



# Simultaneous determination of quality parameters in yerba mate (*Ilex paraguariensis*) samples by application of near-infrared (NIR) spectroscopy and partial least squares (PLS)



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## ABSTRACT

A simple, fast and eco-friendly methodology to determine quality parameters, such as moisture, total ashes and caffeine content, in yerba mate samples was developed using near-infrared (NIR) spectroscopy and chemometrics. The NIR spectra of the yerba mate samples were measured directly on the product contained in the packages, thus avoiding the need of previous pretreatments. In the present study, NIR spectroscopy was used combined with chemometric regression methods based on partial least squares (PLS) algorithm. Performance of the regression models was adequate with very good statistical results, the correlation coefficients ( $R^2$ ) were above 0.90 with a root mean square error of prediction (RMSEP) lower than 0.17% for the three quality control parameters studied. Besides, the quality of the proposed methodology was also evidenced on the basis of the relative error of prediction (REP), which was less than 6.97% in all cases, and the limit of detection (LOD), which ranged from 0.72 to 0.80% for moisture, from 0.74 to 0.76% for total ashes, and from 0.22 to 0.25% for caffeine. Overall, the results demonstrated that NIR spectroscopy with PLS analysis can be successfully applied as a rapid routine method to determine parameters of quality control in yerba mate samples.

## 1. Introduction

The yerba mate or mate (*Ilex paraguariensis*) is a plant that is native to the subtropical region of southern Latin American countries, and is widely consumed and produced in Argentina, Brazil, Paraguay and Uruguay. The herbal infusion beverage is an alternative to coffee and tea in these countries (Heck & de Mejia, 2007). Yerba mate is a food that is considered a rich source of essential elements (Ca, K, Mg, P, Cu, Fe, Mn, etc.); polyphenols (especially chlorogenic acids); alkaloids (caffeine and theobromine); flavonoids (rutin and luteolin) and saponins (matesaponins). These compounds have been associated with health benefits, such as antioxidant activity, and have been reported as anticarcinogenic, antiallergenic, diuretic, hypocholesterolaemic, vasorelaxant, antimicrobial, antiobesity and digestion-improving (Dartora et al., 2011; Burris, Harte, Michael Davidson, Neal Stewart Jr, & Zivanovic, 2012). Yerba mate processing occurs in six steps: harvesting, roasting, drying, milling, aging, and blending/packaging. Argentina is the largest producer and the first significant exporter, cultivating around 165,200 ha of yerba mate per year in the northeastern part of the country (Misiones and Corrientes). This is equal to approximately

280,000 tons per year, of which 43,000 tons are destined for export to Syria, Chile, Lebanon, United States, Spain and Japan (Peralta, 2018).

Quality control is very important in all stages of food processing and fundamentally, in the final marketed product to guarantee quality and safety for the consumer. The most commonly used reference techniques for food quality control are gravimetric methods, liquid or gas chromatography, titrations using specific reagents and colorimetric measurement techniques. All of these present certain complications: they are tedious, slow, difficult to automate for many samples, and require pretreatment of samples using large amounts of organic solvents. A good alternative is near-infrared (NIR) spectroscopy combined with chemometric algorithms, since it enables the development of analytical methodologies that will have many advantages over traditional analysis techniques. The reasons that make this technique attractive are diverse: it allows the registration of solids, liquids and gases; it does not require extensive sample pretreatment; spectral registration is fast; it is a non-destructive technique; routine analysis is fast; it is an economical technique; it does not use toxic reagents and pollutants; and it also allows multicomponent analysis from a single spectrum (Moros, Garrigues, & Guardia, 2010). NIR spectroscopy in association with

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chemometric tools has proved to be an excellent technique for the analysis and monitoring of quality parameters in foods (Chen, Zhao, Huang, Zhang, & Liu, 2006; Ferreira, Galão, Pallone, & Poppi, 2014).

Some previous works have been performed applying NIR spectroscopy and chemometrics in yerba mate samples for quantification of moisture (Mazur, Alves de Oliveira, et al., 2014), phenolic compounds (Frizon et al., 2015), methylxanthines (Mazur, Peralta-Zamora, Demczuk, & Ribani, 2014), and also for classification of yerba mate samples according to their geographical origin (Cozzolino, Restaino, & Fassio, 2010; Alexandre; Kahmann, Anzanello, Marcelo, & Pozebon, 2017; Marcelo, Martins, Pozebon, & Ferrão, 2014).

The Argentine Food Code (CAA), which is responsible for food regulation in Argentina, establishes that the yerba mate that is stored, exhibited or sold must comply with a series of characteristics, between them: 9.5% of moisture as maximum, 9.0% of total ashes as maximum and 0.6% of caffeine as minimum (CAA, chapter XV, 2017). In this context, the aim of the present work is the development of a rapid and friendly methodology by application of NIR spectroscopy coupled with partial least squares (PLS) algorithm. The developed method represents a new alternative to replace the reference methods of quality control, avoiding the use of unsafe organic solvents, and saving experimental time and operator efforts. It is important to highlight that this is the first time that the simultaneous quantification of quality parameters in yerba mate samples is done, using a single spectrum per sample. The results obtained for moisture, total ashes and caffeine are discussed in detail below.

## 2. Materials and methods

### 2.1. Yerba mate samples

This work was carried out with 76 samples of yerba mate of different brands, which were acquired in their commercial packages of 500 g in supermarkets, dietetics, stores and fairs from different Argentine cities. The content of the packages was placed in polypropylene bags and stored in a cool (21 °C) and dark place with low moisture environment controlled with silica gel adsorbents. Before each analysis (reference methods and NIR spectrum measurement), each sample was mixed and homogenized.

### 2.2. Reference methods

The chemical analyses were performed in duplicate, so a total of 152 analyses were performed for each quality parameter studied.

Moisture was measured in accordance with the air oven method 925.19 of the Official Methods of Analysis from the Association of Official Analytical Chemists (AOAC) International, which is based upon the loss of weight after 5.0000 g of sample have been dried in a conventional oven at 100 °C during 3 h until constant weight (AOAC International Arlington, 2019).

Total ashes in yerba mate samples were determined by AOAC method 920.100A (direct method) with a muffle furnace set at 550 °C during 5 h (AOAC International Arlington, 2019).

Caffeine content was measured using the UV spectroscopy method with some modifications (Sinija & Mishra, 2009). A portion of 0.2000 g of each yerba mate sample was extracted in 100.0 mL of boiling ultra-pure water (stirred with a rod and let it boil for 5 min). Then, 5.00 mL of hot water extract of yerba mate samples were taken in separating funnels, and 5.00 mL of chloroform were added to each sample. The separating funnel was shaken vigorously for 5 min and the solutions were then allowed to separate for 10 min at room temperature. Lower chloroform layer was collected to read absorbance at 277 nm against pure chloroform as blank, using UV-Visible spectrophotometer Beckman 120 DU 640 (Fullerton, CA, United States). A standard curve was prepared for caffeine estimation in the concentration range between 0.00 and 25.00 mg L<sup>-1</sup>.

### 2.3. NIR spectra collection

NIR absorbance measurements were conducted by placing the samples inside the quartz cup and were performed in reflectance mode using a FOSS NIRS DS2500 spectrometer (FOSS, Hillerød, Denmark), equipped with a monochromator and a dual Si and PbS detector. This instrument converts the reflectance measurements in absorbance, so the absorbance spectra were recorded with the wavelength mode, ranging from 1100 to 2500 nm with a spectral resolution of 0.5 nm.

### 2.4. PLS algorithm and software

PLS algorithm in its mode PLS1, which was proven to be effective in many quantitative applications, was used in the present work. PLS1 was applied for first-order data and the models of regression were calibrated one at a time (one for each quality parameter analyzed). PLS1 was implemented using the graphical interface MVC1 (Olivieri, Goicoechea, & Iñón, 2004), available on the Internet (MVC1, 2019).

## 3. Results and discussion

### 3.1. Quality parameters obtained by reference methods

The values of moisture, total ashes and caffeine content found by the reference analyses in the yerba mate samples studied ( $n = 76$ , by duplicate) are displayed in the box and whisker plot of Fig. 1. The concentration of moisture presented results between 4.8 and 7.4%, total ashes between 5.5 and 6.2%, and caffeine between 1.0 and 1.9%. Furthermore, in the three parameters studied there are atypical minimum and maximum values. Table 1 shows the range, the mean and the standard deviation of reference values of quality parameters studied for yerba mate samples chosen for the calibration and validation sets. The choice of the samples for the calibration and validation sets was randomly carried out by the Kennard-Stone algorithm (Kennard & Stone, 1969): from the total of 76 yerba mate samples,  $n = 53$  (70%) were selected for the calibration model and  $n = 23$  (30%) for the prediction. Samples included a more broad range in moisture (3.6–8.4%), and one not so wide in total ashes (4.8–6.3%) and caffeine (0.7–2.1%). As can be observed, the values of each parameter are similar for both sets and all of them are in agreement with the values established by the CAA.

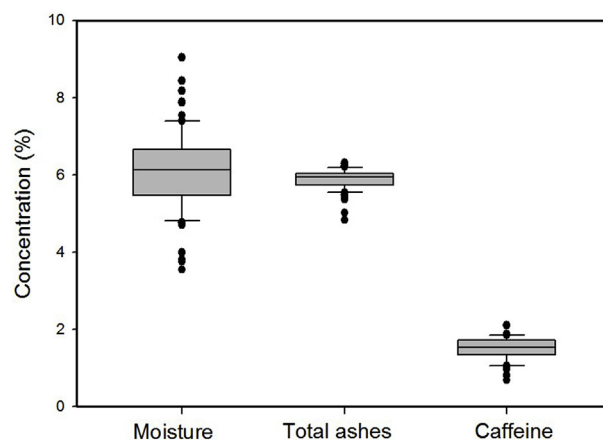


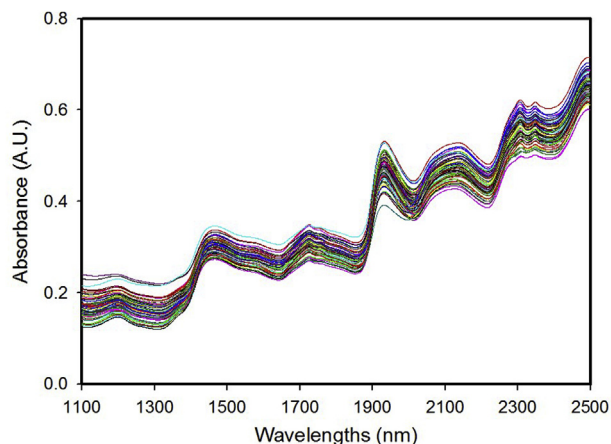
Fig. 1. Box and whisker plot representation of moisture, total ashes and caffeine concentrations obtained with reference methods in yerba mate samples ( $n = 76$ , duplicate analysis). The gray boxes are bounded by the 25% and 75% quartiles, with the median inside, whereas the extreme levels correspond to 5% and 95% quartiles, and the black circles are atypical values.

**Table 1**

Range of values obtained by the reference methods for yerba mate samples in the calibration and validation data sets.

	Calibration				Validation			
	n	Range	Mean	SD	n	Range	Mean	SD
Moisture (%)	51	3.6–8.4	6.0	0.9	23	4.7–8.2	6.3	0.7
Total ashes (%)	53	4.8–6.3	5.9	0.3	23	5.4–6.3	5.9	0.3
Caffeine (%)	50	0.7–2.1	1.5	0.3	23	1.0–1.9	1.5	0.2

n = number of samples; SD = standard deviation.



**Fig. 2.** NIR spectra of the 76 yerba mate samples studied, obtained in the range between 1000 and 2500 nm, without pretreatments. A. U.: arbitrary units.

**Table 2**

Parameters used in the calibration model and statistical results for moisture, total ashes and caffeine in validation samples using NIR spectroscopy and PLS1.

	Moisture	Total ashes	Caffeine
Spectral range (nm)	1100–2500	1350–2500	2200–2500
LV	3	5	4
Treatment (%)	MC	MC-D-d [1,5,25]	MC-SNV-d [1,3,7]
RMSECV (%)	0.30	0.11	0.17
R <sup>2</sup> (calibration)	0.94	0.90	0.94
RMSEP (%)	0.17	0.09	0.10
REP (%)	2.82	1.52	6.97
R <sup>2</sup> (validation)	0.97	0.95	0.90
LOQ (min-max) (%)	2.15–2.41	2.22–2.27	0.65–0.75
LOD (min-max) (%)	0.72–0.80	0.74–0.76	0.22–0.25

D = detrend; d = derivative [order, polynomial degree, moving window]; LOD = limit of detection; LOQ = limit of quantitation; LV = latent variables; MC = mean center; R<sup>2</sup> = correlation coefficient; REP = relative error of prediction; RMSECV = root mean square error of cross-validation; RMSEP = root mean square error of prediction; SNV = standard normal variate.

### 3.2. NIR spectra interpretation

The NIR spectra without pretreatment of the 76 yerba mate samples are presented in Fig. 2. Absorption bands in the NIR region observed around 1200 nm, 1460 nm and 1930 nm are associated with water, and at 1726 nm with oils (e.g. essential oils). The region around 1700 nm is associated with the presence of compounds containing aromatic groups. The bands at 2140 nm, 2302 nm and 2348 nm are associated with amino acids and fatty acids, and could also be associated with aromatic groups, particularly benzene rings (e.g. caffeine) (Cozzolino et al., 2010; Sinija & Mishra, 2009).

### 3.3. PLS regression models

As mentioned before, the complete data of yerba mate samples (n = 76) were randomly split into calibration (n = 53) and validation (n = 23) sub-sets. As observed in Table 1, two outliers were removed from the calibration sample set for the moisture model and three for the caffeine model.

Table 2 shows wavelength ranges, the optimum numbers of latent variables and pre-processing methods for each model. The number of latent variables used for each model was obtained by cross-validation. The analytical performance of the models was evaluated by calculation of the root mean square error of cross-validation (RMSECV), the root mean square error of prediction (RMSEP), the relative error of prediction (REP) and the correlation coefficients (R<sup>2</sup>). Values close to one for R<sup>2</sup>, low values for RMSECV and RMSEP, and values equal to or less than 10% of REP indicate the good performance of the model for the prediction of the quality parameters. The limit of quantification (LOQ) and the limit of detection (LOD) were calculated according to a novel IUPAC-consistent estimator, which adopts the form of a detection interval (Allegrini & Olivieri, 2014). As can be observed in Table 2, the results obtained for the validation set using PLS1 analysis of the NIR spectra are very good and encouraging, since the RMSEPs were low (< 0.17%) and the values of R<sup>2</sup> were from 0.90 to 0.97. It should be highlighted that the simultaneous determination of the three quality parameters in yerba mate samples was achieved quickly and easily. Besides, these results indicate that both LOQ and LOD obtained are appropriate for determining moisture, total ashes and caffeine in yerba mate samples, corresponding to REPs of 2.82%, 1.52% and 6.97%, respectively.

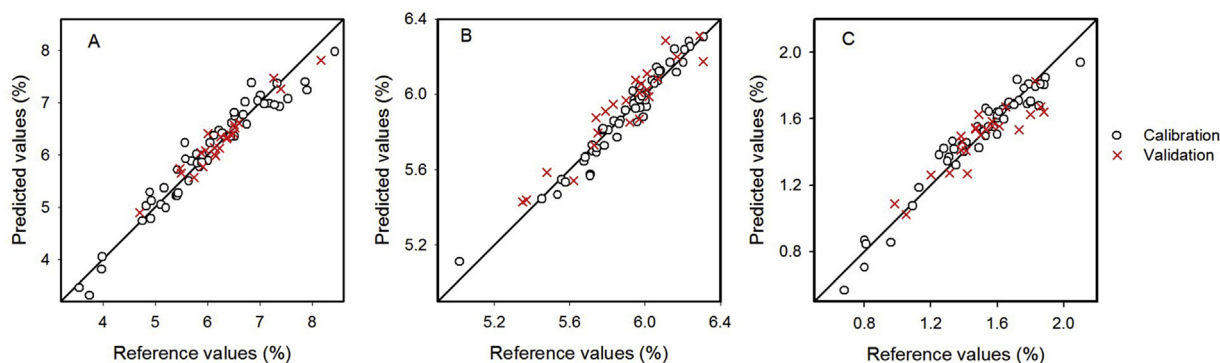
Fig. 3 shows the plots of predicted against reference values for the determination of moisture, total ashes and caffeine in calibration and validation sets. These presented good correlation for the three parameters studied. The correlation coefficients for the models to predict moisture, total ashes and caffeine content were equal to 0.94, 0.90 and 0.94; and 0.97, 0.95 and 0.90 for calibration and validation sets, respectively. Additionally, to verify the good relation between the reference values and the NIR predicted values for the set of 23 validation samples, the relative error (RE) was calculated, which is the absolute ratio between the reference value minus the NIR predicted value divided by the reference value (see Table 3). In general, the RE values for moisture (0.06–6.60%), total ashes (0.01–2.91%) and caffeine content (0.12–12.63%) were low.

Finally, very few works have been published about traceability and authentication of yerba mate samples. No studies with similar purposes, which would describe the simultaneous determination of these three quality control parameters in yerba mate samples or in other foods, were found. In 2014, a study reported by Mazur, Alves de Oliveira, et al. (2014) described a multivariate model based on NIR spectroscopy and PLS regression for the prediction of moisture content in yerba mate samples. A total of 38 commercial yerba mate samples from Brazil were analyzed, resulting in average errors of 2.4% during the external validation phase. Their results are comparable with those reported in this work for moisture content, which once again demonstrates the convenience of associating NIR spectroscopy and PLS algorithm for the establishment of routine quality control with minimal sample manipulation.

## 4. Conclusions

In the present work, near-infrared (NIR) spectroscopy was successfully combined with partial least squares (PLS) and applied to determine simultaneously three quality parameters in yerba mate samples: moisture, total ashes and caffeine content.

The total time required for the complete analysis of one yerba mate sample was about 5 min. It is concluded that the proposed strategy is faster compared to the reference methods, which required more than



**Fig. 3.** Relation between the reference values and predicted values by the calibration models that employed NIR and PLS1 for the content of (A) moisture, (B) total ashes and (C) caffeine. (○) calibration values, (×) validation values and the solid line is the perfect fit.

**Table 3**

Comparison between the reference values and the values predicted by the regression model using NIR spectroscopy and PLS1 in validation samples.

Sample	Moisture			Total ashes			Caffeine		
	Reference values (%)	NIR values (%)	RE (%)	Reference values (%)	NIR values (%)	RE (%)	Reference values (%)	NIR values (%)	RE (%)
1	6.25	6.35	1.58	6.29	6.31	0.34	1.38	1.50	8.36
2	4.70	4.90	4.19	5.97	5.87	1.66	1.49	1.62	9.04
3	7.26	7.47	2.88	5.73	5.73	0.01	1.20	1.26	5.18
4	6.16	5.98	2.89	6.11	6.29	2.91	1.65	1.67	1.28
5	6.36	6.32	0.67	6.01	6.11	1.68	1.47	1.54	4.52
6	6.13	6.14	0.22	5.95	6.08	2.14	1.88	1.64	12.63
7	7.40	7.27	1.82	5.97	6.01	0.63	1.31	1.27	2.92
8	6.50	6.41	1.34	5.75	5.79	0.77	1.42	1.27	10.51
9	5.96	6.09	2.16	6.02	5.99	0.51	1.53	1.54	0.51
10	5.50	5.66	2.85	5.98	6.06	1.30	1.83	1.83	0.12
11	5.91	5.77	2.30	6.31	6.18	2.13	1.86	1.67	9.98
12	6.13	6.02	1.86	6.07	6.08	0.26	1.57	1.58	0.82
13	6.01	6.41	6.60	5.90	5.97	1.14	1.39	1.46	5.01
14	6.23	6.13	1.64	5.74	5.88	2.40	1.50	1.50	0.29
15	5.87	6.05	2.99	5.79	5.91	2.06	1.47	1.55	5.16
16	6.51	6.58	1.07	5.62	5.54	1.39	0.98	1.09	11.23
17	6.45	6.39	0.90	5.83	5.95	2.04	1.80	1.62	9.76
18	5.47	5.74	4.90	5.37	5.44	1.31	1.57	1.56	0.78
19	6.52	6.52	0.06	5.92	5.85	1.16	1.73	1.53	11.37
20	6.60	6.61	0.20	6.01	6.03	0.26	1.05	1.02	2.44
21	8.17	7.81	4.40	5.48	5.59	1.94	1.38	1.41	2.26
22	5.74	5.57	2.91	6.17	6.20	0.48	1.61	1.56	3.40
23	6.38	6.34	0.63	5.35	5.43	1.49	1.41	1.41	0.21

RE = relative error.

6 h per sample. In addition, the method is notably simple, non-destructive and green since the determination is carried out without previous pretreatment, thus avoiding the use of toxic organic solvents, which is essential for the environmental safety.

The satisfactory results indicate that NIR-chemometric techniques can be applied in the control laboratories as an analytical tool to monitor the quality of yerba mate samples.

### Compliance with ethics requirements

This article does not contain any studies with human or animal subjects.

### CRedit authorship contribution statement

**Gianina B. Rossi:** Validation, Formal analysis, Investigation. **Valeria A. Lozano:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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