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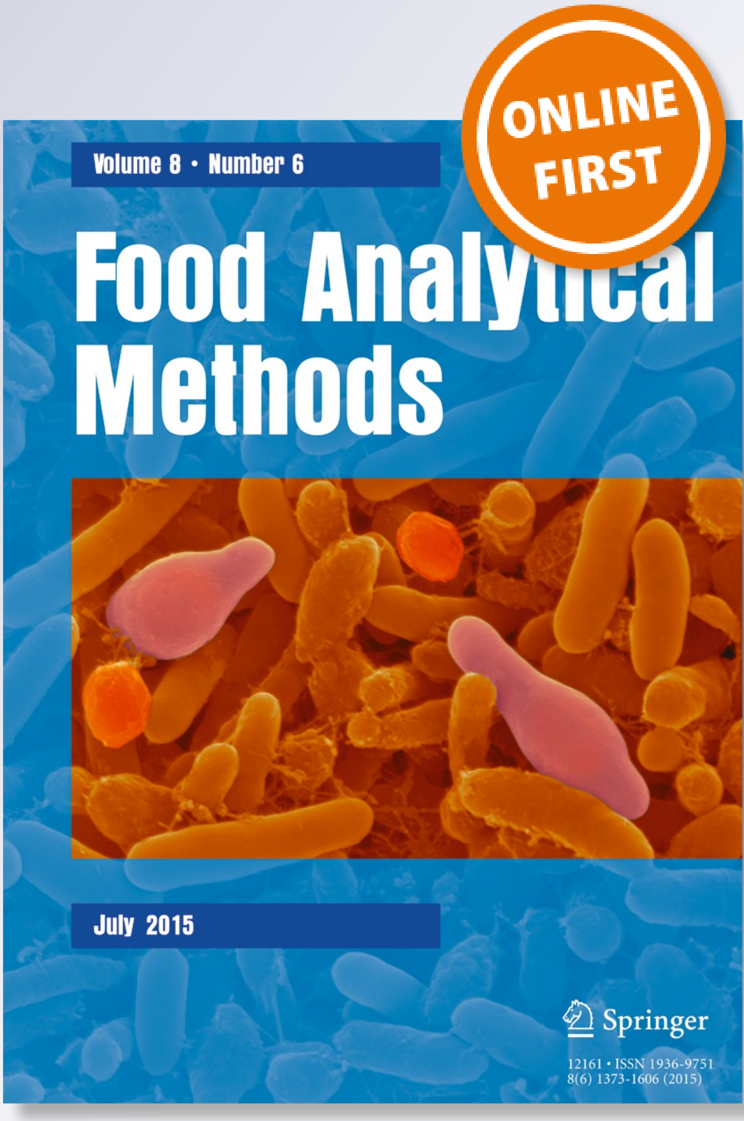
Food Analytical Methods

ISSN 1936-9751

Food Anal. Methods
DOI 10.1007/s12161-015-0217-4



Springer

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Elemental Analysis of Amaranth, Chia, Sesame, Linen, and Quinoa Seeds by ICP-OES: Assessment of Classification by Chemometrics

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Received: 17 March 2015 / Accepted: 1 June 2015

Abstract In this work, 26 elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cs, Cu, Ga, Fe, K, Mg, Mn, Na, P, Pb, Rb, Se, Si, Sr, Ti, V, and Zn) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in seed samples: amaranth, chia, sesame, linen, and quinoa. Elemental analysis showed the presence of toxic elements (As, Cd, and Pb), as well as high mineral content (Fe, Na, P, K, and Mg): The concentrations of toxic elements were below the permissible limits by the WHO. Chemometrics was performed by cluster analysis (CA), principal component analysis (PCA), and partial least squares discriminant analysis (PLS-DA). In all cases, a correct classification of each type of seed was obtained. The combination of elemental analysis (major, minor, and toxic elements) and chemometrics was useful to determine nutritional quality in the studied seeds, as well as to classify them according to the botanical origin. For that, this method can be useful for the analysis of raw material as quality control in food factories and government control labs.

Keywords Amaranth · Chia · Sesame · Linen · Quinoa · Elements · ICP-OES · Classification

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Introduction

Around the world, there is a wide variety of ancient crops, some which were forgotten but more recently rediscovered, such as quinoa, amaranth, linen, sesame, and chia. Quinoa (*Chenopodium quinoa* Willd) is a crop widely studied (Jacobsen 2003), native from the Andes Mountains belonging to Peru and Bolivia. Quinoa has a high content of carbohydrates (71 %), proteins (13 %), and lipids (6 %) (Comai et al. 2007). The Food and Agricultural Organization (FAO) has highlighted the importance of quinoa crops and its contribution in the world feeding; in 2013, quinoa was declared the crop of the year (FAO 2011). Although there are excellent properties of quinoa as food, the presence of toxic elements (Konishi et al. 2004; Ruales and Nair 1993) have been reported. There are few reports about quinoa and chemometrics: A study was performed in quinoa by infrared spectroscopy and chemometrics (Ferreira et al. 2015); also, the study of quinoa, *Amaranthus caudatus*, and purple maize was performed by elemental analysis and chemometrics (Nascimento et al. 2014).

Amaranth (*Amaranthus* sp.) is a plant that was consumed in America before the Spanish conquest. Amaranth is perhaps the ancient crop more widely studied: It presents high protein (16 %), starch (60 %), and lipid (5–8 %) contents (Mendonça et al. 2009; Duarte Correa et al. 1986). Also, the ability of this plant to bioaccumulate metals in contaminated soils was previously studied: The content of Cd in the aerial part and root of *Amaranthus hybridus*, *Amaranthus spinosus*, *Amaranthus viridis*, and *Amaranthus rudis* was assessed as bioaccumulation phenomena (Abe et al. 2008), a conclusion which was achieved by other authors (Li et al. 2010; Olivares and Pena 2009; Chunilall et al. 2005). Also, other pieces of work have reported the elemental content in amaranth from Kenya (Onyango et al. 2008), the content of several metals in

Published online: 10 June 2015

amaranth leaves from South Africa (Pillay and Jonnalagadda 2007), and toxic elements from Argentina (Aguilar et al. 2013a). Moreover, the elemental analysis was performed in a number of foods from France including amaranth (Noël et al. 2012). From the point of view of chemometrics, the classification of several varieties of amaranth seeds was carried out based on elemental analysis (Aguilar et al. 2011) and amino acid profile (Aguilar et al. 2013b).

Linen (*Linum usitatissimum*) has been used as feeding and fiber sources from ancient times in Asia, North Africa, and Europe. Nowadays, linen is harvested in around 50 countries, being Canada the main producer, followed by China, USA, and India (FAO 2015). Linen has high content of protein (22–33 %), lipids, (35–43 %), and fiber (30 %) but low content of carbohydrates (1–2 %) (USDA 2002). Chemometric and elemental analysis was not reported, except the analysis of trace elements in linen fiber (Inoue et al. 2010).

Sesame (*Sesamum indicum* Dc) is a culture native from Africa and India: After Spanish conquest, it was introduced in America. The composition of sesame seeds includes protein (17 %), lipids (50 %), carbohydrates (26 %), and fiber (16 %). Moreover, the lipid profile includes the following fatty acids: linoleic, linolenic, oleic, miristic, palmitic, palmitoleic, and stearic acids (USDA 2002). Elemental analysis has been reported for sesame in roots (Narayanaswamy and Gokulakumar 2010) and edible oil (Iskander 1993).

Chia (*Salvia hispanica* L), is a plant from Central America with a wide genetic diversity (Cahill 2004). Also, it has been indicated that chia is native from the western and central mountains of Mexico in the Chiapas state (Beltrán-Orozco and Romero 2003). Chia has been used as raw material for medicines and paints and as offering in religious ceremonies (Garibay 1989). Due to its use in the present and past, chia is considered a new and ancient culture (Ayerza and Coates 2009). From the point of view of feeding, chia seeds present excellent nutritional composition, including high content of proteins (19–23 %), lipids (30–33 %), carbohydrates (9–41 %), and fiber (18–30 %) (Inoue et al. 2010); however, its elemental content is less known and has not been previously reported.

Based on the lack of information about the elemental content in several crops and the advantages of use of new chemometric methods as classification tools, in this work, the analysis of 26 elements (Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cs, Cu, Ga, Fe, K, Mg, Mn, Na, P, Pb, Rb, Se, Si, Sr, Ti, V, and Zn) was carried out in chia, linen, sesame, amaranth, and quinoa seeds by inductively coupled plasma optical emission spectroscopy (ICP-OES), as well as their classification by use of principal component analysis (PCA), cluster analysis (CA), and partial least squares discriminant analysis (PLS-DA).

Materials and Methods

Instrumentation

Mineralization was carried out using an Anton Paar MW3000 microwave system (Graz, Austria). All elements were determined using a Varian ICP-OES model ICP-OES Vista Pro (Palo Alto, CA, USA), with a Czerny-Turner monochromator, holographic diffraction grid, and a VistaChip charge-coupled device (CCD) array detector. The operation parameters (wavelength) used in the ICP-OES system and the obtained limits of quantification are listed in Table 1. The calibration presented an r^2 coefficient regression range from 0.984 to 0.998 for all elements. The reached LOQ values were in agreement with previously reported values (Dolan and Capar 2002).

Table 1 Selected wavelength for ICP-OES analysis and obtained LOQ

Element	Wavelength (nm)	LOQ μg g^{-1}
Ag	328.068	0.078
Al	396.153	0.314
As	189.043	0.073
B	249.681	0.086
Ba	233.527	0.045
Ca	317.933	0.111
Cd	226.505	0.016
Co	229.623	0.032
Cr	267.716	0.078
Cs	263.251	0.023
Cu	327.393	0.107
Fe	238.204	0.051
Ga	327.251	0.092
K	766.49	0.010
Mg	285.213	0.018
Mn	257.61	0.015
Na	589.592	0.759
P	213.617	0.842
Pb	220.353	0.462
Rb	244.336	0.036
Se	203.991	0.137
Si	251.611	0.097
Sn	189.927	0.064
Ti	283.244	0.773
V	290.880	0.108
Zn	206.207	0.005

Reagents

Nitric and hydrochloric acids were purchased from Ciccarelli (Buenos Aires, Argentina) and purified by means of a Berghof sub-boiling distillation system (Tübingen, Germany). All standard solutions were prepared using spectroscopic-grade reagents from Merck (Darmstadt, Germany). Ultrapure water (18.2 MΩ cm) was obtained using a Millipore Synergy water system (Billerica, MA, USA).

Seed Samples

Fourteen samples of each seed species (amaranth, chia, linen, sesame, and quinoa) were obtained by local producers in the San Luis province (Argentina) from September 2013 to March 2014. Samples were stored in a plastic bag in a dark and dry place until analysis. Seed species were confirmed by an expert botanist before the analyses.

Sample Pretreatment

Mineralization was performed by triplicate as follows: 10 g of the seed samples was ground and passed through a sieve (0.50-mm diameter). Two grams of the obtained powder was transferred into a microwave vessel and mixed with 6 mL HNO_3, 1 mL HCl, and 1 mL 100 mg L^{-1} indium solution (used as internal standard). The mixture was mineralized at 235 °C during 30 min in the microwave furnace, according to the suggestion of the manufacturer. Solutions were

Table 2 Concentration of elements found in the studied species of seeds

Elemental concentration, μg g^{-1}					
Element	Amaranth[a]	Chia[a]	Linen[a]	Quinoa[a]	Sesame[a]
Ag	0.29±0.03	1.07±0.04	0.97±0.15	0.35±0.02	0.61±0.06
Al	27.68±1.55	248.36±5.53	4.88±0.37	<LOQ	<LOQ
As	<LOQ	0.16±0.01	0.08±0.01	0.15±0.01	0.31±0.01
B	<LOQ	4.60±0.12	4.83±0.48	<LOQ	<LOQ
Ba	0.57±0.02	16.41±0.34	16.91±0.22	1.95±0.11	1.32±0.04
Ca	1588.49±14.57	6240.76±121.10	2121.01±13.43	446.49±5.57	10463.47±152.76
Cd	<LOQ	<LOQ	0.21±0.01	0.04±0.01	0.12±0.01
Co	0.10±0.01	0.25±0.03	0.18±0.01	0.11±0.02	0.08±0.01
Cr	1.44±0.02	0.97±0.03	1.38±0.03	0.44±0.04	1.18±0.03
Cs	4.76±0.18	<LOQ	13.14±0.23	0.05±0.01	12.52±0.26
Cu	<LOQ	22.66±0.63	<LOQ	<LOQ	<LOQ
Fe	<LOQ	243.50±4.02	0.08±0.01	<LOQ	0.30±0.01
Ga	107.12±1.10	0.45±0.02	68.43±0.77	131.77±1.01	148.33±1.34
K	5291.10±65.21	6658.33±112.58	8070.05±20.18	6035.02±52.42	5845.53±77.61
Mg	3188.36±34.71	3694.16±50.15	3681.56±28.91	1770.04±19.38	3743.60±49.42
Mn	37.10±0.56	30.31±0.55	31.23±0.31	24.07±0.23	13.73±0.22
Na	<LOQ	10.42±1.70	233.88±7.21	<LOQ	<LOQ
P	5887.24±73.94	7992.98±116.41	6275.23±83.71	4102.34±38.20	8383.36±114.72
Pb	<LOQ	<LOQ	0.52±0.03	<LOQ	<LOQ
Rb	4.22±0.03	4.39±0.09	2.01±0.04	6.94±0.50	1.39±0.02
Se	0.50±0.02	0.78±0.02	<LOQ	<LOQ	0.75±0.02
Si	<LOQ	279.30±7.93	<LOQ	<LOQ	<LOQ
Sn	7.84±0.12	32.22±0.59	7.66±0.09	2.91±0.18	76.54±0.99
Ti	<LOQ	2.68±0.17	<LOQ	<LOQ	<LOQ
V	<LOQ	0.51±0.01	0.26±0.01	0.18±0.01	0.34±0.01
Zn	25.84±0.37	69.79±1.14	48.49±0.93	28.08±0.35	66.06±1.24

LOQ limit of quantification

[a] Mean±SD (*n*=14)

transferred to 50 mL volumetric flasks and completed to mark with deionized water.

Data Analysis

All chemometric analyses (PCA, CA, and PLS-DA) were performed using The Unscrambler X 10.3 software (CAMO AS, Trondheim, Norway).

Results and Discussion

Recovery Assays

As was previously indicated, for the purpose of assessing the recovery grade in the mineralization step, a recovery assay was performed by adding known concentration of indium (100 mg L^{-1}) in each sample. The obtained results were between 94.6 and 103.1 % in all cases, similar those reported to other plant species (Maiga et al. 2005; Abou-Arab and Abou Donia 2000).

On the other hand, to avoid systematic errors and ensure the quality of the obtained results, a second recovery assay was performed by standard addition in all seed species, adding known concentration of every element in triplicate samples: The assay showed a recovery degree range from 93.5 to 105.6 % for all elements, similar to the one achieved by the use of indium.

Elemental Analysis

Table 2 shows the results obtained for the studied seeds (mean±SD for 14 samples for each species). It can appreciate high content for Ca, Mg, K, and P in all samples, as well as the presence of minor elements such as Ag, Al, B, Ba, Co, Cr. Cs, Cu, Fe, Ga, Mn, Na, Rb, Se, Si, Sn, Ti, V, and Zn. Also, there were toxic elements found: As (all seeds except amaranth); Cd was present in linen, quinoa, and sesame, while Pb was found only

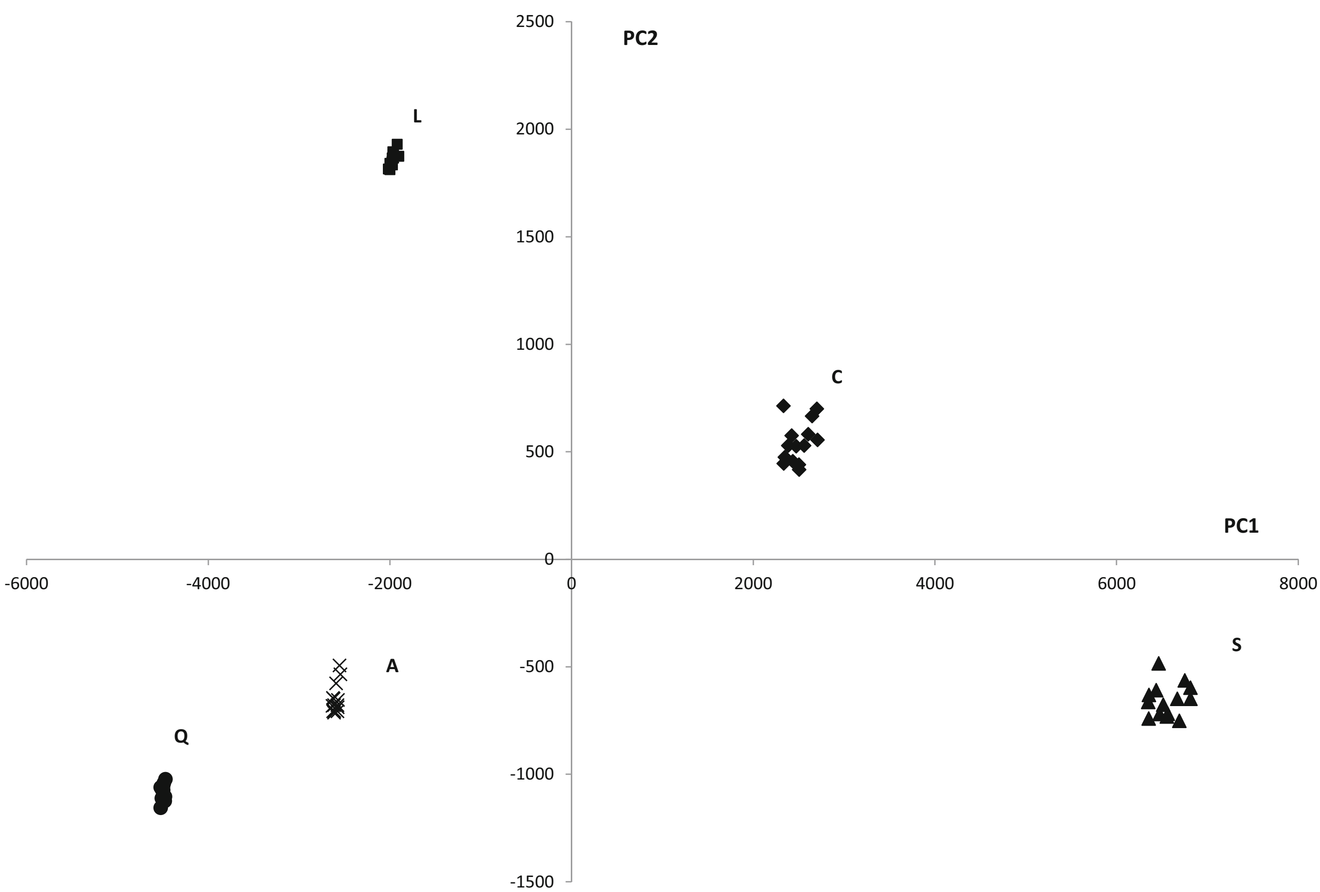

Fig. 1 Cluster analysis performed for seed samples

in linen. The presence and concentration of toxic elements were significantly lower than those reported in other works (Aguilar et al. 2013a, b; Konishi et al. 2004). Moreover, Pb, As, and Cd were under the allowed limit in foods by the World Health Organization in all samples (Pb 10 μg g^{-1}; As 4 μg g^{-1}, and Cd 1 μg g^{-1}) (WHO 1991).

Chemometrics

The concentration values found for every kind of seed were used as variable matrix to obtain all the chemometrics models. In the first place, PCA was performed as exploratory analysis to evaluate the classification models and the influence of original variables. Figure 1 shows the score plot with a clear discrimination for all seed samples: amaranth (A), chia (C), linen (L), quinoa (Q), and sesame (S). The variables used to obtain the final PCA model are shown in Fig. 2 (loading plot), which indicates the influence of each selected variable on the model: Ca, Mg, K, P, and Na. Only two PCs were needed, which explain 99.6 % of variance, indicating a good fit of the final model. Ca had strong influence on sesame, while P and Mg on chia and K on linen; amaranth and quinoa were the less affected for these variables. The influence of variables was in agreement with the relative concentration of each variable in every seed: The major concentration of Ca was found in sesame, the same for P and Mg in chia and K in linen, whereas that amaranth and quinoa were the seeds with the minor concentration of these elements.

Cluster analysis was performed using the same variables in PCA, obtaining a second correct classification shown in the dendogram of Fig. 3. It can also be seen that quinoa, amaranth, and linen were grouped at the left, while sesame and chia at the right, indicating strong differences between both groups, which can mainly be due to the differences in the Ca concentrations (Figs. 1 and 2).

Finally, PLS-DA was used as a supervised method to evaluate the classification errors. Figure 4 shows the classification obtained by the model, in which all seeds were classified again according to their species: The final discriminant model was build using the same

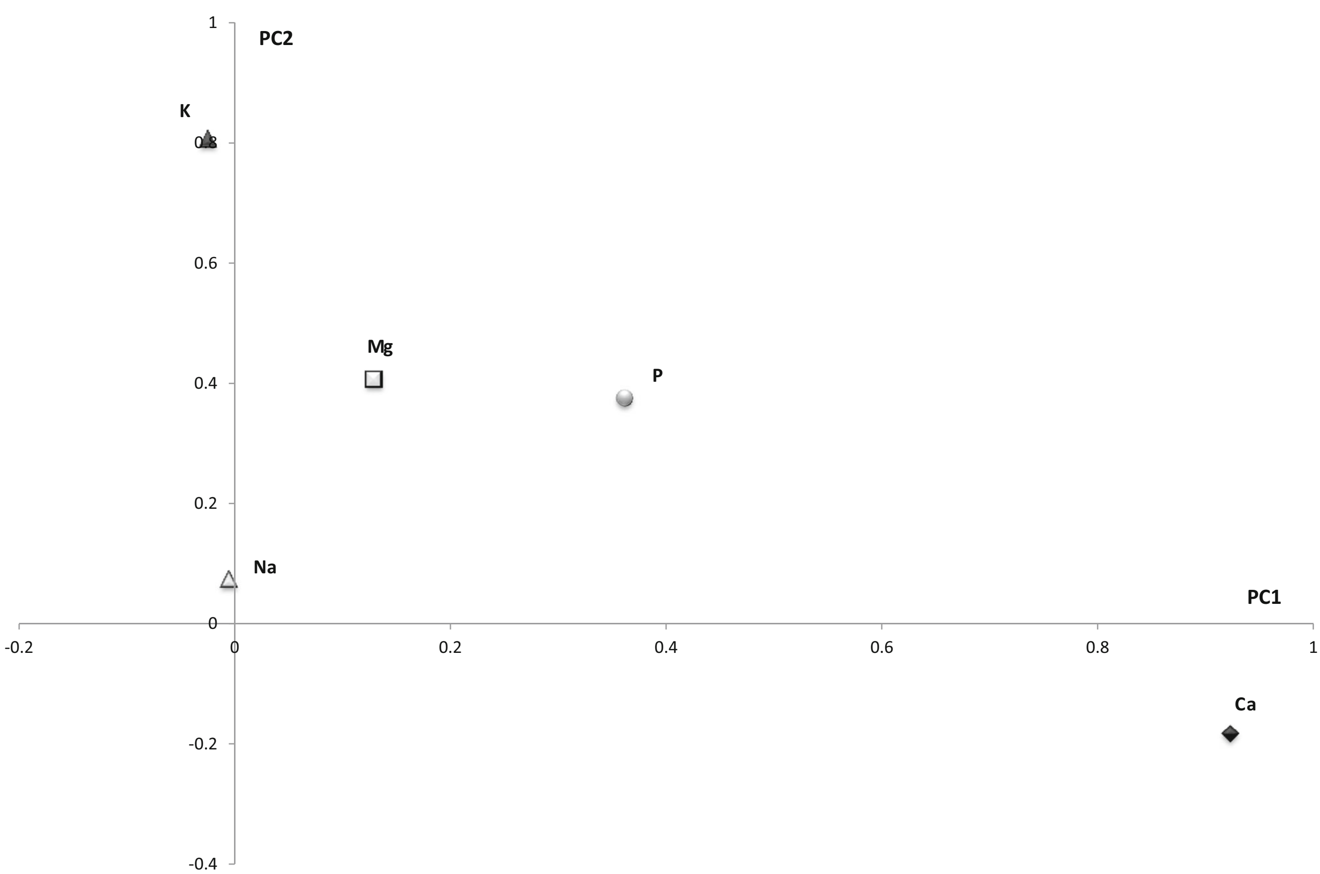

Fig. 2 PCA score plot obtained for the classification of seed samples

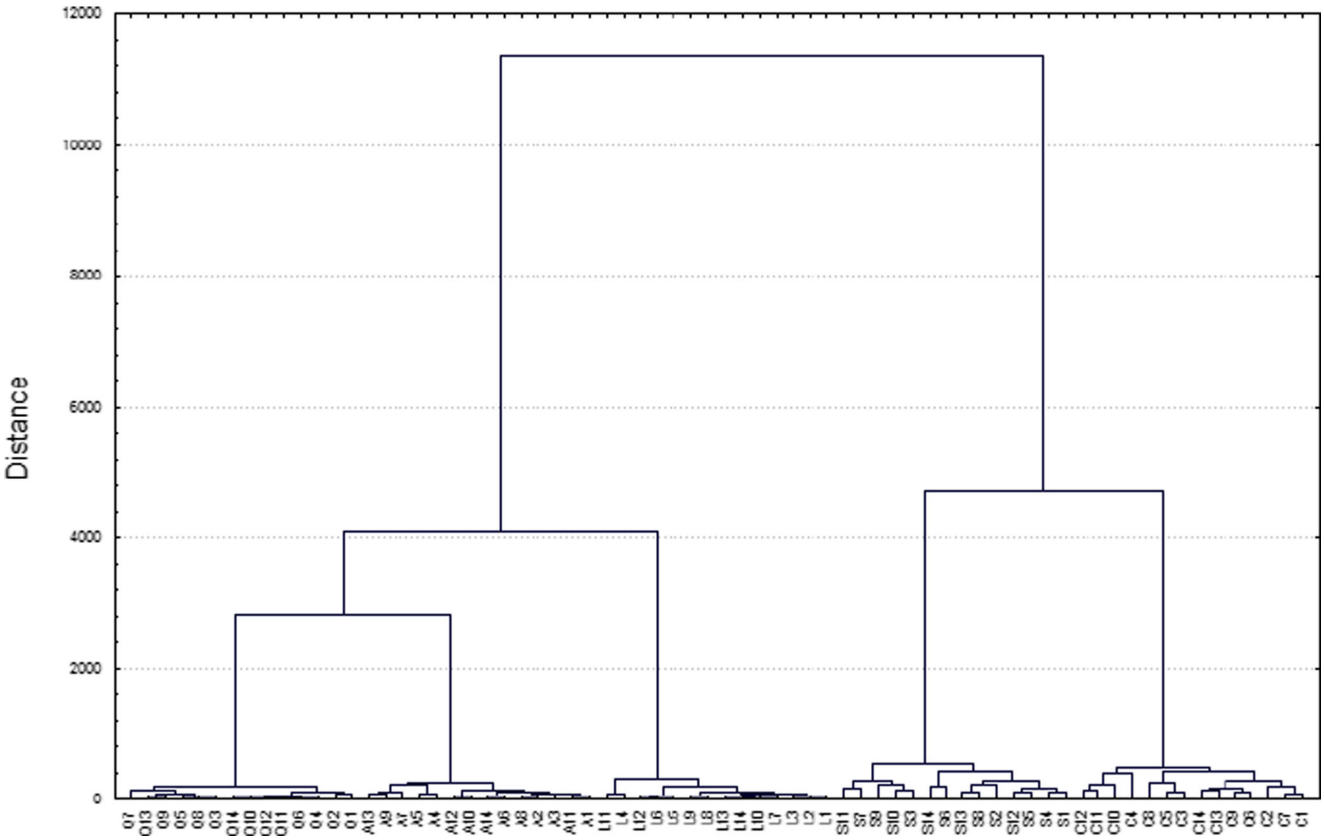

Fig. 3 Loading plot, showing the influence of variables on the PCA model

variables in PCA and CA. After that, a confusion table (Table 3) was obtained, reaching error equal 0 in the classification (10 samples for training) and validation (four samples for prediction) steps. These results indicate a correct classification for all seed species, which is in agreement with Fig. 4, where the distance or separation (in terms of PLS components) between species was high.

Fig. 4 PLS-DA score plot showing the classification of studied seeds

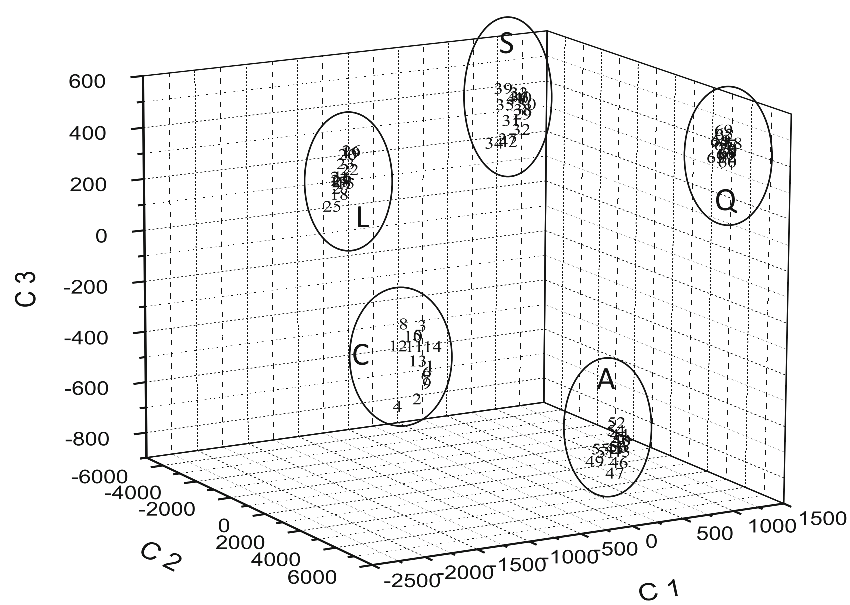

Table 3 Results obtained for training and prediction sets in the PLS-DA model

Training	*A*	*C*	*L*	*Q*	*S*	Total	Error (%)
A	10	0	0	0	0	10	0
C	0	10	1	0	0	10	0
L	0	0	10	0	0	10	0
Q	0	0	0	10	0	10	0
S	0	0	0	0	10	10	0
Prediction	*A*	*C*	*L*	*Q*	*S*	Total	Error (%)
A	4	0	0	0	0	4	0
C	0	4	0	0	0	4	0
L	0	0	4	0	0	4	0
Q	0	0	0	4	0	4	0
S	0	0	0	0	4	4	0

Conclusions

In this work, an elemental analysis was performed in linen, sesame, amaranth, chia, and quinoa seeds, showing, in general, high concentration of major elements and low levels of toxic elements (bellow the permissible limits by WHO). On the other hand, a complete chemometric analysis allowed the classification of seeds based on the concentration of five major elements, which were enough to classify all samples with a 100 % certainty. Due to its simplicity and robustness, the proposed chemometric method can be useful to the analysis of botanical origin of these seeds as raw material in the food factory, as well as government control labs. However, more studies are required to evaluate the effect of other seed plants or the impact of the geographical origin on the results.

Acknowledgments We would like to thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT), Universidad Nacional de San Luis, and Universidad Nacional de La Pampa, Argentina, that supported this research.

Conflict of Interest Daniela Bolaños declares that she has no conflict of interest. Eduardo Jorge Marchevsky declares that he has no conflict of interest. José Manuel Camiña declares that he has no conflict of interest. This article does not contain any studies with human or animal subjects.

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