## The Use of Maltodextrin Matrices to Control the Release of Minerals from Fortified Maté

MIGUEL E. SCHMALKO, MIRYAN G. ACUÑA, AND GRISELDA P. SCIPIONI<sup>\*</sup>

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#### Abstract

The aim of this research was to study the sensorial acceptance of a fortified food containing different minerals (calcium, magnesium and iron) and to determine the actual quantities present (bioaccessibility) when extracted in maté. A sensorial analysis was performed to compare sensorial quality of fortified and non-fortified maté. Although panelists identified differences between the fortified and non-fortified maté, only 3% of them commented on an unpleasant flavor. Sequential extraction assays were performed simulating maté consumption under laboratory conditions. Profile concentration diminished sharply after the second extraction. Magnesium was found to be completely extracted in the first 500 mL. Calcium and Iron were extracted in a very low percentage (29% and 25%, respectively). The outlet rate of the minerals was fitted to two models, and a good fitness (p < 0.001) in all cases was obtained.

Keywords: Ilex paraguariensis, fortification, calcium, magnesium, iron

### 1 Introduction

One way to overcome the lack of nutrients in the daily diet is to consume fortified foods to which nutrients are added to obtain a higher concentration than that naturally available in a given food. If the purpose of producing fortified foods is their general consumption by the population, then the nutrients used must be incorporated into foods that are regularly consumed as part of the daily diet, such as milk, bread, salt, and flour, among others (Martinez-Navarrete, Camacho, Martinez-Lahuerta, Martinez-Monzo, & Fito, 2002; Akhtar, Anjum, & Anjum, 2011).

Minerals can be incorporated into food in the form of salts. This method has been consistently used in order to fortify foods: calcium (Ca) and zinc (Zn) in apple, melon and papaya (Alzamora et al., 2005); Ca in apple (Gonzalez-Fesler, Salvatori, Gomez, & Alzamora, 2008), strawberries, carrots, corn and blueberries (Gong et al., 2010). In other cases, a matrix is formed to control the release of the compounds. Examples of this method are the limonene in matrices formed with xanthan gum and galactomannans (Secouard, Malhiac, Grisel, & Decroix, 2003); limonene and trans-2-hexanal in matrices formed with xanthan gum/propylene glycol alginate and xanthan/AG solutions (Terta, Blekas, & Paraskevopoulou, 2006); Iron (Fe) and Zn in wheat flour to prepare chapatis (Akhtar, Anjum, Rehman, Sheikh, & Farzana, 2008); calcium (Ca), magnesium (Mg) and copper (Cu) in tea-biscuits (Vitali, Dragojevic, & Sebecic, 2008) and stearic acid in matrices formed with starches (Lesmes, Barchechath, & Shimoni, 2008). Martinez-Navarrete et al. (2002) have reported about thirty different foods fortified with Fe.

Yerba maté (*Ilex paraguariensis* Saint Hilaire) is a common plant from which an infusion is

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prepared that is widely consumed in Argentina, Paraguay, Uruguay and southern Brazil. This fortified product could reach a wide segment of the population in these countries. The way of consuming yerba maté is very particular and different from that of other infusions; it is consumed in a drink popularly known as maté. The material (30-50 g) is placed in a gourd and fractions of hot water (70-85 °C) are poured over it. To drink the infusion, a device, similar to a straw with a filter at one end, is used (Scipioni, Ferreyra, Acuna, & Schmalko, 2010).

In order to consume fortified yerba maté, direct addition of fortifying salts results in two problems. One of them is the stratification of the material in the packet due to the different particle sizes. Particles of yerba maté have a relatively large size. The added salts, with a small particle size, position themselves at the bottom of the packet. Consequently, a low uniformity mixture, results. Second, the salts are generally very soluble in hot water, and the infusion has very high salt concentration in the first extractions. This produces a strongly disliked flavour. To address both problems, this research proposes to trap the salts in matrices to control their release.

This method was used in previous research to trap a sweetener for use in maté (Scipioni et al., 2010). Three different agglutinants were used (Arabic gum, maltodextrin and tapioca starch). Powder of yerba maté was used as an inert material. The best results were obtained using a ratio of maltodextrin to powder of 10%. The addition of a fortificant is generally validated with a sensorial analysis in order to evaluate the acceptability to consumers (Akhtar et al., 2011; Luckow & Delahunty, 2004; Martinez-Navarrete et al., 2002; Wang, Zhou, & Isabelle, 2007).

The objectives of this research were to test the sensorial acceptance of a product fortified with three minerals (Mg, Fe and Ca) trapped in a maltodextrin matrix, to determine their release rates and the total extracted quantities (or bioaccessibility) when consumed as maté.

## 2 Experimental

#### 2.1 Materials

The matrix was prepared using yerba maté powder, maltodextrin and the fortifying mineral. Yerba maté powder was obtained from Industry of Misiones, Argentina. It is a byproduct usually discarded due to its small size ( $_{i}425$  m). The maltodextrin was of analytical grade. The fortifying minerals were calcium gluconate ( $CaC_{12}H_{22}O_{14}$ ), magnesium oxide (MgO) and ferrous sulfate ( $FeSO_4$ ); all were analytical grade.

# 2.2 Determination of the mineral quantities

The Argentinean Food Code (CAA, 2008) determines that a portion of a fortified food must contribute from 20 to 50% of the Recommended Dietary Allowances. According to this, the quantities of the different minerals are Ca, 500 mg; Mg, 130 mg; and Fe, 7 mg. In a portion of 50 g, yerba maté contributes 50 mg of Ca, 58 mg of Mg and 2.2 mg of Fe (Ramallo, Smorccewski, Valdez, Paredes, & Schmalko, 1998). The differences between these two quantities (450 mg Ca, 72 mg Mg and 4.8 mg Fe) were added to a portion of the matrix (5 g).

#### 2.3 Preparation of the matrix

To prepare the matrix, 250 g of yerba maté powder, 25 g of maltodextrin and the mineral (265.761 g of  $CaC_{12}H_{22}O_{14}$ ; 6.567 g of MgOand 0.718 g of  $FeSO_4$ ) were used (see 1). The solids were mixed, and 750 mL of water at 60°C were added while stirring. The mixture was then placed in an ultrasonic bath at 60°C for 10 min, followed by drying, during 6 h, in a laboratory oven at 60 C. Glass trays of 0.20 x 0.40 m with a thickness of 0.005 m were used. The dried mixture was ground in a knife mill and the particles were separated in a sieve shaker. The fraction retained in 40 mesh (425 m) was used.

Experiment	Powder	Maltodextrin	Mineral added	Salt or oxide	Mineral quantity of	
				quantity	yerba maté	
	[g]	[g]		[g]	[mg/50g  portion]	
1	not used	0	none	0	0	
2	250	25	Ca	265.761	450	
3	250	25	Mg	6.567	72	
4	250	25	Fe	0.718	4.8	

Table 1: Composition of the matrices used in the experiments

### 2.4 Extraction assays

To study the release rate of the minerals, a device simulating the consumption of maté was used (Scipioni et al., 2010). Fifty grams of yerba maté, 5 g of the matrix (a portion of the fortifying matrix) and a straw were placed in the glass. To this mixture, 100 mL of hot water (at 70 C) was added to moisten the solid (for approximately 30 s). Next, a fraction of 30 mL of water was poured over the mixture and maintained for 20 s. By applying a vacuum, the extract was drawn into an Erlenmeyer flask. This procedure was repeated to obtain an extract volume of 100 mL. Using this method, four other fractions of 100 mL were obtained (Scipioni et al., 2010). The solution was evaporated in an oven at 100 C (for approximately 24 h). The solid was then burnt to obtain the ashes in a furnace at 525 C 25 C for 5 h (IRAM 20505, 1996). The ash was dissolved in 50 mL of HCl (10% v/v), and distilled water was added to a final volume of 100 mL. For each matrix, two separate extraction assays were conducted. These experiments were repeated without a matrix, to be used as a control. The quantity of each mineral in the portion is shown in 1.

## 2.5 Determination of Ca, Mg and Fe

A Perkin Elmer Analyst 200 Atomic Absorption Spectrophotometer was used to measure the ionic concentration of Ca, Mg and Fe (AOAC, 1995). The calibration curve for each mineral was made using four concentrations of the standards. Three measurements were performed for each solution, and the mean values were reported.

#### 2.6 Sensory analysis

The samples were prepared using 15 g of yerba maté and 1.5 g of the matrix. Using the triangle test, the panelists (between 31 and 35) had to distinguish between three samples (two samples were the same, and the third one was different). The results were analyzed using the proportion test. The panelist then had to qualify the different samples using a hedonic scale of 5 levels (like very much, like moderately, neither like nor dislike, dislike moderately, dislike very much).

## 2.7 Models

In this research, the experimental data were fitted to two models previously applied to verba maté. The parameters of these models are appropriate to compare the behavior of the different minerals. First, the model of Pilosof, Boquet, and Bartholomai (1985) was used 1. This model was originally developed to describe the water uptake from a solid matrix, but it had a good fit when it was applied to describe the release rate of soluble compounds from yerba maté (Sabatella, Pokolenko, & Schmalko, 2009; Scipioni et al., 2010). In this case, the accumulated weight of the minerals in the solution (W) was fitted as a function of the volume extracted (V). In 1,  $W_{\infty}$  is the weight of the mineral obtained with a large water volume, and  $V_{1/2}$  is the volume necessary to extract half of  $W_{\infty}$ . This value is related to the extraction rate.

$$W = \frac{W_{\infty}V}{V_{1/2} + V} \tag{1}$$

The experimental data were also fitted to the Spiro and Jago (1982) model 2. This model is similar to a pseudo-first order equation and was

successfully applied to the solid extraction from yerba maté by Linares, Liliana Hase, Laura Vergara, and Liliana Resnik (2010), Scipioni et al. (2010). In this model, the parameter k is related to the extraction rate, and a is the integration constant.

$$W = W_{\infty} - \frac{W_{\infty}}{e^{k*V+a}} \tag{2}$$

In this study, a high value of  $V_{1/2}$  in 1 and a low value of k in 2 were expected. The  $W_{\infty}$  value includes the minerals of the yerba maté and the quantities added in the fortification.

## 2.8 Statistical analyses

To fit the experimental data to the models, a non-linear regression technique was used. The strength of the fit was determined using four statistical parameters: the determination coefficient  $(R^2)$ , the Chi-square value  $(\chi^2, 3)$ , the root square mean error (RSME, 4) and the mean percent error (MPE, 5).

$$\chi^2 = \sum_{i=0}^{N} \frac{(W_{exp_i} - W_{pre_i})^2}{N - np}$$
(3)

$$RMSE = \left(\frac{\sum_{i=0}^{N} (W_{exp_i} - W_{pre_i})^2}{N}\right)^{0.5} \quad (4)$$

$$MPE = \frac{100}{N} \sum_{i=0}^{N} \frac{ABS(W_{exp_{i}} - W_{pre_{i}})}{W_{exp_{i}}}$$
(5)

The  $R^2$  value provides the percentage of the variation explained by the model. The  $\chi^2$  value takes into account the differences between experimental (exp) and predicted (pre) data, the number of data (N) and the number of parameters (np) used in the model (N - np, or degrees of freedom). It was very useful when the models of comparison used different parameters. The RMSE was expressed as the mean absolute difference between the experimental and predicted data, whereas the MPE is related to the relative difference. The StatGraphics statistical package ("Statgraphics," 2009) was used to process the data.

## 3 Results and Discussion

## 3.1 Comparative sensorial analysis

The fortified and non-fortified samples were compared for each mineral using the triangle test. The results are shown in 3.1. The proportion relation between the positive and total results was compared with the theoretical one (0.333). The panelists found significant differences between the two samples in all three cases (p < 0.05).

Table 2: Sensorial analysis results

	$\mathbf{C}\mathbf{a}$	Mg	Fe
Number of panellists	31	33	35
Positive response	16	17	18
Probability	0.0154	0.0113	0.0116

The panelists also qualified the samples using a hedonic scale, to quantify the differences between them. The results are shown in figure 1. For the sample fortified with Ca in figure 1a, the addition of the mineral changed the most frequent response from like moderately to neither like nor dislike. The utilization of a numeric scale from 1 to 5 gave a decrease of 15%for the fortified sample. When the fortified sample with Mg was evaluated, the panelists selected the qualification level of like moderately, but 5 panelists selected the level of dislike moderately (1b). Only one panelist selected the level dislike very much. The fortified sample decreased in panelist preference in 22% compared with the non-fortified sample. The panelist most frequent response in the sample fortified with Fe were like moderately and neither like nor dislike. Only one panelist selected the level dislike very much. The fortified sample decreased in panelist preference by 12% compared with the non-fortified sample. The non-fortified sample was scored in the three cases as 4.2, 4.4 and 3.5, although the same sample and panelists were used in the sensorial analysis. In the three cases, the non-fortified sam-

ples obtained higher qualifications than the fortified ones. Similarly (Luckow & Delahunty, 2004) found, working with orange juice, that consumers always preferred the sensory characteristics of the conventional juices.

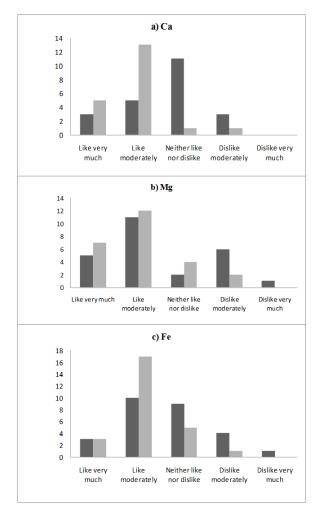


Figure 1: Hedonic test used to compare the differences between the non-fortified (light grey) and fortified (dark grey) samples with Ca (a), Mg (b) and Fe (c).

### **3.2** Mineral extractions assays

Figure 2 shows the mineral concentration variation with the extraction volume in all of the experiments. In both cases, using the fortified and non-fortified samples, the mineral concentration diminishes with the extraction volume. Figure 2a shows the Ca concentration for both materials. In the fortified sample, the two first fractions have a high mineral concentration, while the third fraction shows a substantial reduction in mineral concentration. Ca concentration diminishes in the non-fortified sample to a lesser extent.

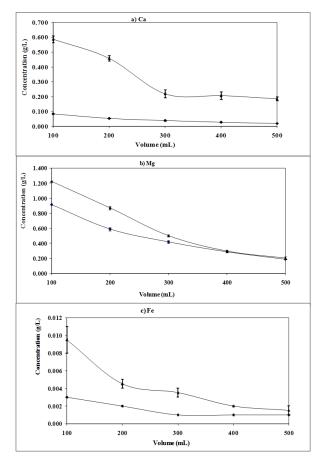


Figure 2: Mineral concentration variation with the extraction volume for Ca (a), Mg (b) and Fe (c).  $\blacktriangle$  Fortified,  $\blacklozenge$  Non-fortified material.

Figure 2b shows the curves of Mg concentration using the fortified and non-fortified samples. In the non-fortified maté, the Mg concentration is higher than the Ca concentration, and the mineral quantity added to fortified sample is less than that added to the Ca one. Consequently, the difference between the curves is less than for the Ca. For the fortified sample, the pro-

file concentration for this mineral is not as sharp as that for Ca. The concentration variations for Fe using the fortified and non-fortified samples are shown in figure 2c. The Fe concentration in the maté using the fortified and non-fortified samples is less than the concentrations of Ca and Mg (about 60-130 times). The Fe concentration profile variation is not as sharp as that of Ca and is similar to the Mg concentration profile. When the panelists quantified the differences between the fortified and non-fortified samples, the sample fortified with Fe showed a minor difference, compared with the non-fortified sample (12%). This is probably due to the very low concentration of the mineral in the maté (< 0.010g/L). The samples fortified with Ca and Mg contained high concentrations of the minerals, which the panelists were able to detect. It is probable that the panelists did not dislike the taste of the sample fortified with Ca because they equated it to the taste of milk. In this case, the difference in preference between the fortified and non-fortified samples was 15%. In the sample fortified with Mg, the panelists found a new strange taste that they did not like, and the difference in preference was higher (22%).

## 3.3 Accumulated mineral weights

Figure 3 presents the total weight of each mineral with the extraction volume in the maté consumption. Mg showed a near complete recovery of the amount added in the first 500 mL. In the case of Ca and Fe, only a fraction of the amount added was extracted, specifically 29% and 25%, respectively. These percentages represent the bioaccessibility of the minerals when they are consumed. The release of the mineral is related to the matrix composition. Yerba maté powder has many components, including proteins (approx. 10%) and polyphenols (approx. 8-10%) (Bravo, Goya, & Lecumberri, 2007; Brumovsky, Hartwig, & Fretes, 2012). Vitali et al. (2008) studied the bioaccessibility of Ca and Mg in tea-biscuits prepared with different components. They found that the bioaccessibility of Ca (from 22.8 to 55.2%) was less than that of Mg (from 64.9 to 78.1). A similar conclusion was obtained in this research. Vitali et al (2008), also

found that polyphenols and proteins diminished the bioaccessibility of these two minerals and depended more on polyphenol concentration. Our research has also determined that the effects were greater for Ca than for Mg.

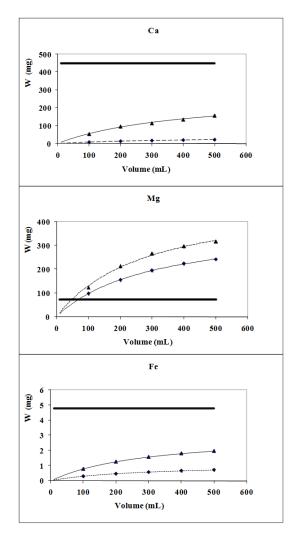


Figure 3: Mineral accumulated weight with the extraction volume for Ca (a), Mg (b) and Fe (c). Experimental and theoretical data obtained with the Pilosof et al. (1985).  $\blacktriangle$  Fortified and  $\blacklozenge$  Nonfortified material. The . The black horizontal line shows the levels of mineral added to the infusion.

Another way to analyze the data is by fitting them to models and comparing their constants. Two models were selected by the physical mean-

Table 3: Constants of the Pilosof et al. (1985) model (Eq. 1). Mean values, confidence limits and statistic parameters  $R^2$ ,  $\chi^2$ , RSME, MPE.

Experiment		$W_{\infty}[mg]$	$V_{1/2}[mL]$	$R^2$	$\chi^2$	RSME	MPE
Ca	Non-fort	$38 \pm 2$	$352 \pm 18$	99.98	0.00427	0.0506	0.31
	Fort	$286 \pm 54$	$370\pm235$	99.59	9.26	2.362	2.16
Mg	Non-fort	$403 \pm 27$	$334\pm46$	99.94	3.045	1.352	0.76
	Fort	$486 \pm 82$	$274\pm101$	99.44	41.317	4.98	2.38
Fe	Non-fort	$1.3 \pm 0.3$	$348 \pm 286$	99.43	0.00028	0.013	0.19
	Fort	$3.1 \pm 0.2$	$215\pm37$	99.84	0.00133	0.0283	1.54

ing of their constants: the model of Pilosof et al. (1985), 1 and the Spiro and Jago (1982) 2. 3 shows constant values of the Pilosof et al. (1985) model, its confidence intervals and values of  $R^2$ ,  $\chi^2$ , RSME and MPE. In all cases, the fit was significant, and values of  $R^2$  higher than 99% were obtained. The other statistics had relatively low values and were higher in the fortified sample than in the non-fortified samples.

Values of (the mineral weight obtained with a great volume of water) for Ca (286.1 mg) and Fe (3.1 mg) were lower than the added quantities (450 and 4.8 mg, respectively). Consequently, the added quantities for these two minerals are not completely bioaccessible (see figures 3a and 3c). A different situation was found with Mg. For this mineral, a total extraction is obtained with 500 mL. This fact can be observed in figure 3c, as the difference between the accumulated weights at 500 mL is equal to the added quantity of this mineral. Values of were not statistically different between the fortified and non-fortified samples. This means that the mineral extraction rate from the matrix is not different than the extraction rate from the yerba maté. 4 shows constant values of the Spiro and Jago (1982) model (Eq. 2), its confidence intervals and values of  $R^2$ ,  $\chi^2$ , RSME and MPE. The values of the statistical parameters were similar to those obtained with the Pilosof et al. (1985) model. The values predicted with this model were lower than those obtained with 1. The values of k for Mg were lower in the fortified sample than in the non-fortified sample. For the other two minerals, no differences in the k values were found. This model includes another constant, a, which indicates the degree of mineral release at the beginning of the extractions (time = 0). In all cases, the confidence limits for this constant include the zero value; consequently, there is no important release of the minerals at the beginning of the extraction. In other cases, such as in tea, high constant values were found for soluble tea compounds. In this case, Linares et al. (2010) conclude that this high initial release is due to the cellular rupture during tea leaf processing.

## 4 Conclusion

Matrices with maltodextrin and minerals (Ca, Mg and Fe) can be used to fortify yerba maté. In the extraction assays, simulating yerba maté consumption, a good recovery of Mg, and low recoveries of Ca and Fe were obtained. In the sensorial analysis, panelists were able to differentiate the fortified sample from the non-fortified sample in all three cases and they did not find an unpleasant savor in the fortified sample. A portion of the fortified yerba maté can contribute up to 50% of the Recommended Dietary Allowances when Mg is used, and up to 14.5% and 12.5% when Ca and Fe are used, respectively.

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Experiment		$W_{\infty}[mg]$	k	a	$R^2$	$\chi^2$	RSME	MPE
Ca	Non-fort	$27 \pm 1$	$0.0033 \pm 0.0004$	$0.036 \pm 0.027$	99.99	0.0335	0.1158	0.71
	Fort	$198 \pm 134$	$0.0034 \pm 0.0287$	$0.015 \pm 0.302$	99.51	18.064	2.688	1.99
Mg	Non-fort	$284\pm10$	$0.0037 \pm 0.0004$	$0.020 \pm 0.029$	99.99	0.379	0.39	0.16
	Fort	$336 \pm 14$	$0.0051 \pm 0.0008$	$0.006\pm0.073$	99.98	75.16	5.48	2.61
Fe	Non-fort	$1.1 \pm 0.7$	$0.0026\pm0.0110$	$0.083\pm0.233$	99.42	0.00046	0.0136	0.33
	Fort	$2.5\pm0.5$	$0.0037 \pm 0.0024$	$0.137\pm0.017$	99.82	0.00074	0.0172	0.81

Table 4: Constants of the Spiro and Jago (1982) model (Eq. 2). Mean values, confidence limits and statistic parameters R2,  $\chi^2$ , RSME, MPE.

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