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Determination of total phenolic compounds in yerba mate (*Ilex paraguariensis*) combining near infrared spectroscopy (NIR) and multivariate analysis



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ABSTRACT

A quick method to determine the content of phenolic compounds (TPC) in yerba mate based on near infrared spectroscopy (NIR) was studied aiming to provide reductions of cost and analysis time for the mate industry without generating laboratory effluents. A total of 111 samples of yerba mate from different regions of the State of Paraná, Brazil (Southeast, South Central and Metropolitan Area of Curitiba) was analyzed by the Folin-Ciocalteu method. The average contents of TPC found were 84.82, 133.31 and 37.00 mg g⁻¹, respectively. The samples were separated into three groups (regarding the different growing regions) using the principal component analysis (PCA). Models were developed using partial least squares (PLS) and some preprocessing strategies of the spectral data were evaluated. The best result was obtained by Multiplicative Scatter Correction (MSC) and first derivative with six latent variables. The best model presented a correlation coefficient of 0.81 with a prediction error of 12%. The results showed that NIR can be applied as an efficient method for the assessment of TPC, which allows classifying samples in relation to its origin of planting, processing and agronomic practices applied, aiding the decision of referral and use of yerba mate in different final products.

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1. Introduction

Yerba mate (*Ilex paraguariensis*) is widely consumed in South America as hot and iced tea, representing an important economic activity in several countries within this region. Yerba mate leaves contain high concentrations of phenolic compounds, mainly tannins, flavonoids and phenolic acids (Bravo, Goya, & Lecumberri, 2007; Vieira et al., 2008), which provide a significant amount of antioxidants to the herb (Filip, Lolito, Ferraro, & Fraga, 2000), decreasing the oxidation of human low density lipoprotein (LDL) either *in vitro* or *in vivo* (Gugliucci, 1996; Gugliucci & Stahl, 1995). Martins and collaborators (2009) observed that rats fed with yerba mate presented lower quantities of thiobarbituric acid-reactive

substances in the liver, suggesting that the treatment with yerba mate extract protects unsaturated fatty acids from oxidation and can especially protect the liver. According to Andersen and Fogh (2001), the yerba mate extract delayed gastric emptying in overweight patients, reducing perception of satiety and leading to significant weight loss after 45 days. Arcari et al. (2009) demonstrated that the treatment with yerba mate extract has an anti-obesity effect on *in vivo* adipose tissue for it controls the expression of various genes involved in the process of obesity, such as inflammatory markers. Inflammation is a factor for many human health disorders such as cancer, cardiovascular diseases, obesity and diabetes. Therefore, the high content of bioactive phenolic compounds in yerba mate encourages its use in foodstuffs.

Currently, the determination of phenolic compounds is carried out by several methods such as high performance liquid chromatography (HPLC) (Berté, Beurx, Spada, Slavador, & Ribani, 2011; Cardozo et al., 2007), gas chromatography (GC), or combinations of these analyses with mass spectrometry (MS) (Jacques, Santos, Dariva, Oliveira, & Caramarão, 2007). These techniques are

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efficient for they provide rapid separation and quantification of phenolic compounds. However, they require sophisticated and expensive equipment, skilled labor and a variety of reagents. Another relevant method includes spectrophotometry since it represents a relatively simple method for quantifying phenolic compounds of plants. The Folin-Ciocalteu assay (FC) bases on a chemical reduction involving a reagent containing sodium molybdate and sodium tungstate (Singleton & Rossi, 1965). The FC reagents react with phenols, as well with other substances, such as ascorbic acid, aromatic amines, sugars and xanthines (Prior, Wu, & Schaich, 2005). This procedure has been used by Mejia, Song, Heck, and Ramirez-Mares (2010) to assess the content of total polyphenols in yerba mate tea. Turner, Cogoi, Isolabella, Filip, and Anesini (2011) evaluated the content of polyphenols in *I. paraguayensis* during the industrial processing. The main phenolic compounds identified in the leaves were chlorogenic acids (5-O-caffeoylquinic, dicaffeoylquinic and 3, 4-isomers) and rutin flavonoids (Filip, López, Gibert, Cousio, & Ferraro, 2001; Mejia et al., 2010). As an alternative to replace the classical chemical analysis, near infrared spectroscopy (NIR) is a simple, fast and non-destructive method that measures the interaction of light with the material, which is in turn determined by the vibration of the chemical bonds of the sample constituents (Pasquini, 2003). In addition, it exempts the use of reagents. This technique has been applied to determine the major phenolic acids in Radix Salvia Miltorrhiza extracts (Li & Qu, 2010), the quality of green tea (Luybaert, Zhang, & Massart, 2003), the caffeine, theobromine and theophylline contents in coffee (Huck, Guggenbichler, & Bonn, 2005), the antioxidant content of bamboo leaves (Wu et al., 2012) and the content of total flavonoids in Ginkgo biloba leaves (Ji-Yong et al., 2012). NIR was also used by Cozzolino and collaborators (2010) to classify yerba mate samples according to its geographical origin – Brazil, Argentina and Uruguay.

According to a recent survey of literature, to date no research has been reported using NIR for the determination of phenolic compounds in yerba mate, which is relevant considering that this analysis can be inserted into the industrial production allowing important conclusions about the use of mate leaves. Within this context, the aim of this work is to evaluate the potential of NIR combined with chemometrics in order to quantify the phenolic compounds in samples of yerba mate (*I. paraguayensis*) grown and processed in different regions of Paraná, Brazil, such as Southeast, South Central and Metropolitan Area of Curitiba.

2. Materials and methods

2.1. Plant materials

In this study, 111 samples of yerba mate were collected from industries located in different zones of Paraná: Metropolitan Area of Curitiba (Region A: $n = 6$, samples 1, 2, 3, 35, 36 and 37), Southeast (Region B: $n = 30$, samples 4–34) and South Central (Region C: $n = 75$, samples 38–111). Samples from region A are native plants with higher leaf mass productivity due to breeding programs conducted by Embrapa Florestas. The plants from region B were cultivated under direct sunlight by small producers in the South Central zone. Samples from area C are plants intercropped with Eucalyptus and grown under different sunlight levels. Before the analyses, the samples from the South Central region and the Metropolitan Area of Curitiba were dried in a home microwave oven operating at 2450 MHz (Philco, model PMW-101) according to the methodology described by Hansel, Domingos, Lima, and Pasquini (2008). The leaves from the Southeast region, provided by a company located at the South-East of Paraná, were industrially dried in a continuous belt for 4–6 h at a temperature between 100

and 110°C. In as much as the samples from regions A and C are part of experimental programs, they were not industrially dried, unlike the mate leaves from region B. The samples from all three regions were crushed in a bench mill (IKA A11, basic model), placed in polypropylene bags and stored in a freezer until the analyses. It is worthwhile to say that the mate leaves from the three distinct regions differ also with respect to the agronomic practices and processing related to each zone.

In order to obtain a comparison between two spectrometers, and therefore evaluate the robustness of the coupled technique proposed herein, all the 111 samples were analyzed by the devices TENSIONER (Bruker Optics, Ettlingen, Germany) – identified with the numbers 01 T–111 T – and VERTEX (Bruker Optics, Bruker Corporation, Billerica, Massachusetts, USA) – identified with the numbers 112 V–222 V. Thus, sample one is represented by both numbers 01 T and 112 V.

2.2. Determination of total phenolic compounds

The extraction of total phenolic compounds (TPC) was performed according to the methodology described by Dutra, Hoffmann-Ribani, and Ribani (2010). 100 mL of water: ethanol 1:1 (v/v) were added to 2 g of yerba mate and kept for 12 h at room temperature. Three extractions were conducted with 25 mL of 50% hydro-ethanolic solution under reflux for 30 min each, producing 250 mL of extract, which were then filtered. The content of TPC was determined spectrophotometrically by the Folin-Ciocalteu procedure in agreement with the methodology published by Singleton, Orthofer, and Raventós-Lamuela (1999). In summary, 500 μ L of extract were mixed with 2.5 mL of Folin-Ciocalteu reagent (1:10) and 2.0 mL of a sodium carbonate (Na_2CO_3) solution (4% w/v). After 120 min of reaction in the absence of light at room temperature, the absorbance was measured at 740 nm. The compound 5-caffeoylquinic acid (5-CQA), brand Sigma, was used as standard, and the results were expressed in mg of 5-CQA equivalent/g of sample.

2.3. Analysis of near infrared spectroscopy

2.3.1. Acquisition of spectra

The samples were analyzed using two spectrometers with different detectors: (a) TENSIONER 37 (Bruker Optics, Ettlingen, Germany), equipped with Fourier transform, integrating sphere and indium gallium arsenide (InGaAs) detector, which has a high detection efficiency ($D^* = 4.41010$), and (b) VERTEX 70 (Bruker Optics – Bruker Corporation, Billerica, Massachusetts, USA), equipped with Fourier transform and deuterated L-alanine doped triglycine sulfate (DLATGS) detector ($D^* = 2.7 \times 10^8$). Both devices were controlled by the software OPUS (versions 6.0 and 6.5, respectively). The spectra of the yerba mate samples were collected by both equipments in the near infrared region, from $10,000 \text{ cm}^{-1}$ to $4,000 \text{ cm}^{-1}$, operating in diffuse reflectance through 64 scans, with a resolution of 4 cm^{-1} and temperature controlled near 20°C. Reflectance data were stored as $\log(1/R)$, being R the reflectance.

2.3.2. Multivariate processing

The software Origin Pro 8.0 (Northampton, MA 01060, USA) was used to construct arrays of spectral data. The spectra were processed in Matlab version 7.1 (Mathworks Inc.) using the package PLS-toolbox 1.5 (Eigenvector Research Inc.) for chemometric analysis. The principal component analysis (PCA) was used to reduce the dimensionality of the data set for some variables – called principal components (PCs) –, which describe the largest variance of the data analyzed. The technique provides a summary of the

similarities and differences between samples regarding the concentration of compounds of interest (Lu et al., 2010).

The data pre-processing is presented in Table 1. In particular, MSC was applied prior to samples discrimination in order to correct the effects of light scattering caused by the non-homogeneity of the samples. Partial least squares regression (PLS) was utilized to build the prediction models of TPC. All the 111 samples were divided into two subsets. The calibration group consisted of 85 samples (80%) and the validation one contained 26 samples (20%). PLS models were developed to correlate the variable X (spectral data) to Y (reference data) and to predict the concentration of the compound of interest within the test validation group ($n = 26$), i.e., the prediction set. The cross-validation was employed with the routine leave-one-out for the set validation. This method involves a single observation from the original sample as validation data and the remaining observations as training data. The process was repeated until all the samples had been used once in the validation set (Xie, Ying, & Ying, 2007). This procedure (leave-one-out/cross-validation) is indicated because it does not waste data (all samples are involved in the model development), and it is more suited to a small amount of samples (Oliveira, Bureau, Renard, Pereira-Netto, & Castilhos, 2014). The prediction set (independent set) was defined to validate the results from the current study (20% of data). Outliers are samples with high leverage and studentized residuals, which attribute significant detrimental effects on the model, so they must be removed from the data (Pedro & Ferreira, 2005). The outliers were detected using the leverage criteria and studentized residuals, according to the equation $3LV/n$ (where n is the number of samples and LV is the number of latent variables), which defines the influence of a given sample on a model. The limit of the studentized residual (± 2.5) indicates low concentration of the sample (Filho, 2009). The performance of the PLS models was evaluated using RMSEC (root mean square error of calibration), RMSECV (root mean square error of cross-validation), RMSEP (root mean square error of prediction) and their respective regression coefficients (R).

3. Results and discussion

3.1. Spectral characterization

The main spectral characteristics of the samples used in the study are visualized from the average spectra presented in Fig. 1. Firstly, it is important to emphasize the high similarity observed in the spectral profile of samples from distinct regions, which showed differences on the intensity of some characteristic bands. Among the characteristic signals, three bands centered at 8.331, 6.853 and 5.164 cm^{-1} can be highlighted, which correspond to the first and second overtones of the water molecule O–H group. The band centered at 5.798 cm^{-1} corresponds to the first overtone of the C–H group, usually ascribed to the presence of lipids, oils and aromatic groups (Miller, 2001). Special attention should be given to the signal centered at 4.670 cm^{-1} , commonly associated with C–H groups of aromatic species (Miller, 2001), particularly from

Table 1
Characterization of the total phenolic compounds of yerba mate by the Folin-Ciocalteu method.

Region	Number of samples	Range (mg g^{-1})	Average (mg g^{-1})	SD*
Metropolitan of Curitiba (A)	06	23.07–49.48	37.00	12.35
Southeast (B)	30	30.36–141.92	84.82	34.07
South Central (C)	75	95.51–168.50	133.31	17.18

*SD = estimative of the standard deviation regarding the amplitude of intervals of TPC for each region studied.

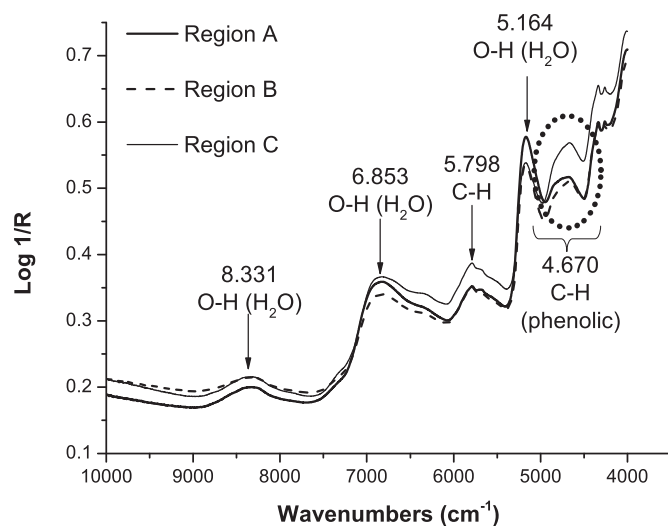


Fig. 1. Spectra of near infrared reflectance of yerba mate from different regions of Paraná (Brazil).

phenolic nature (Li & Qu, 2010). The significant difference in intensity observed specifically in this spectral region suggests important variations in the total phenolic content for the three regions monitored.

In general, the acquisition of spectra in diffuse reflectance mode is strongly influenced by the light scattering phenomena, which in turn depend on the particle size and especially on the homogeneity of the samples, factors that derive from various conditions associated to the region studied, such as the system of cultivation, agronomic practices (light intensity, leaf age and relative humidity), use of different types of fertilizers and sample processing. Even after grinding, there were heterogeneous particles within the samples, which may have influenced the different intensities of the spectra observed in Fig. 1. In addition, NIR determinations were performed in two different spectrometers, aiming to evaluate the robustness of the characterization method regarding different instrumental conditions. The samples identified by 1 T–111 T were analyzed with the equipment TENSIONER 37, and the ones identified by 112 V–222 V (the same samples) were assessed with the equipment VERTEX 70. The investigation was performed by PCA using the whole available spectra set. Firstly, the results show that most of the variance in the spectral data might be represented by only one principal component (PC1: 99.96%), i.e., the introduction of additional PCs contributes only with a representation of spectral details (PC2: 0.02%, PC3: 0.01%).

From the scores presented in Fig. 2A it is possible to note a good proximity between samples 1 T, 2 T and 3 T (highlighted) from Region A, analyzed by TENSIONER, and the same samples 112 V, 113 V and 114 V (highlighted), analyzed by VERTEX. This observation showed the little influence of the instrumental system used for the acquisition of NIR spectra, proving that both devices can be applied in this study. A little variation was observed between the details represented by PC2 and PC3 (Fig. 2B), thus both devices achieved a high repeatability. Considering the similarities of the results obtained by the two spectrometers, proven by the PCA, it was decided to present the results from the equipment TENSIONER starting from this section on.

3.2. Principal component analysis of samples from different growing regions

In order to find similarities or differences associated with different growing regions (and the particularities of each one, i.e.,

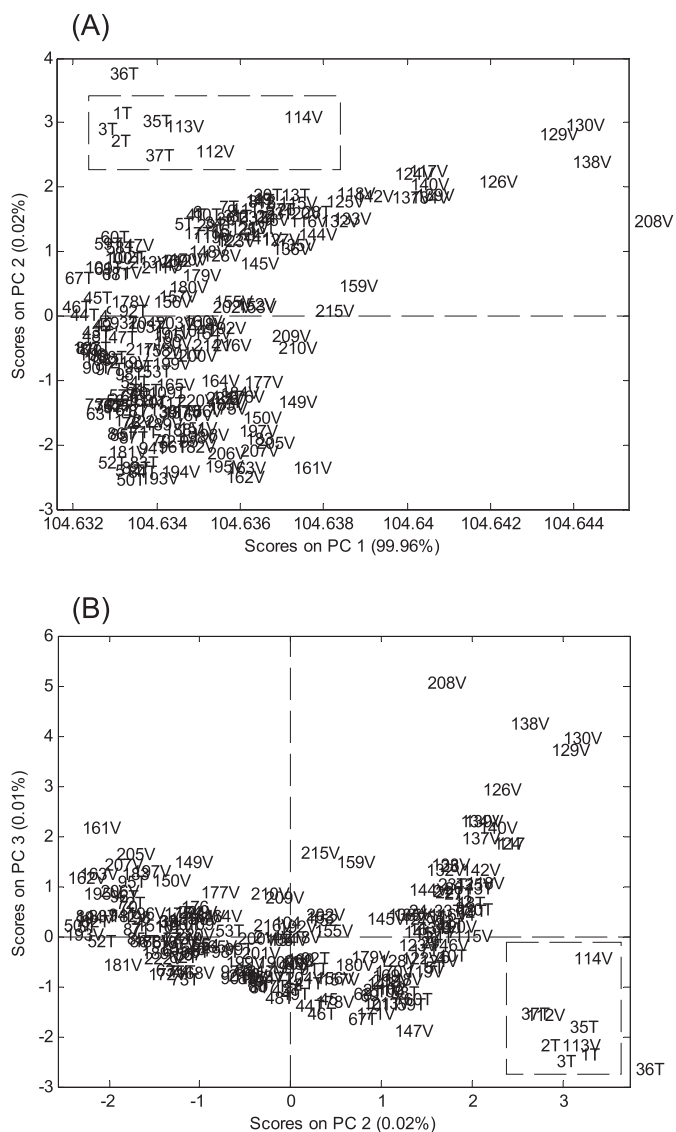


Fig. 2. Scores of the principal component analysis performed with samples of yerba mate from different regions of Paraná (Brazil) using two models: (A) PC1 × PC2 and (B) PC2 × PC3.

agronomic practices and processing system) and to detect outliers (Shin, Craft, Pegg, Phillips, & Eitenmiller, 2010), the PCA was performed with all samples using the NIR spectra acquired with the equipment TENSIONER 37. As shown in Fig. 3A, most of the variance in the spectral data may be represented by only one principal component (PC1: 99.96%). In order to eliminate problems of light scatter caused by the samples' irregular surfaces and particle size heterogeneity, a multiplicative scatter correction (MSC) pre-processing was employed. After correction, the results were located on the same PC-score (PC1-positive), which suggests that the samples had a similar composition. Nonetheless, because all the samples were located in the positive quadrant of this PC, the material must be differentiated based on spectral details described by the second (PC2: 0.03%) and third (PC3: 0.01%) principal components. Thus, the separation of the three groups analyzed is more evident when introducing three principal components, being PC3 particularly important since it enables a clear differentiation of group B.

According to Fig. 3B, the first principal component stresses virtually all the spectral signals, presenting a profile very close to

those of the original spectra. In turn, the second principal component emphasizes the spectral signals centered at 5.164 cm^{-1} , which correspond to the second overtone of the O–H group of the water molecule. Finally, the third main component highlights the characteristic spectral signal of phenolic groups (4.670 cm^{-1}), which is particularly important for the development of multivariate models that aim to quantify the content of total phenolic compounds.

3.3. Determination of total phenols

The results obtained for the TPC in samples of yerba mate from different growing areas, determined by the Folin-Ciocalteu method, are presented in Table 1. These results show significant differences between the mean values for each region, which is justified by the influence of agronomic practices, genetic lineage, climate, soil, altitude, cultivation techniques, harvesting time, plant age and post processing (Joubert, Manley, & Botha, 2006). Therefore, attention should be given to the high values found for the samples from the South Central zone (region C), forasmuch they consist of plants intercropped with Eucalyptus and grown under different levels of sunlight. The average result of 133.31 mg g^{-1} (Table 1) is consistent with the higher intensity observed in the average spectral signal (highlighted) of these samples within the region of phenolic compounds, according to Fig. 1.

As published by Coelho and Mariath (1996), yerba mate grown in shady conditions had improved metabolism of chemicals that inhibit the presence of insects, increasing the lifetime of the plant leaves. Accordingly, the plant can also absorb larger amounts of nutrients. Heck, Schmalko, and Mejía (2008) examined the effects of drying conditions on growth and phenolic composition of yerba mate: they found plantations of yerba mate with high levels of phenolic acids in relation to the mate adult forest, demonstrating that the cultivation and processing methods may have a significant effect on the production and concentration of phytochemicals in mate.

The wide range in the concentration intervals of TPC observed in each location studied may be related with the natural variability and technical processing among species of the same region or with lack of homogeneity among samples. Similar results were observed by Schulz, Engelhardt, Wegent, Drews, & Lazzczynski (1999) regarding the determination of total polyphenols content in samples of green tea (*Camellia sinensis*), for which a variability corresponding to a standard deviation of about 30 g kg^{-1} was obtained. On the other hand, it is important to notice that the method used for the determination of TPC showed an excellent accuracy even though involving an extraction process that is time consuming and subject to non-reproducibility. In general, standard errors of the order of 2 mg g^{-1} were observed in triplicate analyzes, which caused deviations of around 12% for samples with lower levels of TPC.

3.4. Quantification of TPC through PLS models

Multivariate calibration models were built in order to predict the TPC from the NIR spectra using partial least squares regression. Several models have been developed using different types of pre-processing approaches and different number of latent variables (LVs), providing the results summarized in Table 2. The best predictive capacity was achieved for the model developed with six LVs, using a pre-processing based on MSC followed by first derivative. The purpose of applying PCA is to detect anomalous samples and classify groups with similar characteristics. In this case, we worked only with the spectra. MSC pretreatments are commonly used to compensate baseline shifts and to reduce multiplicative effects in the spectral data, which are induced by physical effects such as the

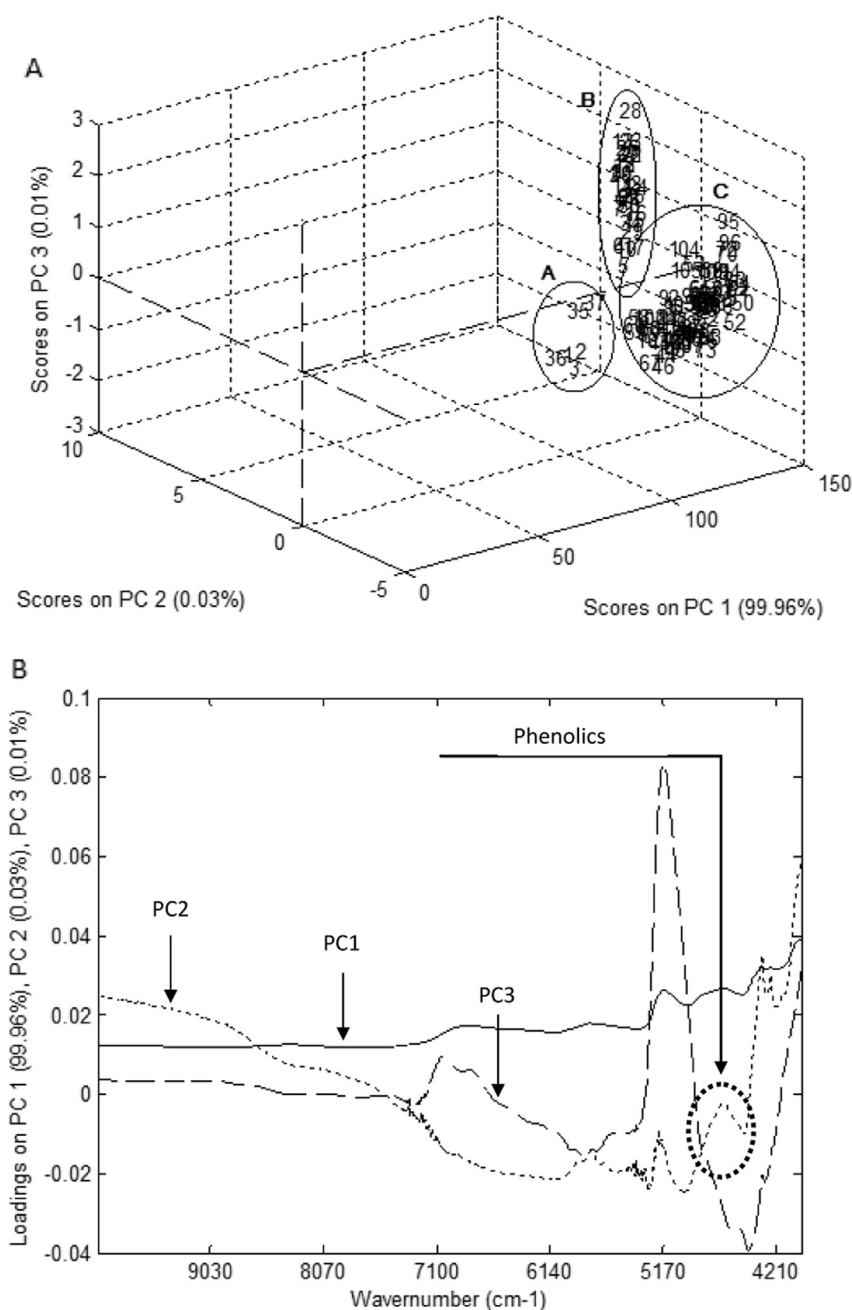


Fig. 3. A) PCA scores (PC1 vs.PC2 vs.PC3) and B) loadings of the three principal components of the spectra of yerba mate from different regions of Paraná (Brazil) pretreated by MSC.

non-uniform scattering throughout the spectrum, radiation wavelength, particle size and refractive index (Nicolai et al., 2007). The first derivative is often used to improve the definitions of bands that are superimposed, to remove noise in the same spectral line and/or to correct the baseline region (Osborne, 2000). By the other hand, the PLS regression is constructed one by one in such a way that the latent variables are oriented along directions of maximal covariance between the spectral matrix X and the response vector Y (Naes, Isaksson, Fearn, & Davies, 2002). Therefore, at this stage the spectral data are correlated with the values obtained by the conventional analysis (Folin-Ciocalteu). As the samples are heterogeneous, presenting average results of TPC of 37.0–133.3 mg g⁻¹, consequently the spectra are also heterogeneous. Hence, the first derivative preprocessing was added to the MSC, which allowed to

remove both additive and multiplicative effects in the spectra. Several other pre-processings were applied, but the best results are shown in Table 2.

In the test validation phase, the model provided a good agreement between real and predicted values, with a correlation coefficient of 0.81 (Fig. 4) and a RMSEP of around 12%. Although this average value is quite close to that observed by Gallice, Messerschmidt, and Peralta-Zamora (2011) for the determination of total phenols in wines, the largest difference between real and target values occur in samples of lower concentration of total phenols (Fig. 4), which significantly increases the average prediction error. Additionally, it is important to emphasize that the determination of phenolic forms by Folin-Ciocalteu shows low selectivity, mainly due to the false positives ascribed to non-

Table 2

Figures of merit of the multivariate models developed as a function of the type of pre-processing and the number of latent variables (LV).

Pre-processing	LV	Calibration (<i>n</i> = 85)		Cross-validation (<i>n</i> = 85)		Test validation (<i>n</i> = 26)	
		<i>R</i>	RMSEC ^a	<i>R</i>	RMSECV ^a	<i>R</i>	RMSEP ^b
No processing	5	0.80	20.41	0.83	22.30	0.73	15.18
MSC	5	0.85	19.75		21.84	0.75	15.71
MSC + 1st derivative	6	0.90	16.07	0.83	20.53	0.81	12.12
MSC + smoothing	5	0.84	19.77	0.81	21.85	0.75	15.73

The pre-processing that provided the best results are shown in bold.

^a Values in mg g⁻¹.

^b Values in %.

phenolic reducing species, such as vitamin C (Oliveira, de Valentim, & Goulart, 2009). Even considering all the changes associated with the different growing regions (such as agronomic and climatic conditions and sample processing), we opted to develop PLS models from samples of three distinct regions in order to build models that are more robust (Table 3).

Recently, Chen, Zhao, Liu, Cai, and Liu (2008) developed a multivariate method for the determination of total phenols in green tea samples using NIR spectroscopy. According to the authors, *R* values of 0.70 justify the association between NIR and multivariate calibration in quality control operations of such products, mainly because of the possibility of implementing control systems *in-situ* and in real time. Páscoa and collaborators (2013) assessed phenolic compounds in coffee residue using a micro plate Folin-Ciocalteu procedure and obtained an average result of 13.0 mg g⁻¹ of gallic acid, with a standard deviation of 5.6. The best PLS model showed RMSEP of 1.48 and *R* of 0.94 with 6 LVs. Bellincontro et al. (2012) analyzed phenolic compounds from three cultivars of olives and found values of *R* of 0.87 and RMSEP of 6.33 mg g⁻¹ with 9 LVs. The content of TPC was computed by summing the specific compounds measured by HPLC. Bala and Singh (2013) evaluated total phenols by the conventional Folin-Ciocalteu method in mustard seeds, obtaining *R* of 0.92 and RMSEP of 0.11 with 6 LVs. With respect to

Table 3

Comparison of the results of TPC (mg g⁻¹) for the samples from the validation set obtained by reference methods and PLS regression model.

Sample	Reference value	Predicted value	RMSEP (%)
1	137.00	130.33	4.87
2	105.56	108.72	2.99
3	77.03	70.63	8.30
4	77.89	73.98	5.02
5	74.28	85.82	15.53
6	105.23	80.97	23.08
7	117.76	103.15	12.40
8	107.70	115.58	7.31
9	112.85	127.82	13.26
10	43.01	52.20	21.39
11	147.53	136.54	7.45
12	163.85	152.86	6.71
13	27.28	44.55	63.29
14	95.83	111.11	15.93
15	141.00	132.88	5.76
16	162.65	136.95	15.80
17	130.91	121.33	7.32
18	136.67	138.27	1.16
19	150.89	136.18	9.74
20	153.20	141.33	7.75
21	136.78	145.21	6.16
22	122.46	119.56	2.37
23	115.28	140.47	21.84
24	145.66	127.90	12.19
25	117.87	109.72	6.92
26	133.38	147.56	10.62
Average	116.91	115.06	12.12

the experimental results and values predicted by the PLS model for the 26 samples from the validation test group, more than half of the prediction errors were less than 10%. However, it is noteworthy that the largest discrepancy occurred in relation to the sample with the lowest concentration of TPC: reference value of 27.28 mg g⁻¹ versus a predicted result of 44.55 mg g⁻¹ (sample from region A).

4. Conclusions

The combination of NIR spectroscopy with multivariate analysis tools for the determination of total phenolic compounds in yerba mate is an interesting approach that has not been investigated to date. In the current work, the principal component analysis (PCA) was able to discriminate samples of yerba mate depending on the area of cultivation (and the agronomic practices and industrial processing associated), while the partial least squares (PLS) regression allowed the development of models for predicting total phenolics with associated errors of 12%. Inasmuch as the spectroscopy in the near infrared region has various advantages over other methods, particularly with respect to the analysis time and cost, sample handling and chemical residues, it may be a suitable tool to the yerba mate industry.

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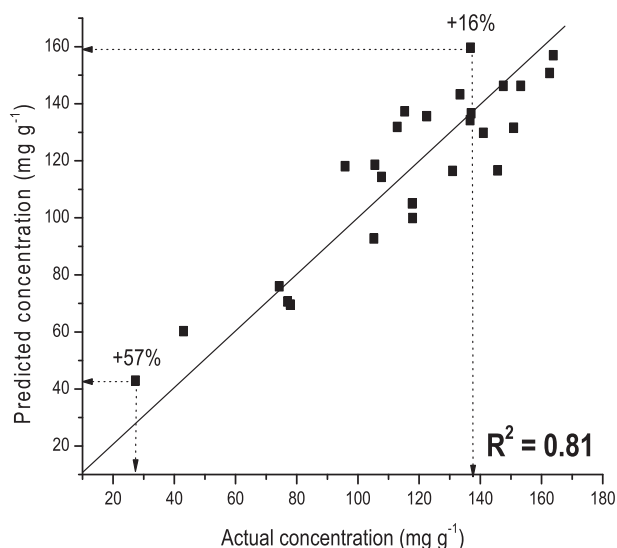


Fig. 4. Correlation between experimental and predicted concentration of total phenols by the multivariate model for the validation set (*n* = 26).

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