ca, Fe, Mg, Mn and Zn contents were performed using a simultaneous ICP OES instrument (PerkinElmer Optima 3000DV, Norwalk, USA) equipped with a peristaltic pump, a cross-flow nebulizer coupled to a Scott camera and a ceramic injector tube with a 2.0 mm internal diameter. This instrument has a solid-state segmented array charge coupled device (SCD) detector and can operate in both the radial and axial torch configurations. The entire system was controlled using the PE Winlab software. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used for the analytical measurements. The instrumental conditions are shown in Table S1. Prior to usage, a check of the plasma conditions was performed to obtain the best sensitivity for all analytes investigated. The choice of the emission line for Mn was based on the signal to background for this element to obtain adequate sensitivity in ICP OES analysis.

Flame atomic absorption spectrometry/flame atomic emission spectrometry (FAAS/FAES)

Measurements of the Ca, Cu, Fe, Mg and Zn contents were carried out using a flame spectrometer (PerkinElmer AAnalyst 200, Shelton, USA) equipped with deuterium background correction and with a flame of air-acetylene. Hollow cathode lamps (Lumina, PerkinElmer) for each element were used. Sodium and K were also determined in this spectrometer, but using emission mode. The instrumental parameters used followed the manufacturer's recommendations and are shown in Table S2.

Graphite furnace atomic absorption spectrometry (GF AAS)

Measurements for the Cd, Cr and Pb contents were carried out using an atomic absorption spectrometer (PerkinElmer PinAAcle 900Z, Shelton, USA) equipped with a graphite furnace, an autosampler (AS900 model) and a Zeeman-effect background corrector. All measurements were made in integrated absorbance, using transversely heated pyrolytic graphite coated tubes with L'vov platforms (PerkinElmer). The operational conditions recommended by the manufacturer were employed. Hollow cathode lamps (Lumina, PerkinElmer) were used operating at 4 mA (Cd), 25 mA (Cr) and 10 mA (Pb). The measurements were performed at wavelengths of 228.8 nm for Cd, 357.9 nm for Cr and 283.3 nm for Pb with 0.7, 0.8 and 0.7 nm spectral band path, respectively. Argon (99.996%, Linde, Barueri, Brazil) was used as the protectant and purge gas. Palladium and Mg were used as chemical modifiers by adding 5 and 3 μg into the graphite furnace for each measurement, respectively. The temperature program was optimized and is shown in Table S3.

The samples were weighed using an analytical balance (Ohaus Adventurer 2140, New Jersey, USA). For sample acid decomposition, a heated digester block was used

(MA-4025 model, Marconi, Piracicaba, Brazil). In each digester tube, a cold finger made of glass (reflux system) was introduced to avoid losses due to volatilization of the analytes and reagents, as described in a previous work.[16] An ETHOS 1 (Milestone, Sorisole, Italy) microwave digestion system equipped with closed polytetrafluoroethylene (PTFE) vessels and sensors for temperature and pressure control was used for microwave sample treatment.

Materials and reagents

Analytical grade reagents were used for all experiments. All solutions were prepared using high-purity water with a resistivity of 18.3 MΩ cm obtained from a Direct-Q 3 Water Purification System (Millipore Corporation, Bedford, USA). Working reference solutions of Al, Cd, Cr, Fe, Na, Pb, Zn and Ca, Mg and Mn were prepared by dilution of a stock solution containing 1000 mg L^{-1} or 4000 mg L^{-1} of each analyte, respectively, in 1% (v/v) HNO_3. Nitric acid (65%, v/v, Synth, Brazil) was purified by double sub-boiling distillation in a MA-075 quartz system (Marconi, Piracicaba, Brazil). Hydrogen peroxide (30%, v/v, Merck, Darmstadt, Germany) was also used. For the analysis of Ca using FAAS, a Cs-La chloride commercial buffer (Fluka, Buchs, Germany) was used to avoid interferences. The concentration added in the standards solutions and samples was 1% (v/v).

Prior to usage, all glass apparatuses were conventionally washed and soaked in 10% (v/v) HNO_3 for at least 48 h and then rinsed with ultrapure water.

Samples and procedures

To determine the analyte concentrations, ten commercial samples of yerba mate were acquired from a local market in Pelotas city in the Southern region of Brazil. These samples were triturated using a blender (non-contaminating kitchen mixer) and passed through a 0.25 mm sieve to obtain a homogeneous sample.

Studies were performed to verify the sampling error and calculate the humidity content of the yerba mate samples. Approximately 1 g of three different samples was dried in an oven at 100 ºC until reaching a constant weight to eliminate the humidity. All samples were prepared in triplicates and were dried and stored in desiccators until weighing for analysis. The humidity content in all samples averaged 6.8 ± 0.3% (m/m). To determine the ash content, approximately 1 g of sample was weighed directly into a beaker and heated in a muffle furnace at 600 °C for one and a half hours. After this period, the beakers containing the ashes were stored in desiccators until weighing. The ash content in all samples averaged 6.7 ± 0.6% (m/m). For ICP OES analysis, the samples were prepared using two different procedures, as described below.

Procedure 1: acid decomposition in an open system with a cold finger

Approximately 500 mg of yerba mate was weighed into a digestion tube, and 9.0 mL of 65% (v/v) HNO_3 was added. The reflux system was coupled to the tubes, and the mixture was heated in a digester block at 220 °C for 2 h. After cooling to room temperature, 1.0 mL of 30% (v/v) H_2O_2 was added, and the solutions were heated again for 1 h at 220 °C. After cooling, the volume was adjusted to 50 mL using ultrapure water for subsequent analysis.

Procedure 2: microwave digestion

For this procedure, approximately 500 mg of sample was accurately weighed into a PTFE vessel. 5 mL of 65% (v/v) HNO_3, 2 mL of 30% (v/v) H_2O_2 and 4 mL of deionized water were subsequently added. The vessels were closed and then placed inside the microwave oven, and the digestion was carried out according to a defined heating program. This program had the following steps: the sample was initially heated from room temperature to 80 °C in 2 min, held at this temperature for 5 min, heated to 120 °C in 4 min, held at this temperature for 5 min, heated to 200 °C in 7 min, and held at this temperature for 25 min. Subsequently, the samples were left to cool, transferred to individual 50.0 mL volumetric flasks, and diluted with deionized water for subsequent analysis. For each sample, this procedure was carried out in triplicate.

To evaluate the availability of metals in yerba mate samples, experiments involving the analysis of barley yerba mate (procedure 3) as well as the water in contact with the yerba mate after the process of infusion (procedure 4) were performed. Here, techniques such as FAAS, FAES and GF AAS were employed, and the samples were prepared via acid decomposition in an open system with a cold finger. The procedures 3 and 4 are described below.

Procedure 3: analysis of barley yerba mate

To determine the Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb and Zn contents in the barley yerba mate, the mate was prepared in a glass bowl. Five different brands/samples of yerba mate (F, G, H, I and J) were used. The water for the mate was heated, and the temperature was maintained in 80 °C (i.e., the ideal temperature for a hot mate). Approximately 74 g of yerba mate was added to a glass bowl. 1.6 L of water was added to each mate sample until the mate was considered weak. Subsequently the yerba mate from the glass bowl was taken out and was spread on watch glasses (in triplicate for each mate) and placed in the oven at a temperature of

80 °C. The samples were kept in the oven for 20 h to remove the humidity. After drying, the samples were homogenized due to the presence of twig fragments of yerba mate.

The samples were decomposed following procedure 1, and the volume was adjusted to 25 mL using ultrapure water for subsequent analysis. For all samples, the concentrations of the analytes were determined by FAES (Na and K), FAAS (Ca, Cu, Fe, Mg, Zn) and GF AAS (Cd, Cr, Pb).

Procedure 4: analysis of water after the infusion process

To determine the amount of analyte that is extracted from yerba mate by the hot water, a leaching procedure was performed, based on the study of Heinrichs and Malavolta.[6] Here, approximately 7 g of each yerba mate sample was weighed in a beaker, and 100 mL of water at 80 °C was added. The mate was kept in contact with water for 15 minutes. Afterwards, the water was separated by filtration using a qualitative filter with 12.5 cm diameter and 14 μm porosity. The resulting liquid was directly analyzed for the determination of the following contents: Na and K by FAES; Ca, Cu, Fe, Mg and Zn by FAAS; Cd, Cr and Pb by GF AAS.

Results and Discussion

Sample preparation by acid decomposition

The comparison between two decomposition procedures was carried out using ICP OES analysis, and the concentrations of Al, Ca, Fe Mg, Mn and Zn were determined in five yerba mate samples (A, B, C, D and E).

Using the open system with a cold finger, 5 mL of HNO_3 and 1 mL of H_2O_2 were initially evaluated for the decomposition of the yerba mate samples. However, it was observed that the final solutions were turbid with high viscosities, and consequently, their analyses using ICP OES gave unsatisfactory results with low precision. Thus, the volume of HNO_3 was increased to 9 mL to promote efficient decomposition and produce cleaner final solutions. Although this volume is larger, the analytical results for the element concentrations agree and are comparable with the conventional method for sample preparation using microwave radiation.

The method for sample preparation using a reflux system introduced in each digester tube was efficient for the decomposition of yerba mate samples, and no loss of acid and/or analyte was observed due to volatilization during heating because the temperature employed in the digester block was higher than the HNO_3 boiling point. This is extremely important because there is no need to replace the acid during the sample preparation process, which would increase the concentration of the analytical blank. Compared to microwave-assisted digestion, the reflux system is inexpensive, and larger sample masses can be used without the risk of explosion because the system operates at atmospheric pressure. Additionally, the analytical frequency is higher and the volume of waste generated is lower.

Analytical results

The figures of merit for the calibration curves for all analytes (Al, Ca, Fe, Mg, Mn and Zn) obtained using ICP OES are shown in Table 1. Good linear correlation coefficients were obtained for the curves ($R > 0.99$). The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as three and ten times the standard deviation of ten measurements of the blank, divided by the slope of the calibration curve, respectively. For all measurements, a single analytical curve was prepared using standard aqueous solutions, independent of the acid decomposition method employed. Thus, it was possible to obtain the same LODs and LOQs because the same sample masses and final volumes of the solutions were used in both methods.

The accuracy of the method was assessed through analyte addition and recovery experiments by adding three levels of concentration of the inorganic standards to a yerba mate sample (E) using both sample decomposition procedures. All the samples were spiked prior to the

Table 1. Figures of merit for the determination of Al, Ca, Fe, Mg, Mn and Zn concentrations by ICP OES in yerba mate samples

Analyte	Linear range / (mg L^{-1})	s[a] / (L mg^{-1})	R[b]	LOD[c] / (mg L^{-1})	LOD[c] / (mg kg^{-1})	LOQ[d] / (mg kg^{-1})
Al	1-6.5	9944	0.998	0.04	3.66	12.19
Ca	10-200	1700	0.999	0.04	4.18	13.93
Fe	1-10	1296	0.999	0.01	1.65	5.49
Mg	10-200	5293	0.999	0.008	0.86	2.87
Mn	10-200	39260	0.999	0.006	0.62	2.07
Zn	0.1-3.0	1707	0.999	0.005	0.54	1.80

[a]s: sensitivity of the calibration curve; [b]R: correlation coefficient; [c]LOD: limit of detection; [d]LOQ: limit of quantification.

decomposition experiments. The results are shown in Table S4. The recoveries ranged from 81 to 113%, showing the accuracy of the methods. The precision, expressed as the relative standard deviation (RSD, %) was verified, and the values were lower than 13.8% and 12.0% for measurements using the reflux system and microwave decomposition, respectively.

To obtain information about the concentrations of Al, Ca, Fe, Mg, Mn and Zn in the yerba mate samples from ICP OES analysis, the samples were decomposed using two procedures: acid decomposition using the reflux system and microwave digestion. The concentrations obtained are shown in Table 2. According to these results and the application of the *t*-test at the 95% confidence level, no significant differences were found between the concentrations of any analyte using the two decomposition procedures. Although some concentrations of the analytes listed in Table 2 showed a high RSD (> 10.0%), the precision was generally better using the reflux system, with a RSD average of 2.7 and 5.3% for procedures 1 and 2, respectively.

Considering that approximately 50 g of yerba is used to prepare the mate and that in many places an adult person drinks this beverage two times a day, a package of one kilo of yerba mate may be exhausted over a period of 10 days. Taking into account this information and the results of Table 2, it is possible to estimate the ingestion of inorganic constituents due to the consumption of yerba mate. It is important to highlight that these values are the total contents of the elements and not the concentration that is extracted when the yerba is used to prepare a hot beverage, as is usually done in the South of Brazil. It is also important to note that the Brazilian legislation only establishes maximum values for As, Pb and Cd in yerba mate (and other vegetables used for infusion drinks), but it is possible to find some recommended values for other inorganic elements.[21-24] As shown in Table 2, high concentrations of Ca (5600-7000 mg kg^{-1}), Mg (2900-4000 mg kg^{-1}) and Mn (1000-2200 mg kg^{-1}) were observed. For Ca, the values found are in accordance with those established as safe (20-25 g for 10 days' consumption). For Mg and Mn, however, the values are higher than those recommended (2.6 g in 10 days for Mg and 0.02 to 0.05 g in 10 days for Mn).

The concentrations of Fe in the analyzed samples ranged from 130 to 360 mg kg^{-1}. This indicates that a greater amount is consumed than is recommended, i.e., 100 to 200 mg in 10 days.[20,22,25] For Zn, the concentrations ranged from 41 to 72 mg kg^{-1}. Recommended values for zinc ingestion are between 100 and 150 mg every 10 days.[20,22,26] For Al, the concentrations found in the analyzed samples varied between 125 and 370 mg kg^{-1}, while the recommended intake of Al is 30 to 140 mg every 10 days.[21,27] The higher values of Al, Ca, Mn and Mg concentrations found in samples of yerba mate are in agreement with the results reported by Wróbel *et al.*[9] and Marcelo *et al.*[28]

The elements that did not present adequate accuracy and precision or sensitivity by ICP OES analysis were then investigated by other techniques of atomic spectrometry.

Table 2. Analytical results for the yerba mate samples obtained using ICP OES and the different treatments (n = 3)

Analyte	Concentration, x ± SD[a] / (mg kg^{-1}, %)				
	Reflux system				
	Sample A	Sample B	Sample C	Sample D	Sample E
Al	308.1 ± 13.0	340.0 ± 6.8	272.7 ± 6.1	130.8 ± 4.8	269.9 ± 6.4
Ca	6823.1 ± 57.6	6874.5 ± 47.5	6542.1 ± 82.7	5771.3 ± 13.6	5689.2 ± 190.2
Fe	243.6 ± 15.5	325.0 ± 7.8	290.8 ± 5.1	134.2 ± 4.3	293.4 ± 6.8
Mg	3679.2 ± 9.4	3840.2 ± 28.5	3978.6 ± 20.3	3148.1 ± 25.2	2939.5 ± 16.8
Mn	2117.3 ± 21.7	1825.9 ± 34.9	1855.5 ± 11.3	1084.4 ± 15.5	1763.6 ± 15.6
Zn	42.9 ± 1.9	48.7 ± 1.2	71.1 ± 0.8	50.8 ± 0.9	58.8 ± 0.4
	Microwave digestion				
	Sample A	Sample B	Sample C	Sample D	Sample E
Al	290.1 ± 23.5	366.0 ± 23.7	276.3 ± 22.2	125.7 ± 2.9	261.3 ± 6.2
Ca	6564.6 ± 407.4	6954.5 ± 216.2	6891.4 ± 897.5	5827.5 ± 209.7	6183.2 ± 378.9
Fe	255.8 ± 10.8	365.6 ± 7.4	313.2 ± 22.8	147.5 ± 17.9	294.5 ± 2.7
Mg	3540.7 ± 222.9	4008.1 ± 190.6	3846.9 ± 352.0	3076.5 ± 17.6	2905.0 ± 22.1
Mn	2157.2 ± 172.6	1964.6 ± 112.8	1829.8 ± 131.8	1112.0 ± 17.1	1773.5 ± 14.2
Zn	41.0 ± 2.5	50.9 ± 1.8	72.2 ± 7.2	53.3 ± 1.0	60.2 ± 0.7

[a]SD: standard deviation.

New analytes were quantified (Na, K, Cu, Cd, Cr and Pb), and availability studies were performed.

To quantify the concentrations of other analytes, such as Na, K, Cu, Cd, Cr and Pb, in the separated yerba mate after the consumption of mate and in the water (after extraction at 80 ºC), five yerba mate samples (F, G, H, I and J) were analyzed using atomic spectrometric techniques. The concentrations of Ca, Fe, Mg and Zn were also determined. The decomposition of the separated yerba mate was performed using procedure 1 (acid decomposition in an open system with a cold finger), as described in the Experimental section. For determination of analytes in the water obtained after infusion, the samples were directly analyzed (without sample pre-treatment). The analytes Na and K, Ca, Cu, Fe, Mg and Zn, and Cd, Cr, Pb were determined by FAES; FAAS and GF AAS, respectively.

The figures of merit obtained are presented in Table 3. The calibration curves were constructed for each analyte using inorganic standards diluted in an acid medium. As seen in Table 3, the calibration curves presented a good linearity ($R > 0.99$) for all analytes investigated. The LOD values obtained for Mg and Zn are better than those obtained by other more sensitive techniques such as ICP OES.[28]

The accuracy of the acid decomposition in an open system with a cold finger for the determination of the Ca, Cu, Fe, K, Mg, Na, Zn, Cr, Cd and Pb contents by atomic spectrometric techniques was evaluated via addition and recovery experiments by spiking two samples of yerba mate (F and I) with aqueous standards at different levels of concentrations. The results are presented in Table S5. The recovery values obtained ranged from 87 to 110% for all analytes, confirming the accuracy of the decomposition method and also showing that this method can be successfully used for the sample preparation of yerba mate, followed by analysis using different atomic spectrometric techniques. In general, the RSD values were lower than 11.0%.

The obtained concentrations of Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb and Zn in five commercial yerba mate samples (F, G, H, I and J) are shown in Table 4.

In the five samples analyzed, it was found that the highest concentrations were obtained for the analytes Ca, K and Mg, in agreement with the results from Heinrichs and Malavolta[6] and Wróbel *et al.*[9] The Na concentration in all samples averaged 0.16 mg g^{-1}. For adults, the recommended daily intake is a maximum of 2 g of Na (20 g in 10 days), and the control of its concentration is important to avoid problems related to high blood pressure.[28,29]

Toxic elements such as Cd, Cr and Pb were also determined in all samples. According to Welna *et al.*[30] the levels of concentration for those elements are normally very low and may vary markedly among different types of tea.

In June 2014, the Sindmate (The Union of Industry Mate in the State of Rio Grande do Sul) released news about the presence of toxic metals such as Pb and Cd in yerba mate in concentrations above those permitted by legislation (0.6 mg kg^{-1} of Pb and 0.4 mg kg^{-1} of Cd). The amount above the established limit was determined directly in the dry yerba mate. However, it is important to know if the metals present in the herb are extracted after the infusion process when the yerba mate comes into contact with hot

Table 3. Figures of merit for the determination of Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb and Zn by atomic spectrometric techniques

	Linear range / (mg L^{-1})	s[a] / (L mg^{-1})	R[b]	LOD[c] / (mg kg^{-1})	LOQ[d] / (mg kg^{-1})
FAES[e]					
Na	0.5-2	9642	0.996	0.60	2.00
K	0.5-2	11450	0.996	0.50	1.50
FAAS[f]					
Ca	1-4	0.018	0.999	80.00	280.00
Cu	1-4	0.078	0.999	0.60	2.00
Fe	1-6	0.043	0.999	3.00	8.00
Mg	0.1-0.5	0.792	0.999	0.10	0.40
Zn	0.5-3	0.253	0.997	0.20	0.80
GF AAS[g]					
Cd	2.5-10[h]	0.024[i]	0.996	0.0013	0.042
Cr	10-50[h]	0.011[i]	0.999	0.088	0.290
Pb	25-100[h]	0.0006[i]	0.999	0.170	0.590

[a]s: sensitivity of the calibration curve; [b]R: linear correlation coefficient; [c]LOD: limit of detection; [d]LOQ: limit of quantification; [e]FAES: flame atomic emission spectrometry; [f]FAAS: flame atomic absorption spectrometry; [g]GF AAS: graphite furnace atomic absorption spectrometry; [h]unit: (μg L^{-1}); [i]unit: (L μg^{-1}).

Table 4. Concentrations of analytes in yerba mate samples obtained using atomic spectrometric techniques (n = 3)

Analyte	Concentration x ± SD[a,b]				
	Sample				
	F	G	H	I	J
FAES[c] / (mg g^{-1})					
Na	0.15 ± 0.01 (6.7)	0.17 ± 0.01 (5.9)	0.15 ± 0.01 (6.7)	0.17 ± 0.01 (5.9)	0.15 ± 0.01 (6.7)
K	13.78 ± 0.86 (6.2)	14.14 ± 0.14 (0.9)	14.16 ± 0.17 (1.2)	12.67 ± 0.33 (2.6)	13.01 ± 0.12 (0.9)
FAAS[d] / (mg g^{-1})					
Ca	14.38 ± 0.24 (1.7)	23.01 ± 1.21 (5.2)	23.24 ± 0.91 (3.9)	20.20 ± 0.12 (0.6)	20.79 ± 0.49 (2.3)
Cu	0.011 ± 0.001 (9.1)	0.011 ± 0.001 (9.1)	0.012 ± 0.001 (8.3)	0.014 ± 0.001 (7.1)	0.012 ± 0.001 (8.3)
Fe	0.52 ± 0.03 (5.7)	0.41 ± 0.04 (9.7)	0.30 ± 0.01 (3.3)	0.41 ± 0.01 (2.4)	0.21 ± 0.01 (4.8)
Mg	8.72 ± 0.87 (9.9)	6.21 ± 0.04 (0.6)	7.42 ± 0.47 (6.3)	7.11 ± 0.11 (1.5)	7.19 ± 0.39 (5.4)
Zn	0.18 ± 0.01 (5.6)	0.053 ± 0.001 (1.9)	0.10 ± 0.01 (10.0)	0.044 ± 0.001 (2.3)	0.042 ± 0.001 (2.4)
GF AAS[e] / (mg kg^{-1})					
Cd	0.66 ± 0.01 (1.5)	0.41 ± 0.02 (4.9)	0.45 ± 0.01 (2.2)	0.161 ± 0.002 (1.2)	0.35 ± 0.01 (2.8)
Cr	1.48 ± 0.02 (1.3)	1.63 ± 0.04 (2.4)	1.64 ± 0.08 (4.9)	1.11 ± 0.01 (0.9)	1.56 ± 0.05 (3.2)
Pb	1.23 ± 0.15 (12.1)	0.66 ± 0.05 (7.5)	< LOQ[f]	1.08 ± 0.01 (0.9)	1.71 ± 0.04 (2.4)

[a]SD: standard deviation; [b]in parenthesis: relative standard deviation; [c]FAES: flame atomic emission spectrometry; [d]FAAS: flame atomic absorption spectrometry; [e]GF AAS: graphite furnace atomic absorption spectrometry; [f]LOQ: limit of quantification.

water. Hence in this work, the concentrations of analytes that remain in the yerba mate barley and also in the water after the infusion process were determined. For the first study, the yerba mate samples were prepared as described in the Experimental section (procedure 3), and the results obtained are shown in Table 5.

Among the ten analytes in the samples investigated, only K, Mg and Na showed a significant decrease in the concentration in the barley mate, with average reductions of 74, 46 and 31% of the initial concentration (Table 4), respectively. This indicates that these analytes are highly available and are leached in hot water. Large variations in the concentrations of other analytes were not observed. As the barley mate was analyzed without any grinding treatment, it can be concluded that the variations in the results can be easily affected by the homogeneity of the samples. Thus, this procedure does not seem to be the most appropriate to evaluate the availability of the analytes in the yerba mate samples.

Subsequently, an analysis of the water after the infusion process (procedure 4) was carried out, and the obtained results are shown in Table 6. The concentrations of Cr, Fe and Pb were lower than the limit of detection of the method for all the investigated samples. Additionally, transferences of Ca, Cd, Cu, K, Mg, Na, and Zn were detected, and lower availabilities were observed for Ca and Cd. We concluded that this method was more effective to assess the transfer of the analytes from the yerba mate to the water. Although the presence of toxic elements was detected, their concentrations were lower than those established by legislation and do not present health risks for the population that consumes the beverage. Thus, we can conclude that to have a more effective quality control, performing analysis on the yerba mate alone is

Table 5. Concentrations of K, Mg and Na, and percentage not transferred in yerba mate samples (n = 3)

Sample	K		Mg		Na	
	Concentration / (mg g^{-1})	PNT[a] / %	Concentration / (mg g^{-1})	PNT[a] / %	Concentration / (mg g^{-1})	PNT[a] / %
F	3.69 ± 0.28	26.8	4.56 ± 0.07	30.2	0.108 ± 0.003	72.9
G	4.26 ± 0.07	30.1	4.18 ± 0.01	67.3	0.112 ± 0.002	66.5
H	2.49 ± 0.01	17.6	3.64 ± 0.02	49.0	0.103 ± 0.004	70.1
I	1.93 ± 0.01	15.2	4.02 ± 0.12	56.5	0.105 ± 0.002	63.7
J	5.48 ± 0.13	42.1	4.65 ± 0.17	64.7	0.114 ± 0.002	73.8

[a]Percentage not transferred.

Table 6. Concentrations of Ca, Cd, Cu, K, Mg, Na and Zn and percentage transferred in water after infusion process (n = 3)

Sample	F		G		H		I		J	
	Concentration	PT[a] / %	Concentration	PT[a] / %	Concentration	PT[a] / %	Concentration	PT[a] / %	Concentration	PT[a] / %
Analyte										
Ca / (mg g^{-1})	0.96 ± 0.05	6.7	0.55 ± 0.02	2.4	0.66 ± 0.03	2.8	0.39 ± 0.03	1.9	0.56 ± 0.01	2.7
Cd / (μg g^{-1})	0.070 ± 0.004	10.6	0.048 ± 0.002	11.7	0.055 ± 0.001	12.2	< LOD[b]	–	< LOD[b]	–
Cu / (mg g^{-1})	0.0031 ± 0.0001	28.2	0.0039 ± 0.0001	35.4	0.0042 ± 0.0002	35.0	0.0050 ± 0.0003	35.7	0.0044 ± 0.0001	36.7
K / (mg g^{-1})	7.44 ± 0.13	54.0	8.01 ± 0.46	56.6	7.54 ± 0.08	53.2	6.29 ± 0.29	49.6	7.02 ± 0.18	54.0
Mg / (mg g^{-1})	3.47± 0.02	39.8	1.54 ± 0.09	24.8	2.47 ± 0.16	33.3	1.13 ±_0.08	15.9	1.73 ± 0.10	24.1
Na / (mg g^{-1})	0.098 ± 0.001	65.3	0.064 ± 0.005	37.6	0.095 ± 0.003	63.3	0.054 ± 0.002	31.8	0.060 ± 0.004	40.0
Zn / (mg g^{-1})	0.040 ± 0.001	22.2	0.016 ± 0.001	30.2	0.025 ± 0.001	25.0	0.025 ± 0.002	56.8	0.027 ± 0.001	64.3

[a]PT: percentage transferred; [b]LOD: limit of detection.

not enough; it is necessary to analyze the water after the infusion process.

Conclusions

The procedure for sample preparation based on acid decomposition using a reflux system for the determination of Al, Ca, Fe, Mg, Mn and Zn in yerba mate by ICP OES showed good results that are comparable with the microwave-assisted digestion system. The procedure is simple, and only HNO_3 and H_2O_2 are used for sample digestion. Due to its simplicity and the capability of ICP OES to analyze multiple elements, the reflux system shows good potential for application to routine analysis (quality control) of this type of sample, and it can also be utilized for the determination of volatile elements, such Pb and Cd. The discrepancies observed in the concentrations in all yerba mate samples analyzed are explained by differences in plant physiology as well as contributions of the external environment during cultivation, i.e., the soil type and climate conditions.[31] To evaluate the availability of analytes in yerba mate samples, the more effective procedure is to analyze the water after the infusion process.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as a PDF file.

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