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Multivariate calibration by near infrared spectroscopy for the determination of the vitamin E and the antioxidant properties of quinoa

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ABSTRACT

Quinoa is a pseudocereal that is grown mainly in the Andes. It is a functional food supplement and ingredient in the preparation of highly nutritious food. In this paper we evaluate the potential of near infrared spectroscopy (NIR) for the determination of vitamin E and antioxidant capacity in the quinoa as total phenol content (TPC), radical scavenging activity by DPPH (2,2-diphenyl-2-picryl-hydrazyl) and cupric reducing antioxidant capacity (CUPRAC) expressed as gallic acid equivalent (GAE).

For recording NIR a fiber optic remote reflectance probe applied directly on the quinoa samples without treatment was used. The regression method used was modified partial least squares (MPLS). The multiple correlation coefficients (RSQ) and the standard prediction error corrected (SEP(C)) were for the vitamin E (0.841 and 1.70 mg 100 g^{-1}) and for the antioxidants TPC (0.947 and 0.08 mg GAE g^{-1}), DPPH radical (0.952 and 0.23 mg GAE g^{-1}) and CUPRAC (0.623 and 0.21 mg GAE g^{-1}), respectively.

The prediction capacity of the model developed measured by the ratio performance deviation (RPD) for vitamin E (2.51), antioxidants TPC (4.33), DPPH radical (4.55) and CUPRAC (1.55) indicated that NIRS with a fiber optic probe provides an alternative for the determination of vitamin E and antioxidant properties of the quinoa, with a lower cost, higher speed and results comparable with the chemical methods.

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1. Introduction

Quinoa (*Chenopodium quinoa* Willd) is a pseudocereal belonging to the Chenopodiaceae family. The Andean region is the center of origin of many varieties of quinoa, which for thousands of years was the main food of the ancient cultures of the region. Their cultivation is expanding to Bolivia, Peru and Ecuador, considered to be the countries with the largest production of this product. However, in the last few years, quinoa production is in a process of expansion into different geographic areas of the entire world (North America, Europe, Asia, Africa and Australia) due to its extraordinary adaptability—FAO [1].

Quinoa has been noted as a foodstuff and it has gained increasing interest in recent years due to its high nutritional value [2,3]; it is rich in proteins (with an average of 13.81%), fat, dietary fiber, carbohydrates, and minerals, and is also a good source of vitamin E [4]. Quinoa is considered to be a functional food, acts as a cell protector and presents an important source of antioxidants, and therefore could be used for medicinal purposes in humans [2,4]. High antioxidant capacity is provided mainly by their phenolic content and the beneficial effects of the polyphenols are known. Due to the beneficial properties that the consumption of this pseudocereal provides it is used as an ingredient in food such as bread, pasta or baby food and also in common diets [5].

Recent studies determined the antioxidant capacity of this pseudocereal [5,6–10]. The methods used to measure the antioxidant capacity in quinoa were based on uptake of various free radicals generated from organic molecules such as 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), and 1,1-diphenyl-2-picrilhydrazyl (DPHH), by Oxygen Radical Absorbance Capacity

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(ORAC). Other less used methods such as Ferric Reducing Antioxidant Power (FRAP) or Cupric Ion Reducing Antioxidant Capacity (CUPRAC) also used to measure the total phenol content and the vitamin E [9]. Some researchers compared the antioxidant potential of the quinoa with other seeds such as wheat, buckwheat, rice, soybean or amaranth [6]. The variation of total phenols and anthocyanins in seeds and sprouts was also studied [7]. The antioxidant activity between fresh and dried samples was also compared [11], and decreasing activity when the pseudocereal is cooked was noted [8]. Most of these reports, concerning the determination of the cereal antioxidant potential, have demonstrated the influence of the type of solvent used. The use of more polar solvents such as methanol could improve the extraction of phenolic compounds, and therefore lead to a reliable assessment of the antioxidant potential [6].

In addition to environmental differences, the nutritional composition of quinoa varies among ecotypes due to the strong genetic variability [3,9,11]. Crops from Japan presented higher antioxidant properties than others from South America [5]. In the same way, the relationship between oxidative stress and abiotic stress caused by environmental conditions was tested [12]. On the other hand, the effect on the sensory and antioxidant properties of bread [10] and of black chocolate [13] have been evaluated when quinoa was added to these products, finding higher vitamin E and very high acceptance by the tasters.

Near infrared (NIR) spectroscopy has been used as a method to predict the quality of different foods and agricultural products due to the speed of analysis, minimal sample preparation and low cost. The NIR spectrum of any food can give a global signature of composition which with the application of chemometric techniques can be used to evaluate compositional characteristics in foods not easily detected by chemical analysis [14–16]. The development of near-infrared spectroscopy reflectance (NIRS) technique combined with chemometric calibration algorithms has allowed that the antioxidant activity and the total polyphenol content can be measured in green tea [17–19] or Chinese hawthorn [20].

The objective of this study was to evaluate the application of near infrared spectroscopy (NIR) to predict the antioxidant capacity and the vitamin E content in quinoa. The NIR spectra were recorded in reflectance mode, applying the fiber-optic probe directly on quinoa samples, with no sample preparation or manipulation. This technique previously was not applied on quinoa matrix and can replace conventional chemical methods of analysis.

2. Experimental

2.1. Samples

To perform the present study three quinoa genotypes (cv. Regalona, ecotype B080, and the breeding line AG2010), obtained from Agrogen EIRL, Temuco, Chile, were used. A total of 48 seed samples were cleaned and stored on a shelf at room temperature (15–18 °C) for 1 month; their nutritional composition was evaluated and their spectra were evaluated.

2.2. Chemical analysis

2.2.1. Quinoa seed extracts preparation

Samples of quinoa seeds were ground on a Thomas-Wiley mill (series 3383-L10, Swedesboro, NJ, USA) using a 60 mesh screen. 1 g sample for each treatment was extracted with 100 mL of methanol 99% (v/v), and shaken for 60 min at 18 °C in an orbital shaker at 190 rpm. The liquid phase of the extracts was filtered through Whatman No. 2 paper and stored at 4 °C until used.

2.2.2. Vitamin E analysis

A methanol–BHT (1 mg mL^{-1}; Merck; Darmstadt, Germany) solution was used to extract vitamin E from quinoa seeds according to Zeng [21]. All samples of vitamin E were run on a sensitive quantitative high-performance liquid chromatographic (HPLC) Shimadzu Eerie 10 (Kyoto, Japan), SCL-10ADvp HPLC system with a Kromasil (Bellefonte, PA, USA) C18 (150 × 4.6 mm; 5 μm particle size) reverse phase column connected directly to the ion source inlet. Chromatographic separation was achieved using elution solvents A=methanol/ethanol (60:40, v/v) HPLC-grade Sigma (St. Louis, MO, USA) and B=Milli-Q water, at a flow rate of 1.5 mL min^{-1}. Initial conditions were 20% B and the solvent gradient began at 0.1 min, 0% B at 5 and 15 min, then 20% B at 17 min and held at 20% B for 3 min. Each injection consisted of 20 plant extract and vitamin E was expressed in mg 100 g^{-1}. All measurements were performed in triplicate.

2.2.3. Total phenolic content (TPC) analysis

Total phenolic content (TPC) in seed extract solutions was determined by measuring the reducing capacity of the Folin–Ciocalteu (FC) reagent (Sigma, St. Louis, MO, USA) according to Velioglu [22] and Miranda [11] with some modifications. Total phenolic assay was conducted by mixing 0.3 mL of quinoa extract solution with 2.25 mL of FC reagent. After 5 min, a volume of 2.25 mL Na_2CO_3 0.56 M in distilled water was added and mixed on a vortex mixer. The mixture was allowed to stand for 90 min at room temperature in dark. The absorbance was measured at 725 nm in a spectrophotometer (Optizen Pop) and compared with a gallic acid equivalent (GAE; 1 mg mL^{-1}) calibration curve. Results were expressed as gallic acid equivalent. All measurements were performed in triplicate.

2.2.4. Antioxidant activity analysis

2.2.4.1. DPPH radical scavenging activity. The free radical scavenging activity of the samples was determined using the 2,2-diphenyl-2-picryl-hydrazyl (DPPH) method with some modifications [11]. For measurement of sample scavenging activity, a volume of 40 μL of extract was added to test tubes and 3.960 μL of DPPH (Sigma, St. Louis, MO, USA) stock solution (absorbance 1.2) was added to each tube [23]. The reaction mixture was vortex-mixed for 20 s and left to stand in dark at 15 °C for 30 min. Absorbance was determined using a UV/VIS spectrophotometer (Optizen Pop) at 517 nm. A standard curve was prepared with gallic acid stock solution (1 mg mL^{-1}). Final results were given as gallic acid equivalent. All measurements were performed in triplicate.

2.2.4.2. Cupric reducing antioxidant capacity (CUPRAC). The CUPRAC assay, a method for determination of total antioxidant capacity, was applied with some modifications according to Çelik [24]. CUPRAC assay required the following solutions: $CuCl_2$ [Cu(II)] 1.0×10^{-2} M (Sigma, St. Louis, MO, USA) in distilled water; ammonium acetate (CH_3COONH_4) 1.0 M in distilled water, pH=7.0; and neocuproine (Nc) 7.5×10^{-3} M (Sigma, St. Louis, MO, USA) prepared in 96% ethanol (v/v). Sample mixture was obtained by mixing 1 mL $CuCl_2$, 1 mL Nc solution and 1 mL NH_4Ac buffer (pH 7.0) in a test tube. Volumes of 0.7 mL antioxidant sample (or standard) solution and 0.4 mL H_2O were added to the initial mixture so as to make the final volume 4.1 mL. The absorbance of the final solution (4.1 mL) was read at 450 nm after 30 min standing at room temperature. A standard curve was prepared with gallic acid stock solution (1 mg mL^{-1}). Final results were given as gallic acid equivalent. All measurements were performed in triplicate.

2.3. NIR spectroscopy

The measurement of the spectra was carried out using NIRS technology and a remote reflectance fiber-optic probe that was applied directly to the quinoa samples with no prior treatment or manipulation. A Foss NIR System 5000 with a standard 1.5 M 210/210 bundle fiber-optic probe (Ref. No. R6539-A) was used. The probe employs a remote reflectance system and uses a ceramic plate as reference. The window is of quartz with a $5 \times 5\ cm^2$ surface area, measuring reflectance in the IR zone close to 1100–2000 nm. The spectra were recorded at intervals of 2 nm, performing 32 scans for both the reference and samples. To minimize sampling error, spectral readings were taken in triplicate for each sample. The mean of these replicates was used in the statistical treatment. For subsequent statistical analysis 42 quinoa samples were randomly selected for the calibration set, while the remaining 6 samples formed the validation set.

2.4. Data statistical analysis

All the statistical analyses were carried out with WinISI II version 1.50 (Infrasoft International, LLC) of the Foss NIR system. Initially, spectral data corresponding to the samples of the calibration set were analyzed by principal component analysis (PCA). PCA transforms the original variables (wavelengths) into new axes called principal components, which are orthogonal, so that the data sets presented on these axes are uncorrelated with each other.

The modified partial least squares (MPLS) regression method was used to obtain the NIR equations for the antioxidant parameters studied. Partial least squares (PLS) regression is similar to principal component regression (PCR), but uses both reference data (chemical, physical, etc.) and spectral information to form the factors useful for fitting purposes [25]. To optimize the multivariate regression equations the spectral scattering effects have been taken into account. This effect was removed using several scattering corrections and mathematical treatments (multiplicative scatter correction, MSC; standard normal variate, SNV; D-trend, DT; or SNV–DT) [26–28]. The correction was performed using the mean spectrum of all spectra of the samples, and a linear least squares regression was applied from the data to each wavelength of the original spectrum and mean spectral data. This treatment allows the minimizing of the scattering effect, since mainly the shift of the maximum and the width changes of the spectra were considered. MPLS is often more stable and accurate than the standard PLS algorithm. In MPLS, the NIR residuals at each wavelength are obtained after each factor has been calculated, and they are standardized (dividing by the standard deviations of the residuals at each wavelength) before calculating the next factor. In order to select the optimal number of factors and to avoid overfitting, the cross-validation is recommended [29]. For this, the calibration set is divided into several groups, and each group is then validated using a calibration developed on the other samples. Validation errors are combined into a standard error of cross-validation (SECV) [30], considering this statistical coefficient the best single estimate for the prediction capability of the equation. It is similar to the average standard error of prediction (SEP) from 10 randomly-chosen prediction sets. In all cases, cross-validation was performed by splitting the population into seven groups.

The performance of the models was quantified by determining the squared correlation coefficient for predicted versus measured compositions in cross-validation and the ratio of standard deviation (SD) to SECV of the data set. The ratio of performance to deviation (RPD) is the relation between SD and SECV, and it is desired to be larger than 2 for a good calibration [31]. An RPD ratio less than 1.5 indicates poor predictions and the model cannot be used for further prediction. The statistics used to select the best equation for each constituent were the highest RSQ (multiple correlation coefficients) and the lowest SECV (standard error of cross-validation).

3. Results and discussion

3.1. Chemical analysis and NIR spectra information

Descriptive analysis (maximum, minimum, mean and standard deviation) of the antioxidant compounds analyzed and the antioxidant capacity in the quinoa samples by the chemical reference methods are shown in Table 1. The data were present according to the two groups established (calibration set and external validation set) for the NIR analysis.

NIR spectra information was obtained using NIRS technology and a remote reflectance fiber-optic probe that was measured directly on the quinoa samples. Fig. 1 shows NIR spectra of the quinoa samples studied. Different mathematical treatments (MSC, SNV, DT or SNV-DT) are necessary to correct scattering. They calculate spectral differences by reducing the confounding effects of baseline shift and curvature.

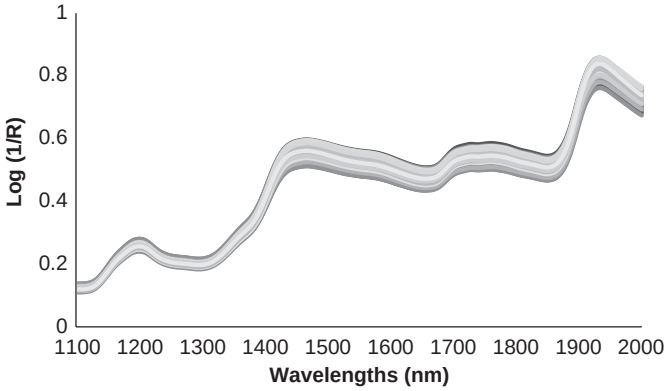

Fig. 1. NIR spectra of quinoa samples.

Table 1
Reference chemical data of the antioxidant properties of quinoa samples in calibration and validation sets.

	Calibration set ($N=42$)				External validation set ($N=6$)			
	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD
Vitamin E (mg 100 g^{-1})	0.51	20.80	4.07	5.28	1.50	16.60	5.18	5.76
TPC (mg GAE g^{-1})	2.87	4.97	3.63	0.39	3.22	4.85	3.79	0.56
DPPH (mg GAE g^{-1})	0.68	5.48	2.87	1.14	1.22	4.31	2.87	1.16
CUPRAC (mg GAE g^{-1})	0.93	2.39	1.79	0.36	1.35	2.29	1.71	0.35

TPC: total phenol content; DPPH: 2,2-diphenyl-2-picryl-hydrazyl; CUPRAC: cupric reducing antioxidant capacity; GAE: gallic acid equivalent.

3.2. NIR calibration equation

To obtain the calibration equations for each antioxidant component analyzed the NIR spectral data and chemical data from 42 samples (samples of the calibration set) were used. Initially, a principal component analysis was applied. In all cases, the spectral variability explained between 97.3% and 99.96%, and 10 principal components were required for the vitamin E, 6 for the total phenolic content, 12 for the DPPH and 8 for the CUPRAC.

Once the number of principal components had been determined, anomalies in the spectra were analyzed using the Mahalanobis distance (*H*-statistic), establishing $H=3.0$ as the limit value. Thus, samples with *H*-value greater than 3.0 were considered different from the spectral population, but the spectra of the samples tested met the criterion of the Mahalanobis distance. Then, all samples can be used to make the prediction. The risk of mistakes in the equations under practical conditions is very low or almost null when the standardized *H*-statistic (Mahalanobis distance) was used during routine analysis of unknown samples.

Modified partial least squares regression (MPLS) were used for the calibrations. The differences between the laboratory values and the NIR predicted values were also evaluated by a chemical criterion, named *T* criterion. The samples with a *T* value greater than 2.5 were removed from the set because they were different from the population. Using the *T* criterion, 1 sample for the vitamin E, 2 samples for the phenolic content, 2 samples for the DPPH and 1 sample for the CUPRAC were removed. The calibration process was implemented with the spectra of the resulting samples and their chemical data. Calculation of the statistical parameters of the calibration equations for each component is shown in Table 2, indicating the number of samples used to obtain the calibration equation after removing the samples for spectral (*H* criterion) or chemical reasons (*T* criterion); the best of the different mathematical treatments, concentration range and standard deviations (for the concentrations of vitamin E, phenols, DPPH and CUPRAC in quinoa) are also shown.

The degree to which the calibration best adjusts the data set was measured by the multiple correlation coefficients (RSQ) and the standard error of cross-validation (SECV). The equations developed for the determination of vitamin E, phenols and antioxidant capacity measured by the DPPH in quinoa had high values for the RSQ coefficient (0.952–0.841). Only the antioxidant capacity measured by CUPRAC showed a lower RSQ (0.592), but the SECV coefficient is small, as occurred with the other antioxidant component evaluated. Therefore, it can be considered that the results of the calibration adjustment were very good. The range of determination was less than that value established by the reference data; based on mathematical criterion the range was set according to the data set around the mean value.

3.3. Internal validation (prediction)

The models obtained were evaluated by cross-validation. The calibration sample set was divided into a series of subsets for their calibration. With the data set a total of seven series were established; of these, six were taken for the calibration set and one for the prediction set. The process was repeated as many times as there are sets, so that all pass through the calibration set and the prediction set. With this process the prediction capacities were checked. Fig. 2 shows the correlation of the values obtained in the laboratory (Ref.) with respect to those predicted by NIR for vitamin E, phenols, DPPH and CUPRAC. The statistical descriptors SEP and SEP(C) showed calibration model for phenols, DPPH and CUPRAC, allowing the determination of these parameters in quinoa of different compositions with excellent result. In the case of the CUPRAC assay as measured of the antioxidant capacity in this product, seems to be worse than the DPPH method.

3.4. Prediction capacity of the model

The prediction capacity of the model obtained was evaluated with the ratio performance deviation (RPD) [31], based on the relationship between the standard deviation of the chemical method (SD Ref.) and the standard prediction error (SEP) encountered in the NIRS model. The model is considered suitable if the RPD is greater than 2.5. The vitamin E, the phenolic content and the DPPH activity exceeded this value, while the RPD value for the CUPRAC was lower.

The main antioxidants in pseudocereals are polyphenols. There were positive and significant correlations between the total phenolic compounds of quinoa and the DPPH radical ($R^2=0.555$; $P<0.0001$), and the total phenolic compounds and the CUPRAC ($R^2=0.430$; $P<0.001$). The results demonstrated the contribution of polyphenolic substances to the antioxidant potential of quinoa. Linear correlation between the phenolic content and the antioxidant potential has also been shown in other works [6,32]. However, there was no correlation between DPPH and CUPRAC. This suggests that there wee different trends in antioxidant capacity by these two methods for their evaluation in the quinoa, justifying the results obtained with NIR. According to Çelik [24] the solvent type and polarity, reaction mechanism, and solubility parameters as well as an essential structural property (i.e. electron-transfer capability) are crucial parameters for the chemical behavior of antioxidant compounds, so the antioxidant capacity and its assays can be limited. In general, the calibration with the NIR spectra data for CUPRAC can be considered acceptable but it is a worse result than for the DPPH. Therefore, the DPPH radical scavenging activity method would be recommended more for the quantification of the antioxidant capacity in quinoa.

3.5. External validation

After obtaining the calibration equations the predicted values were compared with the reference data. The NIR model obtained is tested with the 6 new samples (external validation set), with a different composition and the spectral curve that was used in the calibration.

Table 2
Statistical descriptors of calibration by NIR.

Constituent	Math treatment	*N*	Mean	SD	Est. min	Est. max	SEC	RSQ	SECV	RPD
Vitamin E (mg 100 g^{-1})	SNV only 2,8,6,1	41	3.66	4.63	0.00	17.54	1.84	0.841	4.06	2.51
TPC (mg GAE g^{-1})	None 0,0,1,1	40	3.61	0.39	2.43	4.79	0.09	0.947	0.33	4.33
DPPH (mg GAE g^{-1})	SNV only 2,4,4,1	40	2.90	1.15	0.00	6.35	0.25	0.952	0.71	4.54
CUPRAC (mg GAE g^{-1})	Standard MSC 1,4,4,1	41	1.81	0.34	0.78	2.83	0.22	0.592	0.33	1.57

TPC: total phenol content; DPPH: 2,2-diphenyl-2-picryl-hydrazyl ; CUPRAC: cupric reducing antioxidant capacity; *N*: number of samples; MSC: multiplicative scatter correction, SD: standard deviation; RSQ: multiple correlation coefficients; SEC: standard error of calibration; SECV: standard error of cross-validation; RPD: ratio performance deviation.

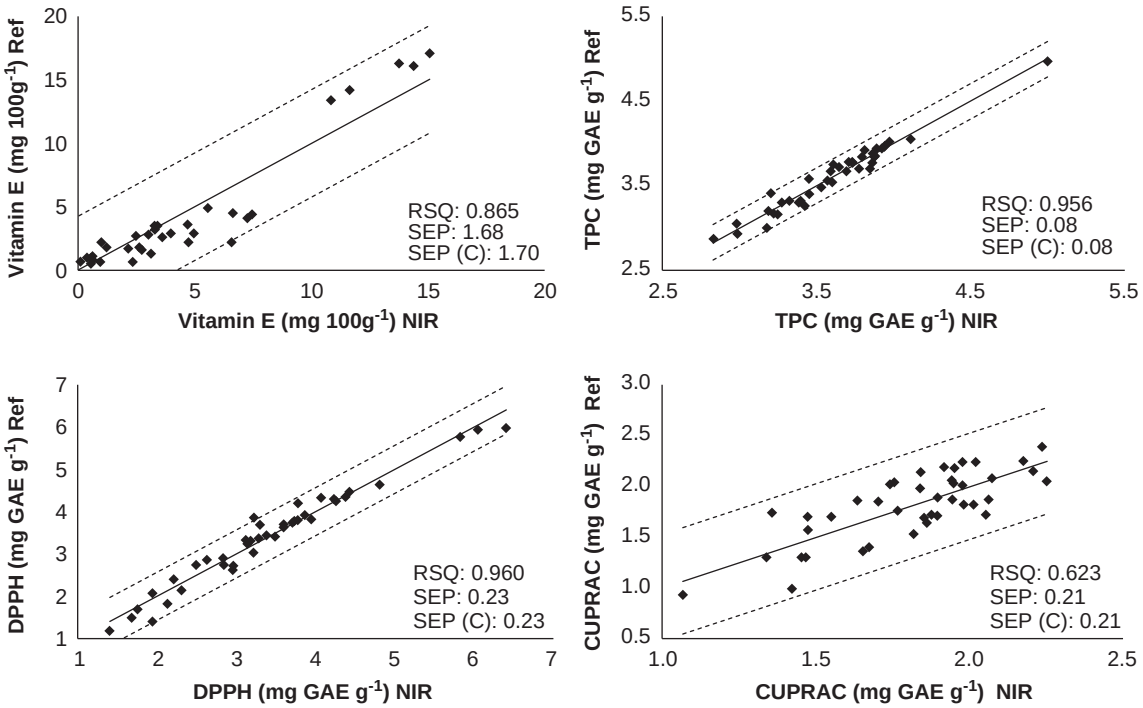

Fig. 2. Comparison of the reference values with the values predicted by the calibration equations. RSQ, multiple correlation coefficients; SEP, standard prediction error; SEP (C), standard prediction error corrected.

Table 3
External validation (6 samples).

Constituent	*P* (level of significance)	Mean residual	RMSE
Vitamin E (mg 100 g^{-1})	0.74	4.60	6.16
TPC (mg GAE g^{-1})	0.39	0.36	0.40
DPPH (mg GAE g^{-1})	0.24	0.48	0.58
CUPRAC (mg GAE g^{-1})	0.57	0.21	0.23

TPC: total phenol content; DPPH: 2,2-diphenyl-2-picryl-hydrazyl; CUPRAC: cupric reducing antioxidant capacity; RMSE: root mean standard error.

The NIRS methodology and the reference data concerning the vitamin E, the phenolic content, the DPPH and the CUPRAC were compared with those of samples not belonging to the calibration model using the Student's *t*-test for paired values. All the constituents studied had significance levels (p) higher than 0.05, with values between 0.74 for the vitamin E and 0.24 for the DPPH (Table 3). There were no differences between the results obtained. So it can be concluded that the method provides significantly identical data to the starting reference data. The means of the residuals were between 4.60 and 0.21 for vitamin E and CUPRAC, respectively. The root mean standard error (RMSE) values were between 6.16 for vitamin E and 0.23 for CUPRAC. With these results it can be concluded that the prediction equations for each component analyzed have been satisfactory.

4. Conclusion

NIR spectroscopy combined with multivariate calibrations analysis can contribute to the determination of chemical compounds in quinoa without previous treatment. The prediction capacity was excellent for the vitamin E, phenols and DPPH, with RPD values higher than 2.5. Statistical analysis showed lower RSQ and RPD for the measurement of antioxidant activity by CUPRAC than with the DPPH method. Therefore, the DPPH radical scavenging activity method would be recommend more for the quantification of the antioxidant capacity in quinoa.

It can be concluded that NIR spectroscopy with optic fiber probe was a rapid and non-destructive method for determination of the vitamin E, phenolic content and antioxidant capacity in quinoa. This is the first work that uses NIR spectroscopy for the determination of these components in quinoa.

Although the results are good and very promising, it is necessary to extend the study with more samples from different geographical areas in order to obtain a model with the greatest applicability.

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