JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Elemental Characterization of Commercial Mate Tea Leaves (*Ilex paraguariensis* A. St.-Hil.) before and after Hot Water Infusion Using Ion Beam Techniques

RAQUEL GIULIAN,* CARLA ELIETE IOCHIMS DOS SANTOS, SAMIR DE MORAES SHUBEITA, LUIZA MANFREDI DA SILVA, JOHNNY FERRAZ DIAS, AND MARIA LÚCIA YONEAMA

Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre (RS), Brazil

Ilex paraguariensis A. St.-Hil. is used to prepare a traditional tealike beverage widely appreciated in Argentina, Paraguay, Uruguay, and southern Brazil. In these countries, the tea is popularly known as *mate* or *chimarrão.* The aim of this work is to characterize the elemental composition of commercial *Ilex paraguariensis* and determine the portion of each element present in the leaves that is eluted in the water during the infusion process and consequently ingested by the drinker. Using the particle-induced X-ray emission technique, we verified the presence of Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, and Rb at different concentrations, which accounts for about 3.4% of the total mass. The results show a loss of about 90% of K and Cl, 50% of Mg and P, and 20% of Mn, Fe, Cu, Zn, and Rb by the leaves after the infusion. The volume of water used in the infusion affects only the concentration of elements such as Cl, P, K, and Mg until the first 600 mL of water, where a steep decrease in the concentration of these elements was observed in brewed leaves. Furthermore, higher water temperatures (typical temperatures used in infusions, between 80 and 100 °C) favor the extraction of K and Cl into the infusion, while the concentration of other elements remains practically constant as a function of temperature.

KEYWORDS: **Mate tea leaves (*Ilex paraguariensis*); hot water infusion process; elemental composition; PIXE**

INTRODUCTION

Ilex paraguariensis A. St.-Hil. leaves are used for the preparation of the most traditional tealike beverage of South America. Popularly known as mate, *I. paraguariensis* is an economically very important plant in South American countries and is widely cultivated in Argentina, Brazil, Paraguay, and Uruguay. Due to its stimulating and tonic properties discovered by the local indigenous people, drinking mate has became a tradition in these South American countries. Known as “chimarrão” in the southern part of Brazil, particularly in the state of Rio Grande do Sul, mate is brewed from the dried and minced leaves and twigs of *I. paraguariensis* (*1*).

In addition to its stimulant and beneficial properties (*2*, *3*), mate can be an important source of dietary nutrients, especially minerals. Indeed, mate drinking constitutes a potentially major source of dietary essential minerals in South American countries. Tea, in general, contains micronutrients such as Mg, K, Mn, and Zn that are essential minerals to human health. For instance, K is an important electrolyte that plays an important role in maintaining a normal blood pressure and in transmitting nerve impulses to muscles (*4*). On the other hand, Mn is a constituent of some enzymes and is involved in a number of physiological processes (*5*). Zn participates in numerous metabolic processes, especially those involved with the metabolism of protein, carbohydrate, fat, and alcohol (*6*). Mg also plays an important role in the structure and the function of the human body and is involved in numerous metabolic reactions (*7*). Therefore, it is very important to identify the mineral composition of teas that are widely consumed. In this context, it is important to bear in mind that the mineral content present in mate leaves depends on several factors such as geographical area where the plant is cultivated, type of soil, water and fertilizers, industrialization process, and storage conditions. Furthermore, the mineral availability in tea infusion also depends on their solubility as well as on the conditions under which the tea infusion is prepared (extraction time and temperature) and drunk. For instance, Tascioglu and Kok (*8*) have shown that the transfer ratio of some elements such as Cu, Fe, Ni, and Cr in the black and green tea infusions depends on temperature as well as on the strength of the infusion and kind of tea.

* Corresponding author. Dept. of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, ACTON, Canberra, ACT 0200, Australia. Phone: (61) (2) 6125 0037. Fax: (61) (2) 6125 0511. E-mail: raq109@rsphysse.anu.edu.au.

10.1021/jf062456r CCC: $37.00
Published on Web 01/04/2007

Several studies have been carried out to determine the elemental composition of *I. paraguariensis* and its infusion by applying different techniques (*9*−*15*). The most commonly used analytical methods to measure the elemental composition of teas are based on the principle of the optical spectrometry (*9*−*11*, *13*), although other techniques such as capillary electrophoresis have also been used to determine inorganic cations in mate leaves (*12*). Nevertheless, one of the drawbacks of these methods is that the sample preparation is somewhat complex as far as solid samples are concerned. Indeed, this kind of sample requires an extra preparation step involving chemical products, with the risk of incomplete dissolution, contamination, and losses. This problem can be overcome by using the particle-induced X-ray emission (PIXE) technique which mainly deals with solid samples.

PIXE is based on the induction of characteristic X-rays by energetic ions (*16*). Chemical bonds, nearest neighbor, bond length, coordination number, and other parameters that characterize the vicinity of the atom play no role in the production of characteristic X-rays. Therefore, PIXE provides elemental concentrations independently of any form of mixture or compound that makes up the sample. PIXE has a truly multielemental capability, that is, all elements with atomic number higher than 11 can be simultaneously detected in a single measurement with the same target (*17*), without any prior knowledge of the elements present in the sample. The sensitivity of this technique is very good and compares to that provided by optical-based techniques such as ICP−MS and ICP−AES (*18*), that is, in the range of a few parts per million (ppm). In addition, unlike optical methods, the sensitivity provided by the PIXE technique varies smoothly as a function of the atomic number. The analysis is relatively fast, namely just a couple of minutes. Since this technique is nondestructive, it preserves the original samples, allowing extra measurements if required. The sample preparation in its solid form (for a variety of samples) does not require either any sophisticated handling or any chemical treatment, thus reducing drastically any chance of contamination. Nowadays, PIXE is widely used to characterize a great variety of materials, including biological, geological, and environmental samples (*19*−*21*).

In this context, the aim of this work is to characterize the elemental composition of 20 different trademarks of commercially available mate produced in industries located in the Brazilian state of Rio Grande do Sul using PIXE technique in two different situations: the product as it is commercialized and the same product after an infusion with hot water in a way that simulates the traditional beverage known as "chimarrão". By exploring some advantages of the PIXE technique, we proposed a different approach in this work to investigate the elemental composition of mate leaves and their infusion. Instead of analyzing the tea infusion itself (*11*−*14*), the solid residues (brewed leaves) were analyzed before and after the infusion. Moreover, a specific trademark was chosen to investigate the elemental concentration of brewed leaves as a function of water volume and temperature.

MATERIALS AND METHODS

Samples. Twenty different trademarks of mate tea leaves produced in industries located in different cities of the RS state were randomly purchased in the local market. The samples consisted of commercial *I. paraguariensis* leaves without any conservative products or sugar. Throughout this work, it has been assumed that the information quoted in the packages is reliable. Finally, the selected trademarks were randomly labeled from 1 to 20 to preserve their identities.

Sample Preparation. Four sets of samples were prepared for the study of elemental composition of the mate leaves. The first set of samples consisted of dried and powdered leaves of *I. paraguariensis* before infusion. The targets were obtained by pressing a homogeneous powder of *I. paraguariensis* into pellets of 25 mm diameter and 3 mm thick. The second and third sets consisted of dried and powdered leaves after infusion with fixed and variable water volumes, respectively. The second set was prepared according to the way the tea is traditionally drunk. In this case, 2 L of distilled water at 70 °C was poured over 20 g of mate mounted on top of a filter that retained the largest part of the product, permitting only the passage of the water and the soluble parts of the material. The remaining portion of the product was removed from the filter and dried in a furnace at 40 °C for 15 h. The third set of samples was obtained in the same way but making use of different water volumes (between 200 and 2000 mL). Finally, the last set was prepared by keeping a constant water volume of 400 mL but at different temperatures, which varied from 10 to 100 °C in steps of 10 °C. For the third and fourth sets, five identical samples were prepared for each water volume and temperature used in the infusion, respectively.

Instrumentation. The measurements were carried out at the Ion Implantation Laboratory of the Physics Institute (UFRGS) using a 3 MV Tandetron accelerator. All PIXE measurements were performed with a 2 MeV proton beam and an average current of 1 nA on target. The samples were placed in a target holder inside a reaction chamber kept at a pressure of about 10^{-4} Pa. The characteristic X-rays induced by the proton beam hitting the samples were detected by a lithium-doped silicon detector, with an energy resolution of about 155 eV at 5.9 keV, which was positioned at an angle of 45° with respect to the beam direction.

Data Analysis. The data were analyzed using the GUPIX code (*22*−*24*). To that end, the standardization procedure was carried out using an apple leaves standard from the NIST (reference material 1515) (*25*). The quantitative PIXE analysis of a sample in a thick target approximation (pellets) requires the knowledge of its matrix composition. For organic materials such as *I. paraguariensis*, its matrix consists basically of C, O, and H, whose X-rays are not detectable by the present setup and, therefore, are considered invisible elements from the PIXE technique standpoint. Therefore, two other ion beam techniques, that is, Rutherford backscattering spectroscopy (RBS) (*26*) and elastic recoil detection analysis (ERDA) (*27*) were employed to obtain the matrix composition of mate tea leaves and apple leaves standard used to calibrate the PIXE analysis.

A standard statistical procedure was adopted to obtain the final values of the elemental concentrations. For each commercial mate tea brand, several independent measurements were carried out. Each experimental PIXE spectrum was fitted using the GUPIX software, which employs the least-square fitting procedure according to Marquardt (*33*). All the final results were assumed to obey a normal distribution, and therefore the mean and standard deviation of the mean were taken as representative values of the whole set of experiments. Finally, the uncertainties stemming from the fitting procedure were convoluted with the statistical uncertainties, yielding the uncertainties quoted in **Table 1**.

RESULTS AND DISCUSSION

Matrix Composition. The RBS spectra of mate leaves and apple leaves standard were obtained to determine the matrix composition of both samples. According to the RBS results, the concentration of these elements is very similar in both samples, which makes the apple leaves a good standard to calibrate the system. After a series of RBS and ERDA measurements, it was found that the matrix of mate tea leaves can be represented by the stoichiometric formula C_7OH_8, which accounts for about 96.6% of the total mass present in the samples.

Elemental Composition of Mate Leaves. The overall composition of 20 different trademarks of commercial mate leaves was evaluated through the PIXE technique. Elements such as Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, and Rb were simultaneously determined in mate leaves before and after infusion. The limit of detection and the mean recovery of the

Table 1. Mean Elemental Concentration of Mate Tea Leaves[a]

element	before infusion (ppm)	after infusion (ppm)
Mg	5025 ± 186	2342 ± 29
Al	413 ± 23	445 ± 29
Si	547 ± 32	898 ± 66
P	1404 ± 73	770 ± 19
S	1035 ± 20	1029 ± 27
Cl	1603 ± 97	113 ± 10
K	15599 ± 422	1185 ± 76
Ca	6785 ± 249	6770 ± 339
Ti	30 ± 3	30 ± 2
Mn	1315 ± 113	932 ± 74
Fe	254 ± 27	203 ± 17
Cu	14 ± 2	11 ± 1
Zn	72 ± 5	59 ± 5
Rb	27 ± 2	24 ± 2

[a] The results, in units of parts per million (ppm), represent an average of all 20 different trademarks analyzed in this work. The uncertainties stem from the statistical variance and the fitting procedure.

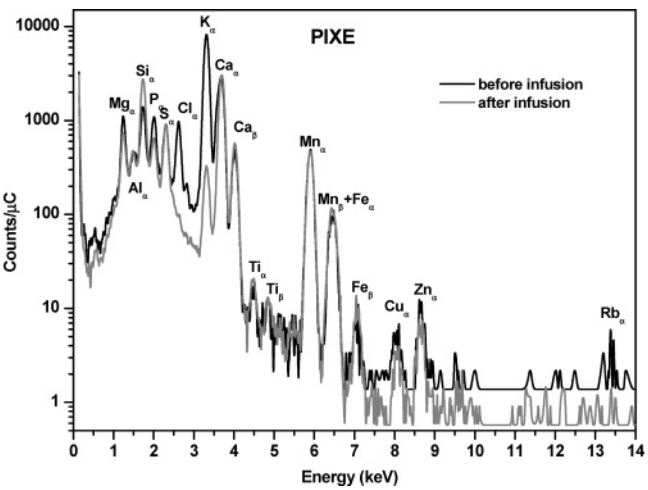

Figure 1. Typical PIXE spectrum obtained from mate tea leaf samples before and after the hot water infusion process. For some elements, both K_α and K_β X-rays lines are shown. The spectra are normalized to the total charge employed in the experiments.

elemental concentrations vary smoothly with the atomic number. For instance, the values corresponding to our PIXE system for Fe are about 8 ppm and 97%, respectively. A typical PIXE spectrum is shown in **Figure 1**. Qualitatively, the peak amplitudes are directly related to the elemental concentration of the elements in the samples. The mean concentration of each element present in mate leaf samples before and after hot water infusion is given in **Table 1**. The results, in units of parts per million, represent the average of all 20 different trademarks analyzed in this work. The uncertainties of the elemental concentrations were relatively small and ranged from 2 to 13%. This variability can be attributed, for example, to factors such as fabrication process, soil quality, and storage conditions.

According to the results shown in this table, the concentrations of K, Ca, and Mg ranged from 16 000 to 5000 ppm approximately. Indeed, it has been observed that these elements are present in large amounts in mate (*9*−*11*). Moreover, significant levels of Cl, P, Mn, and S have been observed (thousands of ppm) in mate leaves before infusion. The concentration of about 1300 ppm found for Mn is higher than the results presented by Heinrichs and Malavolta (*11*). The levels of Al, Si, and Fe ranged from 400 to 250 ppm, while the concentrations of other elements such as Zn, Ti, Cu, and Rb

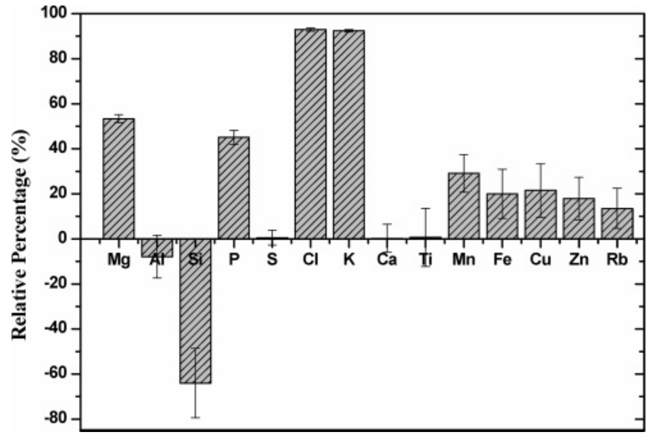

Figure 2. Relative elemental percentage removed from the samples after the hot water infusion process. The negative values indicate an increase in concentration after the process.

ranged from 70 to 15 ppm. A similar level of Al has also been found in mate by Wrobel et al. (*13*). The Zn content observed in mate leaves appears to be much higher than the Zn levels observed in other teas such as green, black, and oolong teas (*28*). Actually, a large variability of Zn content in teas (from few ppb to hundreds of ppm) is observed in the literature (*28 and references therein*). It is important to remark that the Rb content in mate leaves was observed for the first time and its level is similar to the levels observed in black tea leaves investigated by Matsuura et al. (*29*). It is important to bear in mind that Rb is a trace element present in soils and is easily taken up by plants (*30*). Indeed, Rb was observed in a soil sample collected in the region of native mate trees and analyzed by PIXE (data not shown) (*31*). Furthermore, the standard reference material used in this work (*25*) also shows the presence of Rb (10.2 ppm).

Elemental Composition of Brewed Mate Leaves. Figure 2 shows the relative percentage of each element removed from or added to the samples due to the infusion process. The removed amount of material is assumed to be dissolved or carried away with the hot water that was poured over the mate leaves.

According to the results shown in **Figure 2**, K and Cl are the most soluble elements in the infusion. Almost all Cl and K present in the mate leaves before infusion are carried away with water, and consequently, their concentrations in the brewed samples are significantly decreased. Other elements such as Mg and P have their concentrations reduced by around 50% after infusion. The relative variation of Mn, Fe, Cu, Zn, and Rb was between 10 and 30% approximately, while no changes in Al, Ca, Ti, and S content in brewed mate leaves were observed. Moreover, an increase in the Si content was observed in brewed leaves.

Although it is difficult to compare the solubility data obtained under different conditions, a general trend for some elements can be drawn when comparing our data to the results reported in the literature. For mate infusions, a high concentration of K, Mg, and Mn has already been observed (*11*, *13*). The very high solubility of Cl and K in tea infusion can be explained by the fact that both elements are present in plants in soluble forms. Moreover, K is known to be more abundant outside the cells. Furthermore, Matsuura et al. (*29*) have suggested that most of the Ca is accumulated inside the cells and is hardly extracted during brewing. Our data appear to support these facts and, in particular, the claiming of Matsuura et al. concerning Ca.

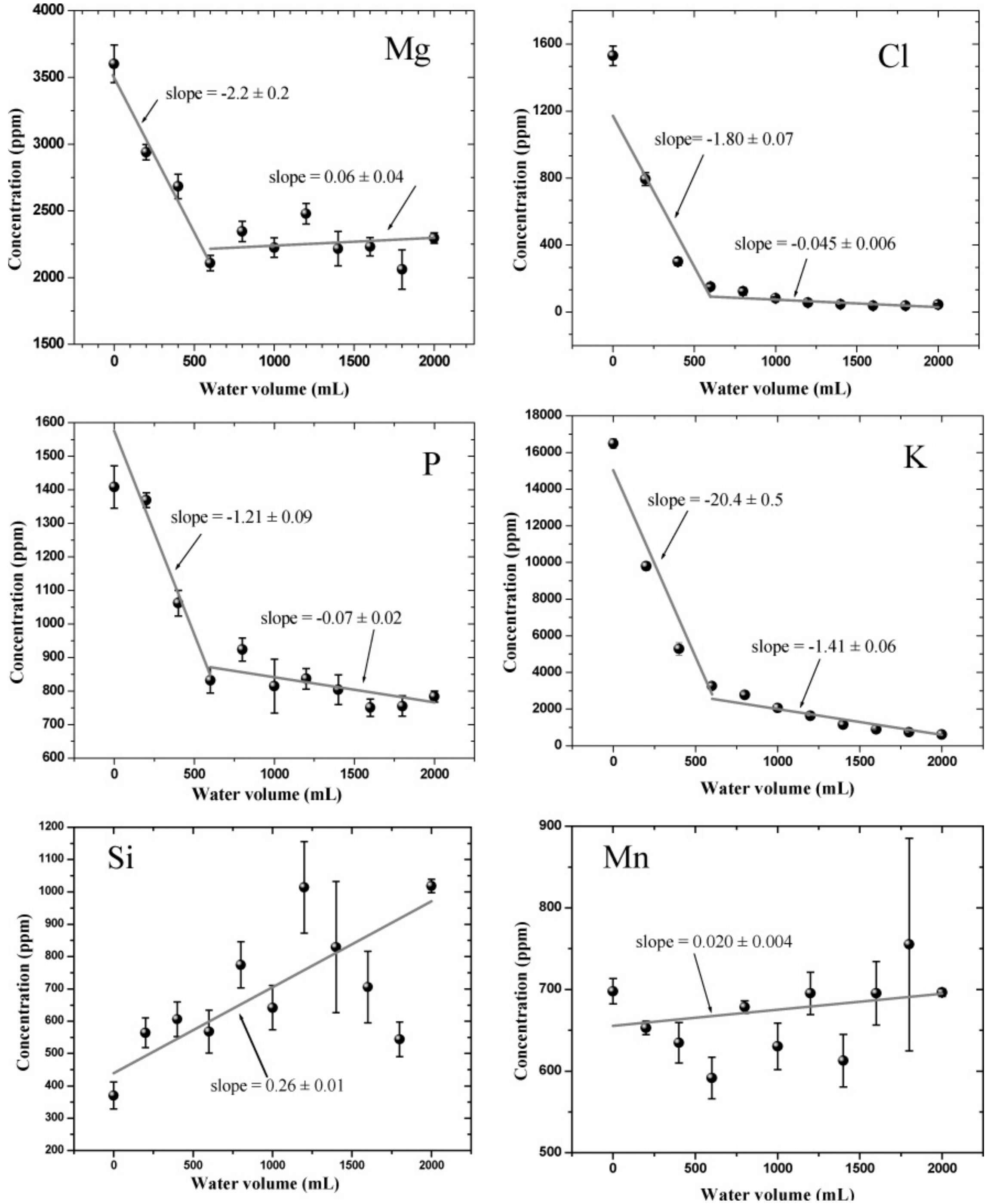

Figure 3. Concentration of metals present in brewed mate leaves as a function of water volume used in the infusion. The straight lines correspond to linear fits of the experimental data.

Due to its nutritional importance, special attention is given to Mn concerning its availability in tea infusion. For example, Wrobel et al. (*13*) have also shown that almost 50% of Mn content in mate leaves is leached to the infusion. Our results suggest that about 30% of Mn is taken to the infusion.

A peculiar result has been observed for Si in brewed mate leaves. For instance, Si has its concentration increased by 65% due to the infusion process. The added amount of material could be explained by the water used in the experiments. Indeed, the water employed in the infusion process was just distilled water, and it could contain a certain amount of Si. During the infusion process, the mate tea leaves could act as a filter retaining part of the Si present in the water, leading to an increasing of the Si concentration.

Elemental Composition of Brewed Mate Leaves: Volume Dependence. Figure 3 shows the behavior of some elements present in the leaves of *I. paraguariensis* as a function of water volume. The volume of water used in the infusion has a strong influence in the concentration of elements such as Cl, P, K, and Mg, for which a specific trend was observed. For these elements, the concentration decreases substantially in a linear fashion until the first 600 mL of water and becomes approximately constant or decreases very slowly for larger volumes. Therefore, these results indicate that Cl, K, Mg, and

P are the most readily extractable elements until the first 600 mL of water. If we consider the tradition in Brazil, where the tea is usually drunk by several people sharing the same vessel, and take into account that a typical vessel has a capacity of approximately 200 mL of water, then our results suggest that the first three people who drink the beverage practically intake most of these elements, while the following drinkers intake a smaller amount.

The Si concentration as a function of water volume increases linearly, suggesting that the Si content in brewed leafy material increases as water volume increases. This result reinforces the statement that the water used in the infusion might be the main source of Si. The concentration of other elements as a function of water volume remained practically constant, as is the case of Mn shown in **Figure 3**.

Elemental Composition of Brewed Leafy Material: Temperature Dependence. The elemental concentration of brewed leaves as a function of water temperature was also investigated. Particularly, for elements such as K and Cl, it seems that higher water temperatures (typical temperatures used in infusions, between 80 and 100 °C) favor the leaching of these elements into the infusion. According to our results, drinkers of mate tereré prepared with water temperature between 5 and 10 °C (*32*) will intake smaller amounts of K and Cl as compared to drinkers of the traditional mate prepared with hot water.

In summary, the elemental composition of *I. paraguariensis* leaves before and after infusion was determined using the PIXE technique. Due to its high sensibility, multielemental capability, and minimal sample preparation, the PIXE technique proved to be a valuable tool to determine the elemental composition of mate tea leaves before and after infusion. Since this technique is nondestructive, PIXE was coupled to other ion beam techniques such as RBS and ERDA to obtain the matrix composition of the samples. The presence of K, Cl, Mg, Al, Si, P, S, Ti, Mn, Fe, Cu, Zn, and Rb was observed at different concentrations, as representing a fraction of 3.4% of the total mass present in the samples. The remaining portion is represented by a combination of C, O, and H also at different concentrations. The comparison between the elemental concentrations of the mate tea leaves before and after infusion suggests that the majority of the elements are leached in the infusion and, therefore, drunk by the consumer. According to our results, the content of some minerals in mate infusion (in particular, K and Cl) depends on water volume and temperature. The first portions of mate (until 600 mL) and mate prepared with hot water contain higher amounts of K and Cl.

Although the general elemental composition of tea leaves is known, climate and horticultural practices, including soil, water, and fertilizers, can be of great influence on the composition of teas. Therefore, teas cultivated in different geographical areas will present significant differences in chemical composition. These facts hamper a proper comparison of the results obtained in this work with those available in the literature.

Further investigation concerning the increase of Si content in brewed mate leaves should be carried out, measuring, for instance, the Si content in distilled water used in the infusion and employing deionized water in the experiments. Our present results suggest that the mate tea leaves absorb Si from the water.

Finally, the influence of the industrial process in the elemental concentration of mate leaves was also investigated by PIXE and will be the subject of a forthcoming publication.

ACKNOWLEDGMENT

We are indebted to the Industria Ervateira Ximango, which kindly provided several samples used in this work.

LITERATURE CITED

(1) Grahan, H. N. Mate. *Prog. Clin. Biol. Res.* **1984**, *158*, 29−74.

(2) Filip, R.; Lotito, S. B.; Ferraro, G.; Fraga, C. G. Antioxidant activity of Ilex paraguariensis and related species. *Nutr. Res.* **2000**, *20*, 1437−1446.

(3) Filip, R.; López, P.; Giberti, G.; Coussio, J.; Ferraro, G. Phenolic compounds in seven South American *Ilex* species. *Fitoterapia* **2001**, *72*, 774−778.

(4) Sheng, H. W. Sodium, Chloride, and Potassium. In *Biochemical and Physiological Aspects of Human Nutrition*; Stipanuk, M. H., Ed.; W. B. Saunders: Philadelphia, PA, 2000; pp 686−710.

(5) Leach, R. M.; Harris, E. D. Manganese. In *Handbook of Nutritionally Essential Minerals*; O'Dell, B. L., Sunde, R. A., Eds.; Marcel Dekker: New York, 1997; pp 335−355.

(6) Cousins, R. J. Zinc. In *Present Knowledge in Nutrition*; Ziegler, E. E., Filer, L. J., Eds.; International Life Sciences Institute Press: Washington, DC, 1996; pp 293−306.

(7) Shils, M. E. Magnesium. In *Nutrition in Health and Disease*, 9th ed.; Shils, M., Olson, J. A., Shike, M., Ross, A. C., Eds.; Williams and Wilkins: Baltimore, MD, 1999; pp 169−192.

(8) Tascioglu, S.; Kok, E. Temperature dependence of copper and chromium transfers into various black and green tea infusions. *J. Sci. Food Agric.* **1998**, *76*, 200−208.

(9) Tenorio Sanz, M. D.; Torija Isasa, M. E. Elementos minerales en la yerba mate (Ilex paraguariensis St. H.). *Arch. Latinoam. Nutr.* **1991**, *41*, 441−454.

(10) Vera Garcia, R.; Basualdo, I.; Peralta, I.; de Herebia, M.; Caballero, S. Minerals content of Paraguayan yerba mate (Ilex paraguariensis, St. Hil.). *Arch. Latinoam Nutr.* **1997**, *47*, 77−80.

(11) Heinrichs, R.; Malavolta, E. Composição mineral do produto comercial da erva-mate (Ilex paraguariensis St. Hil.). *Cienc. Rural* **2001**, *31*, 781−785.

(12) Carducci, C. N.; Dabas, P. C.; Muse, J. O. Determination of inorganic cations by capillary ion electrophoresis in Ilex paraguariensis (St. H.), a plant used to prepare tea in South America. *J. AOAC Int.* **2000**, *83*, 1167−1173.

(13) Wrobel, K.; Wrobel, K.; Urbina E. M. Determination of total aluminum, chromium, copper, iron, manganese, and nickel and their fractions leached to the infusions of black tea, green tea, Hibiscus sabdariffa, and *Ilex paraguariensis* (mate) by ETA-AAS. *Biol. Trace Elem. Res.* **2000**, *78*, 271−280.

(14) Yukawa, M.; Watanabe, Y.; Nishimura, Y.; Wada, M. Determination of Trace Elements in Mate Using PIXE Analysis. *Int. J. PIXE* **1996**, *6*, 505−509.

(15) Marchisio, P. F.; Sales, A.; Cerutti, S.; Marchevski, E.; Martinez, L. D. On-line preconcentration/determination of lead in Ilex paraguariensis samples (mate tea) using polyurethane foam as filter and USN-ICP-OES. *J. Hazard. Mater.* **2005**, *124*, 113−118.

(16) Johansson, S. A. E.; Campbell, J. L. *PIXE: A Novel Technique for Elemental Analysis*; Wiley: Chichester, 1988.

(17) *Particle-induced X-ray emission spectrometry (PIXE)*; Johansson, S. A. E., Campbell, J. L., Malmqvist, K. G., Eds.; Wiley & Sons: New York, 1995.

(18) Saitoh, K.; Sera, K.; Gotoh, T.; Nakamura, M. Comparison of elemental quantity by PIXE and ICP-MS and/or ICP-AES for NIST standards. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *189*, 86−93.

(19) Braga, C.; Teixeira, E. C.; Meira, L.; Wiegand, F.; Yoneama, M. L.; Dias, J. F. Elemental composition of PM10 and PM2.5 in urban environment in south Brazil. *Atmos. Environ.* **2005**, *39*, 1801−1815.

(20) Kern, A. L.; Bonatto, D.; Dias, J. F.; Yoneama, M. L.; Brendel, M.; Henriques, J. A. P. The function of Alrp1 of *Saccharomyces*

cerevisiae in cadmium detoxification: Insights from phylogenetic studies and particle-induced X-ray emission. *BioMetals* **2005**, *18*, 31−41.

(21) Franke, S. I. R.; Prá, D.; Dias, J. F.; Giulian, R.; Yoneama, M. L.; da Silva, J.; Erdtman, B.; Henriques, J. A. P. Influence of orange juice in the levels and in the genotoxicity of iron and copper. *Food Chem. Toxicol*. **2006**, *44*, 425−435.

(22) Maxwell, J. A.; Campbell, J. L.; Teesdale, W. J. The Guelph PIXE software package. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1989**, *43*, 218−230.

(23) Maxwell, J. A.; Teesdale, W. J.; Campbell, J. L. The Guelph PIXE software package II. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1995**, *95*, 407−421.

(24) Campbell, J. L.; Hopman, T. L.; Maxwell, J. A. The Guelph PIXE software package III: Alternative proton database. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, *170*, 193−204.

(25) Outside-Source Reference Materials, Bureau of Analysed Samples LTD; Newham Hall, England, 2001; Catalogue 696, 50.

(26) Chu, W. K.; Mayer, J. W.; Nicolet, M. A. In *Backscattering Spectrometry*; Academic Press: New York, 1978.

(27) *Handbook of modern ion beam materials analysis*; Tesmer, J. R., Nastasi, M., Eds.; Materials Research Society: Pittsburgh, PA, 1995.

(28) Cabrera, C.; Giménez, R.; López, M. C. Determination of Tea Components with Antioxidant Activity. *J. Agric. Food Chem.* **2003**, *51*, 4427−4435.

(29) Matsuura, H.; Hokura, A.; Katsuki, F.; Itoh, A.; Haraguchi, H. Multielement determination and speciation of major-to-trace elements in black tea leaves by ICP-AES and ICP-MS with the aid of size exclusion chromatography. *Anal. Sci.* **2001**, *17*, 391−398.

(30) Pais, I.; Jones, J. B., Jr. In *The Handbook of Trace Elements*; CRC Press: Boca Raton, FL, 1997; pp 128−129.

(31) Giulian, R. Estudo da composição elementar da erva-mate (Ilex paraguariensis). M.S. Thesis, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, 2005.

(32) Santa Cruz, M. J.; Garitta, L.; Hough, G. Sensory Descriptive Analysis of Yerba Mate (Ilex Paraguariensis Saint Hilaire), a South American Beverage. *Food Sci. Technol. Int.* **2002**, *8*, 25−31.

(33) Marquardt, D. An algorithm for least-squares estimation of nonlinear parameters. *SIAM J. Appl. Math.* **1963**, *11*, 431−441.

Received for review August 28, 2006. Revised manuscript received November 22, 2006. Accepted November 24, 2006. We are grateful to CNPq and FAPERGS for their partial financial support of this work.

JF062456R