

Simultaneous determination of sulfur, nitrogen and ash for vegetable tannins using ATR-FTIR spectroscopy and multivariate regression

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ARTICLE INFO

Keywords:

Vegetable tannins
Multivariate regression
Fourier transform infrared spectroscopy
Partial least square

ABSTRACT

The quantification of sulfur, nitrogen and ash content in tannins of mimosa (*Acacia mearnsii*) and quebracho (*Schinopsis* sp.) is of fundamental importance for its industrial use. Thus, an analytical method capable of identifying these properties by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) was developed using multivariate regression methods. Partial least squares regression (PLS) method was used as well as the interval partial least squares (iPLS) and the synergy interval partial least squares (siPLS). The developed models were compared based on the root of the mean square errors (RMSE) and determination coefficients (R^2). The results showed that both the iPLS and the siPLS, using the infrared data, obtained satisfactory results, but having a small improvement with the use of the siPLS. In general, the proposed method does not require reagent consumption, being much faster than traditional techniques, allowing potential applications for simultaneous determination of sulfur, nitrogen and ash contents for routine analysis of plant tannins by FTIR data.

1. Introduction

The term “vegetable tannins” was first used to identify the natural products used in the production of leather. Vegetable tannins are plant extracts with high affinity for the collagen of the leather, increasing the thermal, physical and biological stability [1–4]. Tannins are compounds with polyhydroxylated structures present in various parts of plants, with molecular weight in the ranges between 500 and 3000 Da. The polyhydroxylated structure of this class of compounds ensures high solubility in water and polar organic solvents [5]. They are formed mainly by secondary metabolism in different parts of plants, exerting an antimicrobial and phage-inhibitory function against herbivores [6–9]. The two main groups of this class of compounds are hydrolysable and condensed tannins [3,10,11].

Hydrolysable tannins are a class of natural compounds that hydrolyze easily in aqueous media, being formed mainly by esters of gallic acid or ellagic acids with a glucose in the central nucleus. The hydrolysable tannins most used are the chestnut and tara. These extracts present low availability, being less than 10% of the world production of natural tannins, resulting in high prices and lower attractiveness when compared to condensed tannins [12,13].

Condensed tannins or proanthocyanidins are flavan-3-ol oligomers condensed in the C4-C6 and C4-C8 sense and represent more than 90% of the world production of vegetable tannins [3,11,14,15]. Although they are widely found in the plant kingdom, the two main sources for the industrial production of these extracts are mimosa (*Acacia mearnsii*) and quebracho (*Schinopsis* sp.), where it is extracted from the bark and the wood, respectively. [13,15–17].

Quebracho extracts are obtained by extraction from the woodchips of quebracho trees which grow wild in the Gran Chaco region of Argentina, Bolivia, and Paraguay [1–18]. Currently, the main mimosa producers in the world are Brazil, with 170,000 ha planted, followed by South Africa with 110,000 ha [17].

The polysaccharides of these extracts are poorly soluble in water and are usually present in small amounts in the fraction of extractable tannins [19]. The quebracho proanthocyanidins (PACs) have low solubility in water, being necessary the sulfitation process at the time of extraction and in later stages. This process increases the solubility of the extract in cold water and the rate of penetration into skins during the tanning process, as well as increases water retention in adhesive films, ensuring slower drying [1,20,21].

The literature has presented some works for the qualitative analysis

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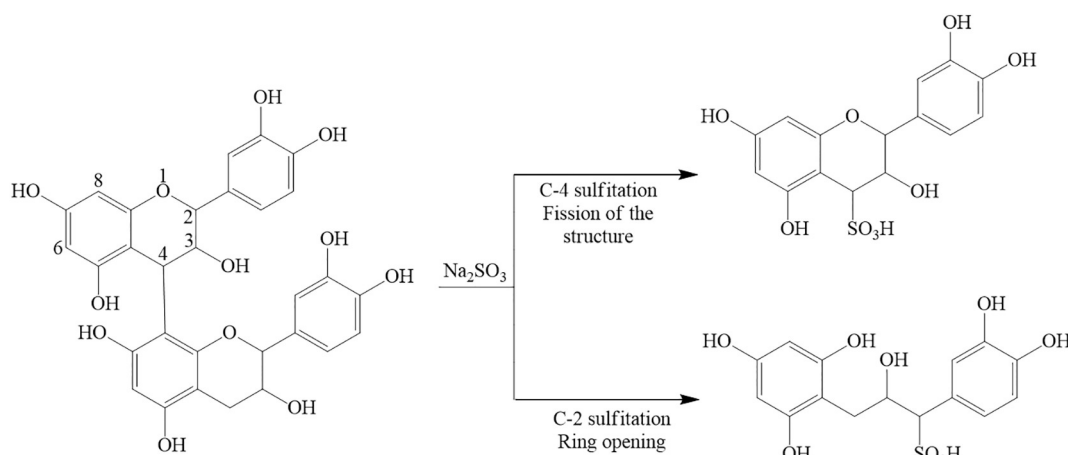
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<https://doi.org/10.1016/j.microc.2019.103994>

Received 24 March 2019; Received in revised form 6 June 2019; Accepted 7 June 2019

Available online 08 June 2019

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Scheme 1. Schematic representation of the sulfitation at the C-2 or C-4 position in the flavonoid.

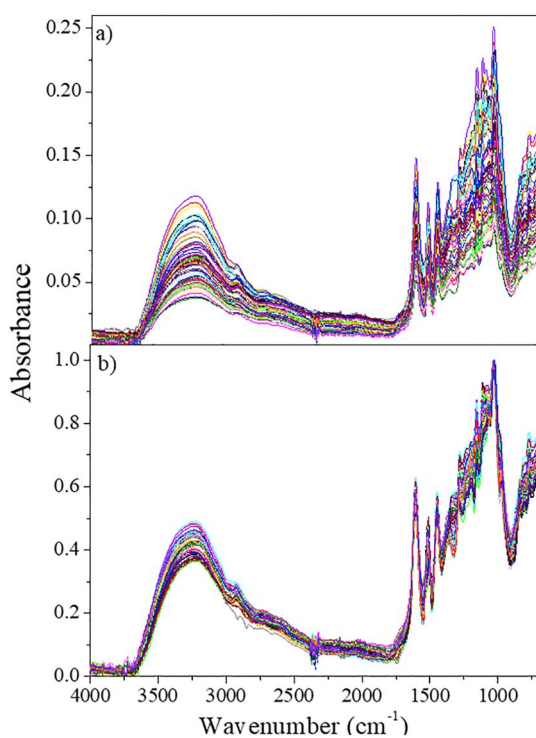


Fig. 1. ATR-FTIR spectra for tannin samples: a) spectra without processing; b) preprocessed spectra.

of tannins with FTIR and unsupervised multivariate analyzes, such as hierarchical cluster analysis (HCA) and principal component analysis (PCA) [7,9,22].

In a study carried out for vegetable tannins using unsupervised multivariate analyzes (HCA and PCA), it was possible to observe a good separation between the hydrolysable and condensed tannins, as well as a greater proximity between the extracts with more similar chemical composition (chestnut and valonea) [4].

In quantitative analyzes of properties of natural extracts, Velasco et al. (2018) report the development of multivariate models using PLS regression and FTIR for the quantification of total phenolic, total flavonoids, free radical scavenging activity, and total antioxidant capacity of the two species of *Physalis* of the family Solanaceae. The FTIR-PLS models showed coefficients for prediction between 0.756 and 0.905,

Table 1

Results of the merit figures of the regression models by PLS, iPLS and siPLS for determination of the sulfur content by with MSC.

Model	Intervals (cm^{-1})	LVs ^(a)	Rcv ^{2(d)}	RMSECV (%) ^(b)	Rp ^{2(e)}	RMSEP (%) ^(c)
PLS	4000–700	7	0.852	0.353	0.847	0.360
iPLS2	2349–700	6	0.861	0.343	0.960	0.235
iPLS4	1524–700	6	0.865	0.338	0.981	0.179
iPLS8	1523–1112	3	0.870	0.329	0.955	0.268
iPLS16	1317–1112	9	0.878	0.321	0.927	0.284
iPLS32	1214–1112	8	0.838	0.371	0.932	0.267
si2PLS8	1523–1112	5	0.875	0.323	0.964	0.234
	3174–2762					
si3PLS8	1111–700	7	0.869	0.331	0.974	0.206
	1523–1112					
	4000–3588					
si4PLS8	1523–1112	7	0.873	0.326	0.952	0.259
	2348–1936					
	3174–2762					
	3587–3175					
si2PLS16	1317–1112	5	0.871	0.328	0.939	0.237
	2965–2760					
si3PLS16	1317–1112	5	0.890	0.303	0.970	0.235
	1523–1318					
	1935–1730					
si4PLS16	1111–906	5	0.890	0.303	0.973	0.248
	1317–1112					
	1523–1318					
	2141–1936					
si2PLS32	1008–906	6	0.882	0.314	0.968	0.166
	1317–1215					
si3PLS32	905–803	9	0.923	0.254	0.914	0.284
	1317–1215					
	3792–3689					
si4PLS32	905–803	11	0.939	0.227	0.839	0.418
	1317–1215					
	3068–2966					
	3584–3481					

^aLV = Latent variables; ^bRMSECV = Root Mean Square Error of Cross Validation; ^cRMSEP = Root Mean Square Error of Prediction; ^dRcv² = determination coefficient of cross-validation; ^eRp² = determination coefficient of prediction; non-MS = without Multiplicative Scatter Correction.

representing a versatile tool for quantitative assessment in natural extracts, being fast and with good accuracy [23].

Applying the FTIR-PLS technique for the determination of wood properties, Fahey et al. (2017) quantify the polysaccharide compositions and lignin contents of the cell walls of the gymnosperm *Pinus*

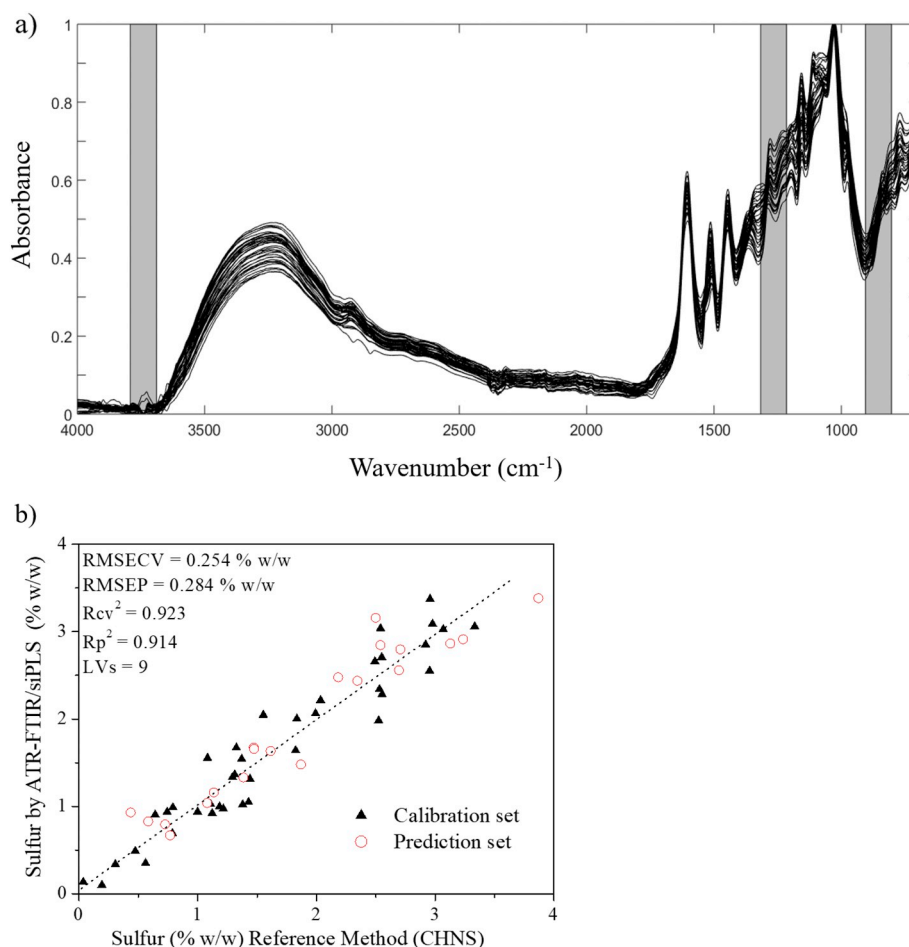


Fig. 2. Results for si3PLS32 model for prediction of sulfur: (a) Spectral regions selected to build the model and (b) Sulfur (% w/w) values by the reference method versus predicted ATR-FTIR/siPLS values, with nine latent variables (LVs).

radiata. The results show the feasibility of using FTIR spectroscopy for the rapid prediction of both the parameters [24].

The authors Tsuchikawa and Kobori presented in review that the research with NIRS spectroscopy associated with multivariate calibrations has increased exponentially in recent times in the application of wood characterization. Properties such as chemical composition, moisture, density, anatomical characteristics, mechanical properties, degradation, paper and pulp were studied, showing that these techniques are extremely important, especially for the industry [25].

This work aims to develop a fast, clean methodology according to the concepts of green chemistry for the simultaneous determination of ash, nitrogen and sulfur by ATR-FTIR and multivariate calibration methods for sulfated proanthocyanidins of mimosa (*Acacia mearnsii*) and quebracho (*Schinopsis* sp).

2. Experimental section

2.1. Tannin samples

The mimosa and quebracho samples were obtained from Tanac S/A (Brazil) and Silvateam (Argentina), respectively. In total, 64 samples were evaluated, being 31 of quebracho and 33 of mimosa. The extracts are dried in spray-dryer and marketed as powders, with particle size less than 210 μm and moisture content of 4.0 to 6.0%.

2.2. Total nitrogen and sulfur determination

Firstly, the samples are placed in the oven during 24 h at 60 °C to obtain constant weight. This methodology is used to avoid degradation of organic matter. Then, the sample is macerated in a porcelain capsule and the samples are powdered into a sieve of 60 mesh, which corresponds to a maximum granulometry of 250 μm . Afterwards, approximately 5 g of sample is placed in a 50 mL falcon tube and the volume is raised with Milli-Q water until 45 mL. Subsequently, the tube is agitated for homogenization of the sample and then the tube is inserted in the centrifuge at 3000 rpm for 5 min. After this process, the water of tube is withdrawn, and the washing process is repeated three times. The washing process is necessary for the removal of possible halogens (fluorine and chlorine). At the end of the washing process, the falcon tubes are opened in an oven at 60 °C for 24 h and then macerated again and sent for analysis of Total Nitrogen and Total Sulfur in the elemental analyzer.

The determination of the percent of total nitrogen was realized through burning sample in the LECO (United States of America) elemental analyzer, model TRUSPEC non-dispersive, equipped with an infrared detector. In this equipment, samples are burned in oxygen atmosphere with purity 6.0 (99.9999%) and flow of 101 per minute (lpm) at temperature of 950 °C. The determination of percent of total sulfur was realized through burning sample in the LECO SC-632

Table 2

Results of the merit figures of the regression models by PLS, iPLS and siPLS for determination of the nitrogen content by ATR-FTIR without MSC.

Model	Intervals (cm ⁻¹)	LVs ^(a)	Rcv ^{2(d)}	RMSECV (%) ^(b)	Rp ^{2(e)}	RMSEP (%) ^(c)
PLS	4000–700	6	0.897	0.050	0.863	0.077
iPLS2	2349–700	8	0.925	0.043	0.924	0.055
iPLS4	1524–700	7	0.931	0.041	0.917	0.055
iPLS8	1111–700	4	0.926	0.042	0.917	0.055
iPLS16	1111–906	9	0.925	0.043	0.933	0.048
iPLS32	1420–1318	6	0.908	0.047	0.910	0.062
si2PLS8	1111–700	7	0.931	0.041	0.918	0.056
si3PLS8	1523–1112	8	0.926	0.042	0.916	0.057
	1111–700					
	1523–1112					
si4PLS8	3174–2762	9	0.923	0.044	0.916	0.056
	1111–700					
	1523–1112					
si2PLS16	2671–2349	6	0.935	0.040	0.912	0.051
	3174–2762					
	1111–906					
si3PLS16	1111–906	7	0.936	0.039	0.927	0.052
	1523–1318					
	4000–3794					
si4PLS16	1111–906	8	0.938	0.039	0.933	0.053
	1523–1318					
	2141–1936					
si2PLS32	4000–3794	5	0.917	0.045	0.895	0.067
	1420–1318					
	1317–1215					
si3PLS32	905–803	6	0.936	0.039	0.927	0.050
	1008–906					
	1111–1009					
si4PLS32	802–700	9	0.946	0.036	0.914	0.060
	1111–1009					
	1523–1421					
	1626–1524					

^aLV = Latent variables; ^bRMSECV = Root Mean Square Error of Cross Validation; ^cRMSEP = Root Mean Square Error of Prediction

^dRcv² = determination coefficient of cross-validation; ^eRp² = determination coefficient of prediction; non-MS = without Multiplicative Scatter Correction.

elemental analyzer, equipped with an infrared detector. The samples are fired in an oxygen atmosphere with purity 4.0 (99.99%) and flow of 5 lpm at temperature of 1350 °C.

2.3. Reference method for ash determination

Analysis of the parameters of ash was carried out as per the procedure given in ABNT NBR 11042:2013 Insumes — Dyes, binders, pigmented pastes, greases substances and tanning — Determination of ash content (ABNT NBR 11042, 2013) [26]. This procedure was performed in duplicate and the result matched the arithmetic average on a dry basis.

2.4. Infrared spectroscopy

The infrared analyses were performed using a Perkin Elmer Spectrum 400 spectrophotometer equipped with a DTGS detector and a universal attenuated total reflectance accessory. The spectral range of 4000–700 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans was used. The samples were analyzed as received, without previous treatment. The spectroscopy analyses were performed in duplicate and for the multivariate regression models were used the average spectra.

2.5. Multivariate regression

The multivariate analysis of the tannin samples was performed from the ATR-FTIR data, with these data being constructed multivariate regression models by iPLS and siPLS for the concentrations of nitrogen, sulfur and ashes.

The software used for these studies was Matlab 7,11 (MathWorks Inc., Natick, MA) with iToolbox package (<http://www.models.kvl.dk/>). All spectra were smoothed (Savitsky-Golay algorithm, 15 points, first-order polynomial) and normalized (between 0 and 1). In the construction of the models, it was used the average of duplicates of the spectra.

Considering the total of 64 tannin samples, 42 samples were selected for the construction of the calibration models and 22 samples were used to evaluate the prediction of the models using the Kennard-Stone algorithm [27].

For the building of the regression models by PLS, iPLS and siPLS the application of two preprocessing alternatives to the spectra was evaluated: only mean centering or the multiplicative scatter correction (MSC) treatment combined with mean centering [28]. The iPLS models were built by performing 2, 4, 8, 16, 32 equidistant divisions of the spectrum, in each case being selected only one interval, according to the lowest values of Root Mean Square Error of Cross Validation (RMSECV), coefficient of determination for cross validation (Rcv²) and the lowest number of latent variables (LVs). The regression models by siPLS were obtained by performing 2, 3 or 4 combinations between spectral divisions that were 8, 16 and 32 intervals, we chose the combination of intervals that obtained the model with lower RMSECV, of Rcv² and the smaller number of latent variables and considered the regions that had more relevant spectral information.

The number of latent variables for each regression model was determined by the leave-one-out cross validation procedure, choosing the lowest number of LVs with which the regression models presented the lowest RMSECV. Taking care that there was no overfitting.

After the construction of the regression models by iPLS and siPLS, the best model was defined as the one with the lowest values of RMSECV and Root Mean Square Error of prediction (RMSEP). It was hoped that there would not be large differences between the errors in order to avoid an overfitting. It was also considered the number of LVs, where the ideal is to use as few numbers as possible, as well as the highest values of Rcv² and the coefficient of determination for prediction set (Rp²).

3. Results and discussion

The ash and sulfur contents are related to the salts content added during the extraction process. During the extraction process of the polyflavonoids, bisulfite salts or sodium sulfite are added, as well as during the process of clarifying the extract.

Polyflavonoids of long chains end up being insoluble in aqueous medium and the sulfitation process assists the extraction leaving the extracts more soluble by insertion of group sulfite and decrease of the chains of the polyflavonoids. This process can occur at position C-2 or C-4, according to the Scheme 1 [1,29,30].

Moreover, the sulfited extracts have a much-enhanced pelt penetration, higher hygroscopicity of tannin adhesive allowing the film to dry more slowly [1,20].

The ash content is related to the salts added during the process of extracting or modifying the extract, in addition to the micronutrients that the plant absorbs during growth.

The nitrogen content is related to the complex polysaccharide-proteins with low- and high-molecular-weight fractions present in the extracts [19]. The higher the polysaccharide content, the lower the

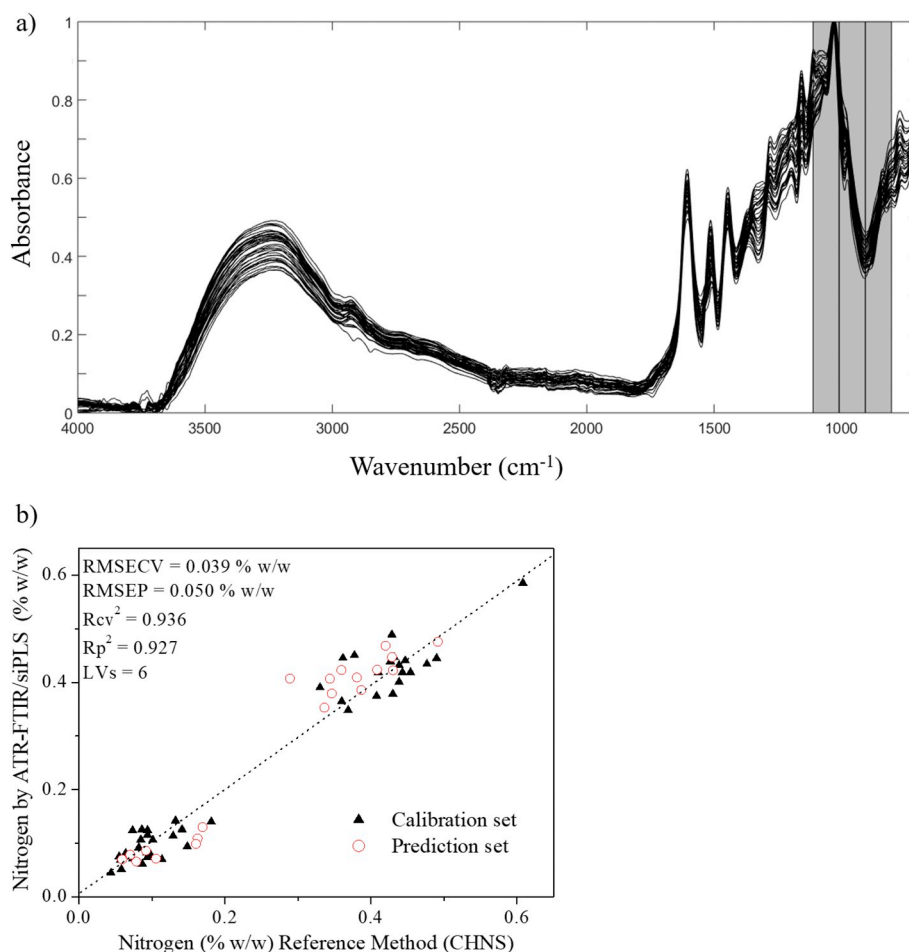


Fig. 3. Results for si3PLS32 model for prediction of nitrogen: (a) Spectral regions selected to build the model and (b) Nitrogen (% w/w) values by the reference method versus predicted ATR-FTIR/siPLS values, with six latent variables (LVs).

polyphenol content, e.g. lower purity.

The ash, nitrogen and sulfur contents vary in the range of 2.410–8.753%, 0.044–0.628% and 0.098–3.383%, respectively.

The ATR-FTIR spectra were obtained in the region of 4000–700 cm^{-1} from the tannin samples, Fig. 1. The Fig. 1a represents the untreated ATR-FTIR spectra of the data and the Fig. 1b represents the preprocessed ATR-FTIR spectra.

3.1. Multivariate regression models for sulfur content

Commercial extracts of acacia and quebracho proanthocyanidins (PACs) are often sulfited by treatment with sodium hydrogen sulfite.

The selection the best model, the set of the all factors, that is, a small number of LVs, low values of RMSECV and RMSEP and high values of R_{cv}^2 and R_p^2 , and regions that had more relevant spectral information, were considered for all multivariate regression models.

Table 1 shows the number of LVs and the values of RMSECV, RMSEP, R_{cv}^2 and R_p^2 , and the selected intervals used in the PLS, iPLS and siPLS models to determine the sulfur of both tannins (acacia and quebracho).

For sulfur content, the best model was the si3PLS32 (which used intervals 3, 27 and 31 when the spectrum was divided into thirty-two equidistant intervals). The spectral regions that were select were

905–803, 1317–1215 and 3792–3689 cm^{-1} . The optimal combinations of subintervals select are shown in Fig. 2a. There exist 306 variables in the combinations of spectral subintervals selected by siPLS.

The region of 905–803 and 1317–1215 cm^{-1} are attributed to the vibrational bands of S–O bonds of the sulfonic groups in different chemical environments. In the region of 3792–3689 cm^{-1} can be OH stretching of SO–H [31–36].

In Fig. 2b, we observe good correlation between the reference and predicted values for both the calibration and external validation sets. The result of RMSECV is 0.254% (w/w) and determination coefficient (R_{cv}^2) is 0.923 in the calibration set.

3.2. Nitrogen content

Nitrogen is related to the percentage of complex polysaccharide-proteins. The determination of nitrogen in PACs is of great importance, since it has an inverse relation with the amount of polyphenols present, being ideal low nitrogen values to have high values of polyphenols [19].

Table 2 shows the values off RMSECV, RMSEP, the number of LVs, the values of R_{cv}^2 and R_p^2 , and the selected intervals used in the PLS, iPLS and siPLS models to determine the nitrogen of tannins of acacia and quebracho.

Table 3

Results of the merit figures of the regression models by PLS, iPLS and siPLS to determine the ash content by ATR-FTIR with MSC.

Model	Intervals (cm ⁻¹)	LVs ^(a)	Rc ^(d)	RMSECV (%) ^(b)	Rp ^(e)	RMSEP (%) ^(c)
PLS	4000–700	5	0.758	0.90	0.879	0.65
iPLS2	2349–700	5	0.804	0.81	0.919	0.54
iPLS4	1524–700	4	0.770	0.97	0.888	0.60
iPLS8	1523–1112	4	0.798	0.83	0.899	0.58
iPLS16	1317–1112	6	0.835	0.75	0.857	0.66
iPLS32	1214–1112	9	0.803	0.81	0.890	0.58
si2PLS8	1111–700	5	0.818	0.78	0.899	0.66
si3PLS8	1935–1524	5	0.810	0.80	0.916	0.55
	1111–700					
	1523–1112					
si4iPLS8	1935–1524	9	0.906	0.79	0.877	0.60
	1111–700					
	2761–2349					
	3174–2762					
si2PLS16	4000–3588	7	0.840	0.74	0.855	0.69
	1317–1112					
	1729–1524					
si3PLS16	1111–906	8	0.857	0.69	0.774	0.82
	3172–2966					
si4PLS16	3793–3587	10	0.856	0.70	0.851	0.74
	1111–906					
	3172–2966					
	3586–3380					
si2PLS32	3793–3587	4	0.855	0.69	0.898	0.56
	1008–906					
si3PLS32	1317–1215	12	0.919	0.52	0.861	0.74
	2759–2657					
	3068–2966					
si4PLS32	1317–1215	10	0.918	0.52	0.848	0.72
	2759–2657					
	3068–2966					
	3274–3172					

^aLV = Latent variables; ^bRMSECV = Root Mean Square Error of Cross Validation; ^cRMSEP = Root Mean Square Error of Prediction
^dRc² = determination coefficient of cross-validation; ^eRp² = determination coefficient of prediction; MSC = Multiplicative Scatter Correction.

The best model was si3PLS32 when intervals 29, 30 and 31 were used. The si3PLS32 model combined three neighboring spectral regions ranging from the 1111–803 cm⁻¹ region [19].

The nitrogen content can be determined indirectly by determining other signals of the polysaccharides present in the sample. The 1111–803 cm⁻¹ region is characteristic of C–O bond stretching, skeletal vibrations of six members (pyranose) ring, C–O–C stretching of the polysaccharide ring and symmetrical deformation of amide [37–41].

Therefore, the selection of significant regions for the nitrogen models was verified and them optimal combinations of subintervals select are shown in Fig. 3a. There exist 306 variables in the combinations of spectral subintervals selected by siPLS. In Fig. 3b, we observe good correlation between the reference and predicted values for both the calibration and external validation sets. The result of RMSECV is 0.039% (w/w) and determination coefficient (Rc²) is 0.936 in the calibration set. Therefore, it is possible to observe good results. The division of the nitrogen content into two groups is possibly because they

are two different plant species in the same model, confirming that it is quite robust.

3.3. Ash content

During the process of extraction and chemical modifications of PACs some inorganic salts are added, as for example, sodium bisulfite. One of the important analyzes for the quality control of these extracts is the ashes analysis, because it indicates how much of inorganic material was added on the product.

Table 3 shows the values off RMSECV, RMSEP, the number of LVs, the values of Rc² and Rp², and the selected intervals used in the PLS, iPLS and siPLS models to determine the ashes of tannins of acacia and quebracho.

The best model was si2PLS32 when intervals 27 and 30 were used. The si2PLS32 model combined two spectral regions, 1008–906 and 1317–1215 cm⁻¹.

The region of 1008–906 and 1317–1215 cm⁻¹ are attributed to the vibrational bands of S–O bonds of the sulfonic groups in different chemical environments [31–36]. This indicates, in this case, that the ash percentage is probably the result of the sulfitation of the extract. It should be noted that this behavior was observed for the set of evaluated samples, and it is not possible to guarantee that samples of different species will behave in the same way.

The optimal combinations of subintervals select are shown in Fig. 4a. There exist 204 variables in the combinations of spectral subintervals selected by siPLS. Fig. 4b is the scatter plot that displays the correlation between the reference values and the PLS/ATR-FTIR prediction values. The result of RMSECV is 0.69% (w/w) and determination coefficient (Rc²) is 0.855 in the calibration set.

From the PLS regression models it can be observed that the best method of variable selection was the siPLS.

The results were better for the determination of sulfur and nitrogen than for ash determination (see Table 1–3). This behavior probably occurs because the sulfur and nitrogen contents were determined by instrumental techniques, while the ashes were determined by thermogravimetric analysis and presented higher errors.

The models generated from this method of selection of variables presented smaller errors of cross validation and prediction and higher values of coefficients of determination when compared to the methods of selection of variables by iPLS.

4. Conclusions

In this work, it was possible to demonstrate that the multivariate regression method associated with ATR-FTIR spectroscopy was efficient in the determination of sulfur, nitrogen and ashes in samples of *Acacia mearnsii* and quebracho tannins.

The iPLS and siPLS algorithms were able to select appropriate regions for each property of interest.

This methodology showed advantages because it is not destructive, very fast compared to traditional methods and does not require toxic reagents and sample preparation.

Therefore, for the levels of nitrogen, sulfur and ashes the multivariate analysis technique using PLS regression with infrared data presented satisfactory results, being possible to be easily implemented in the production process.

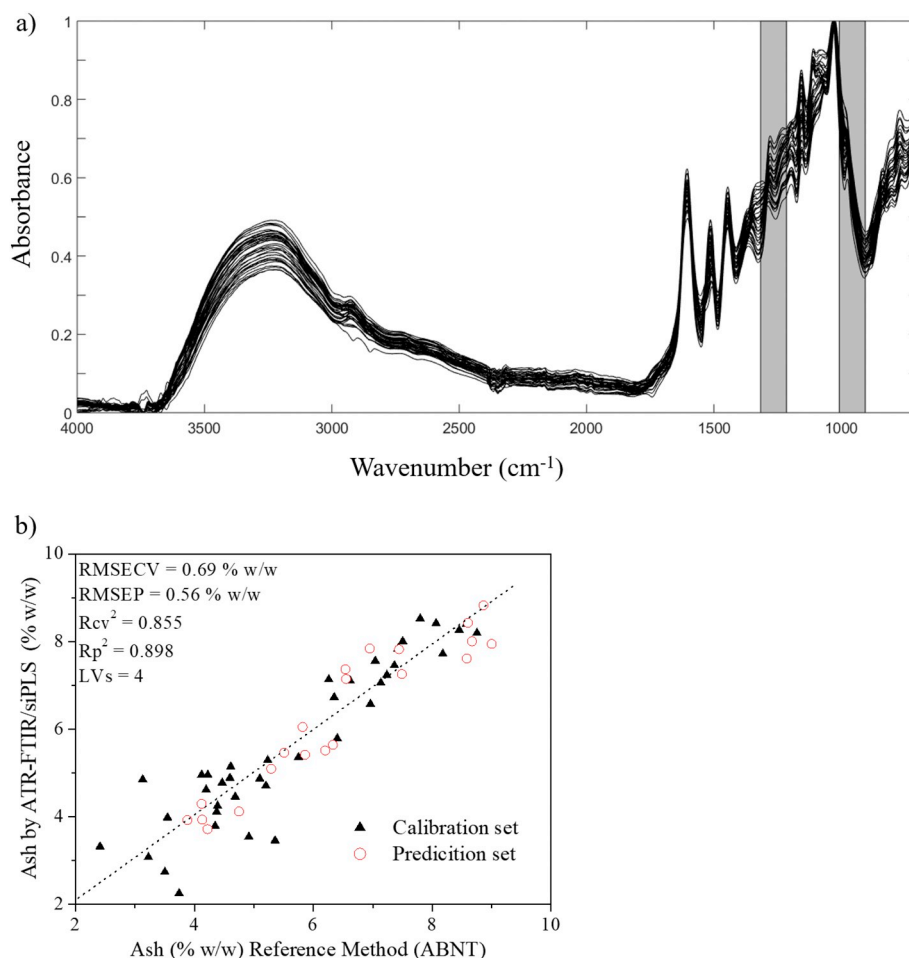


Fig. 4. Results for si3PLS32 model for prediction of ashes: (a) Spectral regions selected to build the model and (b) Ashes (% w/w) values by the reference method versus predicted ATR-FTIR/siPLS values, with four latent variables (LVs).

Acknowledgements

The authors thank the Federal University of Rio Grande do Sul for all support, as well as the company TANAC S/A for the samples and support.

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