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## Fractionation of Aluminum in Commercial Green and Roasted Yerba Mate Samples (*llex paraguariensis* St. Hil.) and in Their Infusions

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Different trademarks of green mate and mate tea (*llex paraguariensis* St. Hil.) were employed in this work, the aim of which was to compare the fractionation of Al from green mate and mate tea (roasted mate) and from their infusions. Using the flame atomic absorption spectrometry technique, contents determined for Al leached to green mate and mate tea infusions varied from 12.8 to 18.1% and from 5.9 to 10.6%, respectively. The concentrations of phenolics in infusions were determined using the Folin–Ciocalteu method, and the presence of melanoidins was also evaluated. The results showed that phenolic compounds are the major contributors to the leached Al in green mate infusions, but melanoidins also contribute in the case of infusions prepared from the mate tea. By employing a chelating resin batch procedure, it was observed that Al was predominantly in relatively inert forms, mainly in the case of mate tea infusions (50–70%).

KEYWORDS: Green mate and mate tea (*llex paraguariensis* St. Hil.); infusions; fractionation of aluminum; phenolics; melanoidins

#### INTRODUCTION

Ilex paraguariensis St. Hil. is a tea plant of the Aquifoliaceae family cultivated in South American countries, which is commonly named "mate" or "yerba mate", where it is popularly used to prepare hot infusions. Yerba mate is not consumed as a raw material but instead it is processed before commercialization. Two distinct products named "green mate" and "mate tea" can be obtained from the industrial processing of yerba mate, which are used to prepare mate infusions. Green mate is obtained after blanching (operation performed with hot gases at temperatures above 500 °C), crushing, and drying of leaves and twigs of yerba mate (1-4), and mate tea is obtained by the roasting of green mate (160 °C for approximately 12 min) (3). The green mate is used to prepare the most traditional tealike beverage of South America known as "chimarrão". The production and consumption of yerba mate occurs predominantly in South American countries; however, other countries, such as the United States (5), Germany, and Japan, started to import it at a rate of 1000 tons per year at the end of the 1990s (6).

Several beneficial effects for human health are attributed to the infusions of yerba mate, due to their claimed antiinflammatory, choleretic, diuretic, hepatoprotective, and mild stimulant properties among others (7, 8). The infusions are also considered as an important source of dietary antioxidants (caffeoyl derivatives and other phenolic compounds) and essential minerals such as K, Mg, Mn, and Zn (9).

On the other hand, in opposition to the beneficial effects, yerba mate contains a high concentration of aluminum (9), which seems to be a toxic element to humans, and its contamination appears to be linked to the Alzheimer's disease among other neurodegenerative disorders (10, 11). In green mate infusions, Al and other elements could form complexes with polyphenolic compounds, and its efficiency of leaching to the infusions appears to be strongly related to the polyphenol content (12). According to Flaten (13), polyphenolic compounds are the most important Al-complexing ligands in the *Camellia sinensis* infusions or green tea.

The polyphenol content of the green mate could be decreased by thermal degradation due to the roasting process employed to obtain the mate tea product (14). Clifford and Ramirez-Martinez (15) found that the brewed green mate in Europe provided 107-133 mg of chlorogenic acids per approximately 200 mL of infusion; in contrast, roasted mate provided 16-41mg under the same conditions. As a result, it could be expected that the concentration of soluble Al of the green mate leached to the infusions could be different in comparison with that leached from the roasted mate (mate tea). To evaluate the toxic effects of Al, not only is it important to consider the total concentration of soluble Al present in a sample, but it is also necessary to investigate the distribution of its species, because both bioavailability and toxicity of an element depend on its speciation (16, 17). Free Al species related to the monomeric

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positively charged ones seem to be mainly responsible for its toxicity (17). On the other hand, ligands such as polyphenols contribute to decreasing its toxicity by means of complex formation (13). By using speciation methods, it is possible to investigate the fractions of the Al species with higher toxic importance, that is, those species related to hydrated ions of free Al as well as the very or moderately labile Al complexes.

Generally, information on the variable physicochemical forms in which metals are distributed in a certain sample is obtained by employing an operational fractionation protocol, which provides a speciation study based on the classification of a metal or a group of metals according to physical and/or chemical properties, instead of providing exact and detailed information on the metal species by defining molecular forms of metals and the structure of metal complexes (*18, 19*).

One of the experimental approaches used for metal species fractionation is based on the application of solid sorbents with chelating ion-exchange properties, and Chelex 100, an iminodiacetic chelating resin, has been the most commonly used. By using this resin, it is possible to discriminate between the noninert metals (hydrated ions of free metal, very or moderately labile metal complexes, and kinetically labile metals) and very stable or inert forms of complexed metals present in an aqueous sample, considering that inert forms are not sorbed on the resin even when the sample is kept in contact with the resin for a long time of 24 h (20).

The approach proposed in this paper is based on the comparison of the fractionation of Al from green mate and mate tea samples and from their infusions obtained under the same conditions, so that the effect of the industrial processing of yerba mate on the Al speciation could be evaluated. Effects of the roasting process of green mate to obtain mate tea on the Al fractionation have not been described.

#### MATERIALS AND METHODS

**Chemicals.** All reagents used were of analytical grade (Merck), unless specified. Deionized distilled water obtained in a Milli-Q system (Millipore, Bedford, MA) was used throughout the work. A stock standard solution of Al (Titrisol, Merck) containing 1000 mg L<sup>-1</sup> was used to prepare reference solutions. Total polyphenol determinations were made by using Folin–Ciocalteu reagent (Aldrich-Sigma). Chelex 100 (Bio-Rad Laboratories) with a particle size of 50–100 mesh was purchased in sodium form. All glassware was soaked with 10% v/v HNO<sub>3</sub> for 24 h and then rinsed thoroughly with deionized distilled water prior to use.

**Samples.** Three different trademarks of green mate and three different trademarks of mate tea (*Ilex paraguariensis* St. Hil.) produced in industries located in Paraná state, Brazil, were purchased in the local market, and the available trademarks of green mate and mate tea were randomly labeled from 1 to 3 to preserve their identities. The samples were minced and homogenized by employing a mortar and pestle of agate prior to the analyses.

**Digestion Procedure.** The digestion was carried out using a hot plate operating at 80 °C. Triplicate samples (5 g) were digested by employing 10.0 mL of concentrated HNO<sub>3</sub> and 1.0 mL of H<sub>2</sub>O<sub>2</sub> (30% v/v), and the digestion procedure was repeated until a clear acid-digested solution was obtained. After cooling, the solution obtained was transferred to a volumetric flask, and the volume was made up to 50 mL with deionized distilled water together with the addition of potassium chloride in a final proportion of 1% (w/v). The digestions were carried out in triplicate. The reliability of the digestion procedure was verified by recovery of Al (4.0 mg L<sup>-1</sup>) from the yerba mate samples spiked with Al standard solution.

**Infusion Preparation.** Green or mate tea (roasted mate) samples (5 g) were weighed into 250 mL Erlenmeyer flasks, 150 mL of hot water (85 °C) was added, and the samples were left at 85 °C for 10 min. After cooling, the infusions were filtered through a 0.45  $\mu$ m

membrane filter (Millipore) so that the supernatant was separated. A volume of 25.0 mL of the filtered infusion solution was transferred to a volumetric flask, and the volume was made up to 100 mL with deionized distilled water together with the addition of both KCl and concentrated HNO<sub>3</sub> in final proportions of 1% (w/v) and 1% (v/v), respectively. Infusions were prepared in triplicate.

Aluminum Determination. Measurements were made by employing a SpectrAA 50 flame atomic absorption spectrometer (Varian). The hollow-cathode lamp of Al was used as radiation source, and a D<sub>2</sub> lamp was used for background correction, because the measurements were made below 330 nm. Al was measured under optimized operating conditions by FAAS in a N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame, using the following instrumental parameters: wavelength of 309.3 nm, slit width of 0.5 nm, and hollow-cathode lamp operating at 12 mA. To avoid possible ionization interferences for Al determination, KCl was added to all solutions (acid-digested, filtered fresh infusion, and reference solutions) in a final proportion of 1% (w/v). The Al determined in the filtered infusions was considered to be operationally available (soluble). The determinations, the recuperation of Al (1.0 mg L<sup>-1</sup>) from the infusions spiked with Al standard solution was verified.

**Total Polyphenol Determination.** The total soluble polyphenols extracted from the green mate and mate tea to the aqueous infusions were determined in the filtered ones according to the Folin–Ciocalteu method (21), using gallic acid as the standard of calibration. Filtered infusion samples (100  $\mu$ L) were introduced into volumetric flasks, to which were added 5.0 mL of Folin–Ciocalteu reagent and 4.0 mL of sodium carbonate (7.5% w/v), and the volume was made up to 10 mL with deionized distilled water. The solution was allowed to stand for 30 min, and then the absorbance at 765 nm was measured by employing a UV–vis spectrophotometer (UVmini-1240 Shimadzu) and a 3 mL capacity cuvette (1.0 cm length). Reference solutions were prepared in the range of 3–15 mg L<sup>-1</sup> gallic acid. The total polyphenol determinations were carried out in triplicate by using filtered fresh infusions.

Particulate Aluminum Determination in the Yerba Mate Samples. Particulate Al concentrations were calculated as the difference between the total Al concentrations (obtained from the acid-digested samples) and soluble Al concentrations obtained from the fresh infusions filtered through a 0.45  $\mu$ m membrane filter (18).

**Spectrophotometric Measurements.** Spectrophotometric analysis was performed to verify the presence of melanoidins in green mate and mate tea infusions by measuring their absorbances at 420 nm (22). Mate infusions were diluted 1:100 in deionized distilled water prior to analysis. The spectrophotometric measurements were carried out by employing a UV–vis spectrophotometer (UVmini-1240 Shimadzu) and a 3 mL capacity cuvette (1.0 cm length).

Fractionation of Noninert and Inert Aluminum from the Infusions by Sorption in Chelex 100. Chelex 100 was washed with 1.0 mol  $L^{-1}$  HNO<sub>3</sub> and converted to NH<sub>4</sub><sup>+</sup> form by treatment with 1.0 mol  $L^{-1}$  NH<sub>3</sub> prior to sorption studies, which were carried out by using a batch procedure (20). A 25.0 mL volume of filtered fresh infusions obtained from green mate and mate tea samples were kept in contact with 1 g of the Chelex 100 for 2, 4, 6, 8, and 24 h on a shaking plate at room temperature. The final pH was measured after equilibration, and no attempt was made to keep it at a fixed value. After equilibration, the aluminum not retained on the resin was determined in the solution phase by FAAS employing the optimized conditions described before. The inert fraction of aluminum was calculated as the difference between the concentration of Al not retained on the resin and total soluble Al present in the filtered fresh infusions before contact with the resin.

The amount of resin (1 g) used in the experiments was determined from a batch sorption study using a 25.0 mL volume of a 10 mg  $L^{-1}$ Al standard solution buffered at pH 5.5 by using acetic acid/ammonium acetate buffer, which was equilibrated with known amounts of Chelex 100 (0.10–1.5 g of dry resin) employing a contacting time of 24 h at room temperature.

**Statistical Analysis.** Statistical analysis to comparison of the results expressed as means  $\pm$  standard deviations obtained for the yerba mate samples and their infusions was performed by employing the Tukey test at a 5% significance level (p < 0.05). All statistical analyses were performed using the Statistica 6.0 software.

**Table 1.** Concentrations of Total, Particulate, and Dissolved AI in Yerba Mate Samples and Percentage of Leaching AI to Their Infusions (Mean  $\pm$  Standard Deviation, n = 9)<sup>*a*</sup>

sample	total Al	soluble Al	particulate Al	leached Al
	(mg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(%)
mate tea 1 mate tea 2 mate tea 3 green mate 1 green mate 2 green mate 3	$\begin{array}{c} 413 \pm 2 \ a \\ 612 \pm 13 \ b \\ 254 \pm 6 \ c \\ 370 \pm 8 \ a \\ 391 \pm 3 \ a \\ 586 \pm 3 \ b \end{array}$	$\begin{array}{c} 44 \pm 2 \ a \\ 50 \pm 1 \ a \\ 15 \pm 3 \ c \\ 67 \pm 6 \ b \\ 68 \pm 3 \ b \\ 75 \pm 2 \ b \end{array}$	$369 \pm 2 a$ $562 \pm 12 b$ $239 \pm 4 c$ $301 \pm 6 ac$ $323 \pm 2 ac$ $509 \pm 3 b$	$\begin{array}{c} 10.6 \pm 0.4 \text{ ac} \\ 8.2 \pm 0.3 \text{ cd} \\ 5.9 \pm 0.5 \text{ d} \\ 18.1 \pm 0.6 \text{ b} \\ 17.4 \pm 0.6 \text{ b} \\ 12.8 \pm 0.4 \text{ a} \end{array}$

<sup>*a*</sup> Mate tea or green mate 1, 2, and 3 correspond to three different commercial trademarks; in each column, different letters indicate significant differences (p < 0.05) among results.

#### **RESULTS AND DISCUSSION**

**Concentration of Al in Yerba Mate Samples and in Their Infusions.** The total Al concentrations were determined from the acid-digested solutions of three different trademarks of green mate samples and from three different trademarks of mate tea samples. The soluble Al concentrations were determined from the filtered fresh infusions, and the particulate Al concentrations were calculated as the difference between the total and soluble Al concentrations. Significant differences (p < 0.05) were observed for the total Al concentrations in the different mate samples (**Table 1**). Mate tea labeled 2 presented nearly 2.5 times the Al contained in mate tea 3.

Reissmann et al. (23) determined Al values for the green mate that varied from 167 to 1235 mg kg<sup>-1</sup> of dry weight; these values are much higher or much lower than those determined by Wrobel et al. (12) and Giulian et al. (9), who determined that the contents of Al in the green mate were 369 and 413 mg kg<sup>-1</sup> of dry weight, respectively. In the present work, the Al content of the green mate varied from 370 to 586 mg kg<sup>-1</sup> of dry weight, respectively (Table 1). Malik et al. (24) found that the content of Al in leaves of roasted mate was  $241 \pm 18 \text{ mg kg}^{-1}$  of dry weight, and the values determined in this work for the mate tea (roasted mate) varied from 254 to 612 mg kg<sup>-1</sup> (**Table 1**). The wide variability observed for the results obtained in the present work for the green mate and mate tea samples and also for the results reported by Reissmann et al. (23) on the Al values for the green mate could be due to the soil Al content and the soil pH (25) where the plants of yerba mate were cultivated, among other factors such as industrialization process and storage conditions (9). López et al. (25) reported results on the Al content in 72 samples of 17 different spices and aromatic herbs and also found a wide variability of results for the same type of samples as well as between the different types of spices and aromatic herbs investigated. To verify the reliability of the procedure used to determine the total Al concentrations, the recovery of Al was evaluated by adding Al standard solutions prior to the digestions, and the recovery yields varied from 99 to 101%.

In the comparison of the Al concentrations in the filtered fresh infusions with the total Al of dry samples of green mate and mate tea, it was observed that 12.8-18.1 and 5.9-10.6% of soluble or dissolved Al from green mate and mate tea samples were transferred to infusions, respectively. These results were significantly different (p < 0.05), as shown in **Table 1**, and they allow us to suggest that the roasting step employed in the industrial processing of green mate to obtain the mate tea contributes to a decrease of the concentration of soluble Al present in the mate tea when compared with the higher concentrations of soluble Al obtained from the green mate. The Al concentrations in mate infusions may depend on the levels

of organic chelating species such chlorogenic acids, tannins, and other phenolic compounds present in the dry yerba mate, which may be modified or degraded during the roasting step (14).

According to Flaten (13), the Al concentrations in tea infusions generally range from 1 to 6 mg  $L^{-1}$ , and the Al concentrations determined in green mate and mate tea infusions (Table 2) were in accordance with this range of values, because they varied from 2.23 to 2.50 mg  $L^{-1}$  and from 0.50 to 1.67 mg  $L^{-1}$ , respectively. Thus, it was found that the mate tea infusions could supply lower concentrations of Al as compared to green mate infusions. However, all filtered infusions presented higher concentrations of soluble Al than the maximum permissible concentration of  $0.20 \text{ mg L}^{-1}$  fixed for drinking water (20, 23), but it is important to consider the total concentration of soluble Al leached to the infusions, because the bioavailability and toxicity of Al depend on its speciation. The reliability of the procedure employed to determine the soluble Al in the infusions of green or mate tea was evaluated by employing Al standard solution additions, and the recovery varied from 92 to 104%.

**Concentration of Total Phenolics in Infusions.** A calibration curve of gallic acid (ranging from 3.0 to 15.0 mg L<sup>-1</sup>) was prepared, and the concentrations of total soluble phenolics were determined from the regression equation of the calibration curve  $(y = 0.0962 \pm 0.0017, r^2 = 0.9996)$ . The concentration of total soluble phenolics varied from 14.0 to 30.3 mg and from 42.0 to 46.7 mg of gallic acid/g on dry basis of mate tea and green mate, respectively (**Table 2**), under the conditions employed to prepare the infusions. The obtained results indicated that mate tea contained significantly (p < 0.05) lower levels of soluble phenolics as referred to green mate. This may be due to the thermal degradation of phenolics caused by the roasting process employed to obtain the former.

As can also be seen in **Table 2**, the concentrations of soluble phenolics ranged from 467.0 to 1010.0 mg  $L^{-1}$  and from 1401.6 to 1555.4 mg  $L^{-1}$  in the mate tea and green mate infusions, respectively. The most important conclusion that can be drawn from these results is that phenolic compounds have a great influence on the concentrations of soluble Al present in the infusions, because their concentrations were proportional to the amount of phenolic compounds present in the green mate and mate tea infusions.

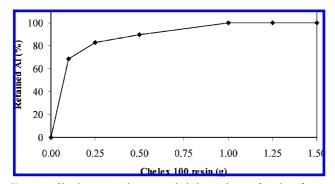
Bastos et al. (4) evaluated the content of total phenolics in one sample of green mate infusion and in one sample of mate tea infusion, and the values determined were 1130 and 710 mg mL<sup>-1</sup>, respectively, and they suggested that the lower concentrations of total phenolics observed for the mate tea infusions were due to the roasting stage used to obtain the mate tea from the green mate. In this work, according to the expectation, the phenolic contents for the green mate were higher that those obtained for the mate tea infusions, and they varied from 1401.6 to 1555.4 mg  $L^{-1}$  and from 467.0 to 1010.0 mg  $L^{-1}$ , respectively, according to the results shown in Table 2. Lima et al. (27) found that the concentration of total soluble phenolics in a nonfiltered infusion of mate tea was 78.56 mg  $g^{-1}$  of dry weight, by employing a time of extraction of 5 min; this value is in disagreement with the lower values obtained in this work  $(14.0-30.3 \text{ mg g}^{-1})$ , when the infusions were analyzed after filtration through a 0.45 µm membrane filter.

Moreover, it was found that the percentages of soluble Al leached to green mate infusions and to mate tea infusion labeled 3 were related to the phenolic concentrations in these beverages ( $r^2 = 0.8186$ ) with the exception of mate tea infusions 1 and 3, when they were considered in the correlation. For lower phenolic

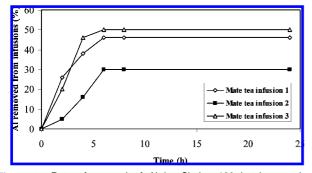
Table 2. Concentrations of Dissolved AI and Phenolic Compounds in Mate Infusions and Absorbance Measurements at 420 nm (Mean  $\pm$  Standard Deviation, n = 9)<sup>a</sup>

infusion	soluble phenolics (mg L <sup>-1</sup> )	soluble AI (mg L <sup>-1</sup> )	melanoidins A <sub>420nm</sub>
mate tea 1	519.3 $\pm$ 48.9 (15.6 $\pm$ 1.5 mg g <sup>-1</sup> ) a	$1.47 \pm 0.05  a$	$1.048 \pm 0.037$ a
mate tea 2	1010.0 $\pm$ 53.0 (30.3 $\pm$ 1.6 mg g $^{-1}$ ) b	$1.67\pm0.02$ a	$0.858\pm0.029$ b
mate tea 3	$467.0 \pm 33.1$ (14.0 $\pm 1.0$ mg g <sup>-1</sup> ) a	$0.50\pm0.09$ b	$0.335 \pm 0.031~{ m c}$
green mate 1	$1401.6 \pm 85.9$ (42.0 $\pm 2.6$ mg g <sup>-1</sup> ) c	$2.23 \pm 0.10$ c	$0.304 \pm 0.022~{ m c}$
green mate 2	1437.0 $\pm$ 25.9 (43.1 $\pm$ 2.3 mg g <sup>-1</sup> ) c	$2.27\pm0.04~\mathrm{c}$	$0.310 \pm 0.016  \mathrm{c}$
green mate 3	$1555.4 \pm 115.7~(46.7 \pm 3.5~{ m mg~g^{-1}})~{ m c}$	$2.50 \pm 0.03$ c	$0.328 \pm 0.015 \mathrm{c}$

<sup>a</sup> Values in parentheses represent the concentration of soluble phenolic compounds on dry basis of mate samples; in each column, different letters indicate significant differences (p < 0.05) among results.



**Figure 1.** Aluminum retentions on a chelating resin as a function of mass of Chelex 100 by employing a batch procedure. Conditions: standard solution containing 10.0 mg L<sup>-1</sup> Al<sup>3+</sup> in 0.10 mol L<sup>-1</sup> acetic acid/ammonium acetate, pH 5.50 buffer.



**Figure 2.** Rate of removal of Al by Chelex 100 batch procedure. Conditions: 25.0 mL of filtered fresh mate tea (roasted mate) infusion kept in contact with 1 g of resin; infusions were prepared from three different trademarks labeled 1, 2, and 3.

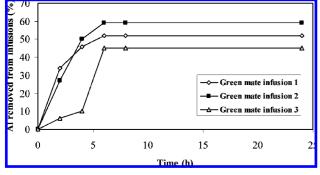
concentrations, better leaching was observed. In accordance with this result, Wrobel et al. (*12*) found that for the lower tannin level in *I. paraguariensis* was observed a better leaching of Al, Cu, Fe, and Mn.

The presence of melanoidins in mate infusions was also evaluated to verify their probable contribution to the amount of soluble Al leached to the infusions. Brown color is characteristic of melanoidins, and this attribute was used to detect the soluble melanoidins present in mate infusions prepared from the green mate and from the mate tea samples by measuring their absorbances at 420 nm (18). Table 2 shows significant differences of the compared absorbance measurements at 420 nm. Significantly different absorbances were not obtained among the green mate infusions labeled 1, 2, and 3 and the mate tea infusion labeled 3, for which values varied from 0.334 to 0.335. On the other hand, significant differences (p < 0.05) of absorbance between mate tea infusions labeled 1 and 2 were obtained (Table 2), and besides, their absorbance values were higher and also significantly different in comparison to the values shown for the other infusions. Therefore, on the basis of these results, it can be suggested that mainly in the case of mate tea samples, soluble melanoidins together with soluble phenolic compounds had influence over the percentage of Al leached to them. However, further research is needed to evaluate the influence of melanoidins on the amount of Al leached to the mate tea infusions as well as the influence of other compounds formed during the roasting process employed to obtain the mate tea from the green mate. Effects of melanoidins on the fractionation of Al in the yerba mate or in another tea plant have not been described.

**Fractionation of Noninert and Inert Aluminum from Infusions.** The optimum amount of Chelex 100 necessary to perform fractionation studies with the green mate and mate tea infusions was found previously by sorption on a chelating resin. This amount was determined using a batch procedure by keeping a 25.0 mL volume of a 10.0 mg L<sup>-1</sup> Al standard solution in contact with different masses of Chelex 100 (NH<sub>4</sub><sup>+</sup> form) for 24 h, and the results are shown in **Figure 1**. From these results it can be observed that a 1.0 g mass of chelating resin was sufficient to ensure the complete sorption of the total Al present in the standard solution. Consequently, this mass was considered to be the optimum amount of resin, because it was sufficient to promote the complete sorption of a higher content of Al when compared with those present in the different infusions prepared in this work, the contents of which varied from 0.50 to 2.50 mg L<sup>-1</sup> (**Table 2**).

In Figure 2, increases of Al removals from mate tea infusions versus time are shown for the batch procedure by using the optimized mass. It was observed from these experiments that the sorption equilibrium of Al on Chelex 100 occurred after 6 h, and the Al removals from mate tea infusions labeled 1, 2, and 3 related to the labile or noninert aluminum, which are composed of all the Al species completely sorbed on the resin, were 46, 30, and 50%, respectively. These results indicated that relatively large proportions of Al (50-70%) were not sorbed by Chelex 100 from the mate tea (roasted mate) infusions, probably due to the formation of relatively stable complexes with organic ligands present in these infusions, which are unable to be dissociated by interaction with the active groups of the sorbent, even by employing a long contact time of 24 h. On the basis of these results, it can be observed that most soluble Al present in these mate tea infusions were found as relatively inert species, which are considered to be less toxic. Some investigations for the determination of Al fractionation in tea infusions have demonstrated that Al is present mostly linked to organic compounds. In a fractionation study of Al, Alberti et al. (20) found that the major part of Al present in black and green tea infusions was associated with very strong ligands such as large polyphenolic compounds that do not compete with the Chelex 100 for the metal complexation, suggesting that the strong complexes formed with Al could contribute to the low toxicity of this element in tea. In another work, Ruszczynska et al. (28) found that up to 40% and up to 60% of Al in black and green tea infusions were present in the form of organic complexes, respectively.

Increases of Al removals from green mate infusions versus time are shown in **Figure 3**. As shown in this figure, the sorption



**Figure 3.** Rate of removal of Al by Chelex 100 batch procedure. Conditions: 25.0 mL of filtered fresh green mate infusion kept in contact with 1 g of resin; infusions were prepared from three different trademarks labeled 1, 2, and 3.

equilibrium of Al on Chelex 100 was also reached after 6 h, and the proportions of the total soluble Al from the green mate infusions labeled 1, 2 and 3, which are completely sorbed on the resin, were 52, 59, and 45%, respectively. As a consequence, 41-55% from the total soluble Al in these infusions was not sorbed on the resin. On the basis of these results obtained with Chelex 100, it could be suggested that up to 70% in the case of mate tea infusions and up to 55% in the case of green mate infusions of the total amount of soluble Al were probably present in the form of stable organic complexes. It should be stressed that the proportion of noninert and inert forms of Al in the different infusions prepared from green mate and mate tea depends not only on the industrial processing steps used to obtain the products of the yerba mate but also on the different soil conditions where the yerba mate plants were cultivated as well as on the different harvesting periods. All sorption experiments were carried out in triplicate, and the relative standard deviations of determinations ranged from 0.5 to 3.6%. There are no reports in the literature on the fractionation of noninert and inert Al from mate infusions.

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