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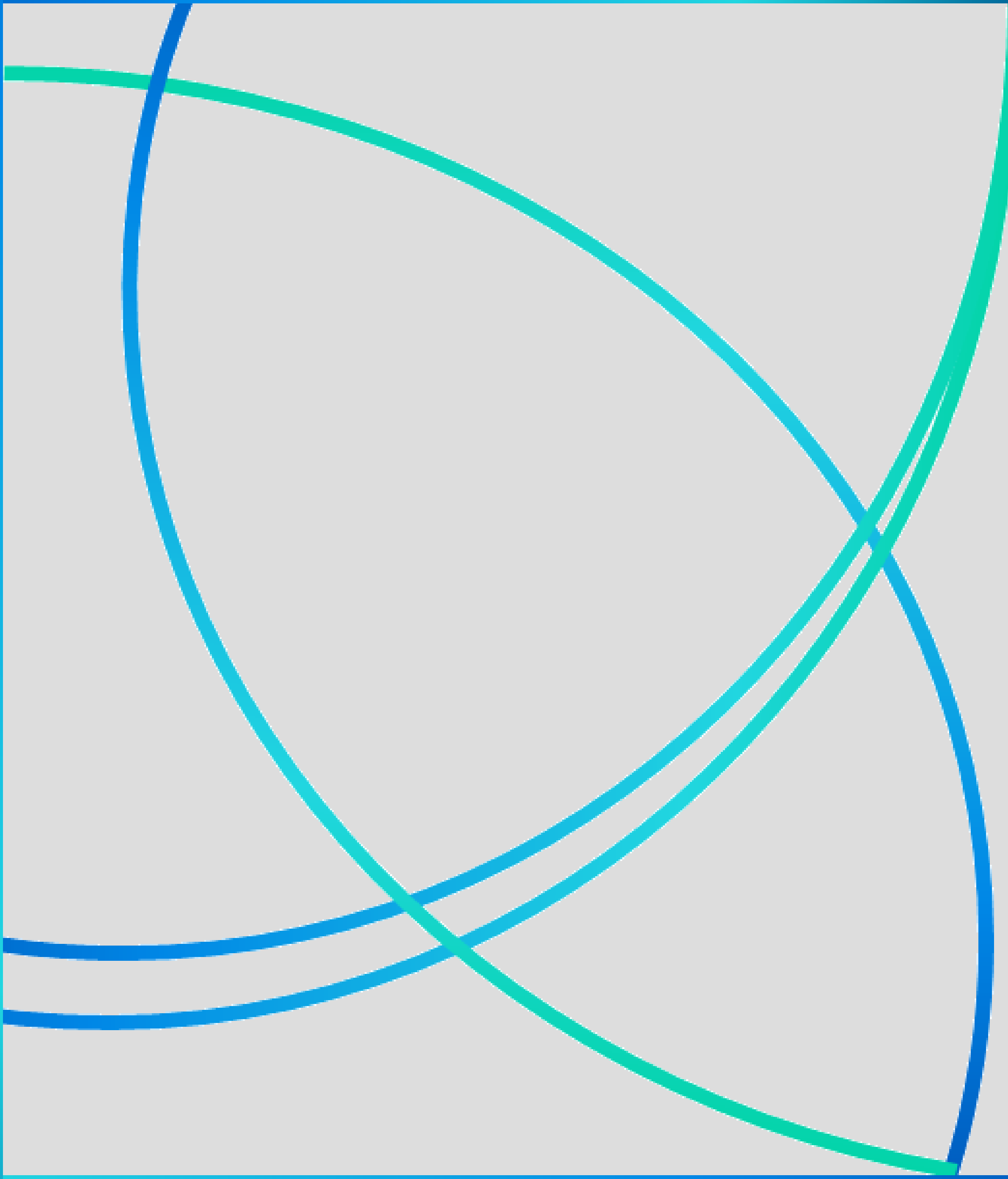

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Authentication of the protected designation of origin “Kaki Ribera del Xúquer” from its mineral profile

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Abstract

Protected designation of origin (PDO) “Kaki Ribera del Xúquer” samples were discriminated from those produced in other five origins concerning: towns surrounding Valencia, Alicante, Andalucía, Castellón and also Ribera, produced outside the PDO frame. Multivariate analysis tools; such as principal components analysis (PCA), hierarchical cluster analysis (HCA), linear discriminate analysis (LDA) and classification and regression trees (CARTs) were evaluated in order to achieve a correct sample classification of the six sample origin groups considered. Chemometric analysis was conducted with 14 variables (content of different elements in mg kg-1, determined by ICP-OES and ICP-MS). HCA and CART cannot authenticate the origin of kaki fruits at 100 %; CART provided a separation of 79 % for the PDO samples. PCA only discriminated well the samples as a function of their different harvest but LDA provided quite satisfactory results obtaining a classification rate of 100 % for samples of the calibration set and 67 % for those included in the validation set.

Keywords: Protected designation of origin (PDO), mineral profile, inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), kaki fruit.

Autenticación de la denominación de origen protegida “Kaki Ribera del Xúquer” a partir de su perfil mineral

Resumen

Muestras de caqui con denominación de origen protegida (DOP) “Kaki Ribera del Xúquer” fueron discriminadas de otras con distinta procedencia española: de ciudades cerca de Valencia, Alicante, Andalucía, Castellón y la Ribera producidas fuera de la DOP. Se usaron herramientas de análisis multivariante como el análisis de componentes principales (PCA), análisis jerárquico de clústers (HCA), análisis discriminante lineal (LDA) y árboles de clasificación y regresión (CARTs) para evaluar la correcta clasificación de los seis grupos de origen. Para el análisis quimiométrico se utilizaron 14 variables (contenido mineral en mg kg-1, determinado por ICP-OES e ICP-MS). HCA y CARTS no permiten la total autentificación de caquis; CART proporciona una separación del 79 % para las muestras de DOP, mientras que PCA sólo permite discriminar bien las muestras a partir de su año de cosecha. LDA proporciona unos resultados bastante satisfactorios ya que se obtiene una clasificación correcta del 100 % para el set de calibración y de 67 % para el set de validación.

Palabras clave: Denominación de origen protegida (DOP), perfil mineral, espectroscopia de emisión óptica con plasma de acoplamiento inductivo (ICP-OES), espectrometría de masas con plasma de acoplamiento inductivo (ICP-MS), caqui.

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1. Introduction

Kaki is a seasonal fruit whose origin is China and Japan, and it was brought to Spain during the 19th century. One of the main geographical locations of kaki fruit production is the river Xúquer region (Valencia, Spain). The local variety “Rojo Brillante” has the protected designation of origin (PDO) “Kaki Ribera del Xúquer” from the European Union.

Authenticity is a quality criterion for food which importance increases within Europe as a result of legislative protection of regional foods, based on the approval of different labels (1,2). The PDO label is used to describe foodstuffs, with regional identity, that are produced, processed and prepared in a specific geographical area (3,4). From the economic point of view, food authenticity has great importance, for the sectors involved in food production and also for the consumer. This is a very important factor because the authenticity helps to guarantee the characteristics and quality of food products and to prevent overpayment (5,6).

The use of analytical techniques is the best way to authenticate foods without any doubt in order to determine their geographical origin. There are many papers that try to discriminate foods between PDO areas to those produced outside the PDO, using different analytical methods. The most commonly analytical techniques used are GC-MS (7-11) and HPLC (12-14) for the determination of organic compounds, but organic compounds vary easily due to a lot of factors: fertilization, climatic conditions... So, it is sometimes very difficult to have definitive authentication. The mineral profile of foods is characteristic due to the soil type and the climatic conditions. Therefore, the determination of the mineral profile is a good technique to assure the geographical origin of food samples (5). The most commonly techniques employed to determine mineral elements in food in order to do their authentication are flame atomic absorption spectrometry FAAS (15,16), inductively coupled plasma optical emission spectrometry ICP-OES (17-20) and inductively coupled plasma mass spectrometry ICP-MS (21,22).

The main purpose of this study is the authentication of kaki fruit samples produced from PDO “Kaki Ribera del Xúquer” using their mineral profile information together with multivariate analysis.

2. Material and methods

2.1. Apparatus

An ICP-OES Optima 5300 DV inductively coupled plasma optical emission spectrometer Perkin Elmer (Norwalk, CT, USA) equipped with an auto sampler AS 93-plus, and an ultrasonic nebuliser U6000AT$^+$ Cetac (Nebraska, EEUU) was used for mineral determinations. ICP-MS measurements were carried out with a Perkin-Elmer SCIEX Elan 6100 DRCII apparatus, equipped with a Meinhard nebuliser and an autosampler Perkin-Elmer AS-91 was used for sample introduction.

The apparatus employed for sample pre-treatment was a microwave laboratory system, Ethos SEL from Milestone (Sorisole, Italy), equipped with a thermocouple for automatic temperature control, and an automatic gas leaks detector.

2.2. Reagents

Argon C-45 (purity higher than 99.995%) supplied by Carburos Metálicos (Barcelona, Spain), was employed as plasmogen and carrier gas for ICP-OES and ICP-MS.

Stock solutions of a multi-element standard solution (100 mg L^{-1}) containing 26 elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Na, Sr, Tl, Ti, V and Zn) dissolved in 5% HNO_3 obtained from Scharlau (Barcelona, Spain), and a multi-element solution containing 20 mg L^{-1} Dy, Er, Eu, Gd, Ho, Lu, Sm, Sc, Tb, Tm, Yb and Y and 100 mg L^{-1} Ce, La, Nd and Pr dissolved in 5% HNO_3, also from Scharlau, were employed to prepare the calibration standards.

For sample digestion it was employed HNO_3 69 % for trace analysis and H_2O_2 35 % reagent grade, both from Scharlau, and nanopure water with a minimum resistivity of 18.0 MΩ cm, obtained from a Milli-Q Millipore system (Bedford, MA, USA).

A 1000 mg L^{-1} ruthenium standard solution for ICP and a 1000 mg L^{-1} rhodium standard solution for ICP both from Scharlau, were used as internal standards.

2.3. Samples

162 kaki fruit samples from different Spanish agricultural cooperatives were collected during 2010 and 2011 harvests. Each sample corresponds to a mixture of 2-4 pieces of kaki fruit obtained from the same producer but from different trees. 114 samples were produced under the PDO "Kaki Ribera del Xúquer", four samples from Alicante, 12 from Andalucía, 10 from Castellón, nine from Ribera (outside the PDO) and 13 from Valencia (see Figure 1). The samples were taken from October to December, for each harvest. The edible parts were lyophilised, pulverised and stored in polyethylene bottles until analysis.

Figure 1. Map of Spain indicating the different regions where the kaki fruit samples employed through this study were produced

The microwave-assisted treatment was adapted from that provided by Mir-Marqués et al., 2012 (23) according to the microwave laboratory system manufacturer recommendations and our experience.

Freeze-dried samples (0.5 g) were digested with 8 mL of concentrated nitric acid and 2 mL of H_2O_2 into the Teflon vessel inside the microwave oven. The digestion step of 15 min at 180 °C (700 W) was employed. The resulting solution was quantitatively transferred to a plastic flask and made up to 20 mL with ultrapure water. All samples were analysed in triplicate to eliminate any specific error, to verify the homogeneity of samples and to evaluate the repeatability of the procedure. Blanks and certified material (NIST 1573a Tomato Leaves from the National Institute of Standards and Technology (Gaithensburg, MD, USA)) were prepared in the same way than the samples.

2.4. Analytical procedures

The calibration range for all the 42 elements evaluated was established from 0.05 to 2 mg L^{-1} and ruthenium (1 mg L^{-1}) was used as internal standard and added to all samples, blanks and standards for ICP-OES analysis. Digested samples were measured with a final dilution of 40 mL. For ICP-MS analysis, the calibration range for all the 42 elements evaluated was from 2 to 400 µg L^{-1} and rhodium (10 µg L^{-1}) was used as internal standard and added to samples, blanks and standards. In this case, digested samples were measured with a final dilution of 100 mL. Additional, control standards were measured for every series of 10 independent sample measurements and a reference material every series.

The average measurement of blanks was subtracted from the analytical signals of digested samples after interpolation on the calibration graphs. Results were expressed as a basis of dry weight.

2.5. Statistical analysis

Both, univariate and simple multivariate methodologies were employed through this study for the authentication of the origin of samples from their mineral profile.

Univariate analysis

Analysis of variance was applied to all variables studied considering only those elements present in the samples over the detection limit of the method employed. In cases where the concentration was below the detection limit, this value was taken as data for the chemometric studies. The mean values obtained for samples with different origin were compared by using one-way ANOVA and two-way ANOVA including the production year.

Multivariate analysis

Statistical multivariate analysis was performed by using the software XLSTAT2008 from Addinsoft (Barcelona, Spain). Principal component analysis (PCA), hierarchical cluster analysis (HCA), linear discriminate analysis (LDA) and classification and regression trees (CART) were performed on the mineral elements concentration of the studied samples.

Although 42 elements were evaluated in the 162 kaki fruit samples analysed, calculations were performed using only 14 variables considering the content of Al, Ba, Ca, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Sr, Ti and Zn, in mg kg^{-1}, determined by ICP-OES and ICP-MS. The concentrations of other elements were lower than the detection limit (LOD) in almost samples analysed in this study and thus they were not used in data treatment.

3. Results and discussion

3.1. Mineral content of kaki fruit

Table 1 shows the maximum, minimum, mean and median concentration of elements (Al, Ba, Ca, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Sr, Ti and

Zn) present in all samples at concentration levels higher than the LOD as a function of their production region (Alicante, Andalucía, Castellón, PDO Ribera del Xúquer, Ribera outside PDO, Valencia) expressed in mg kg^{-1} of dry weight.

3.2. Statistical analysis

3.2.1. Univariate analysis

ANOVA was used to compare elemental profiles of food in different origin (6). We performed a one-way ANOVA for each one of the 14 analytes present in all samples over the LOD of the employed method: Al, Ba, Ca, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Sr, Ti and Zn, to find whether there were significant differences between samples produced in different regions. ANOVA analysis shows that the differences were statistically significant at a probability level of 95 % ($p<0.05$) since F calculated is greater than F critic (F critic 2.16) for all elements except for

Table 1. Mineral composition of kaki fruit samples from different Spain production

		Al	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Sr	Ti	Zn
PDO “Kaki Ribera del Xúquer” n= 114	**min**	< 0.12	0.4	210	0.1	< 0.3	6800	< 0.005	240	0.4	< 1.2	< 0.10	0.3	< 0.04	0.4
	max	8.6	4.8	540	2.2	11.0	12600	1.0	500	14.2	200	2.3	9.8	3.6	4.5
	mean	3 ± 2	1.7 ± 0.8	380 ± 70	1.1 ± 0.5	3 ± 2	9600 ± 1400	0.2 ± 0.2	400 ± 50	5 ± 3	50 ± 30	0.7 ± 0.4	4.6 ± 1.7	2.3 ± 0.7	1.7 ± 0.6
	median	2.4	1.6	380	1.0	2.4	9700	0.09	400	4.4	40	0.7	4.5	2.5	1.6
Alicante n= 4	**min**	1.2	0.14	500	1.32	0.57	9400	< 0.005	420	4.3	40	0.85	1.8	2.6	1.70
	max	2.7	7.8	1000	2.10	3.68	11600	0.06036	540	11.1	110	2.55	3.0	3.3	2.77
	mean	1.9 ± 0.8	3 ± 3	800 ± 200	1.6 ± 0.3	2.0 ± 1.6	10300 ± 900	0.02 ± 0.03	480 ± 50	8 ± 3	70 ± 30	1.7 ± 0.7	2.3 ± 0.5	3.0 ± 0.3	2.4 ± 0.5
	median	1.9	2.4	800	1.49	1.87	10100	0	480	7.5	70	1.63	2.3	3.0	2.50
Andalucía n= 12	**min**	0.5	< 0.07	230	0.3	0.6	9200	< 0.005	380	2	30	0.3	0.2	1.4	1.1
	max	9.3	4.0	550	2.0	8.7	15517	0.56	610	35	90	2.5	5.1	3.7	3.0
	mean	3 ± 3	2.2 ± 1.2	400 ± 80	1.1 ± 0.5	4 ± 2	11200 ± 1800	0.2 ± 0.2	440 ± 70	9 ± 10	60 ± 20	0.9 ± 0.6	2.6 ± 1.6	2.6 ± 0.6	1.8 ± 0.5
	median	2.6	2.3	400	1.3	4.2	10600	0.09	410	6	50	0.8	3.0	2.6	1.7
Castellón n= 10	**min**	< 0.12	0.46	240	0.19	0.33	6500	< 0.005	330	3.1	10	< 0.10	2.0	1.0	< 0.14
	max	2.60	2.51	430	1.04	4.05	11200	0.194	420	11.6	40	0.75	4.1	3.2	1.44
	mean	1.1 ± 1.0	1.5 ± 0.7	350 ± 60	0.7 ± 0.3	2.2 ± 1.4	9000 ± 1300	0.07 ± 0.08	360 ± 30	6 ± 3	20 ± 10	0.4 ± 0.3	3.1 ± 0.7	2.3 ± 0.6	0.8 ± 0.5
	median	0.69	1.51	340	0.72	2.10	8900	0.041	360	5.0	20	0.39	3.2	2.3	0.95
Ribera outside PDO n= 9	**min**	< 0.12	< 0.07	210	0.7	< 0.3	7600	< 0.005	330	3	20	< 0.10	1.2	1.5	1.0
	max	10	3	520	2.1	13	11100	1.0	500	10	130	1.2	7	3	3
	mean	3 ± 4	2.0 ± 0.8	410 ± 90	1.2 ± 0.4	4 ± 4	9000 ± 1100	0.4 ± 0.3	410 ± 60	7 ± 2	50 ± 30	0.8 ± 0.3	4.0 ± 1.6	3.0 ± 0.7	2.0 ± 0.5
	median	2	2	400	1.2	3	9100	0.43	400	7	50	0.8	3	3	1.4
Valencia n= 13	**min**	< 0.12	0.5	270	0.6	< 0.3	8000	< 0.005	340	0.7	3	0.4	1.0	1.7	0.7
	max	14.3	5.1	660	3.3	6.3	12300	0.77	630	22	60	5.1	9.3	4.2	2.9
	mean	3 ± 4	2.0 ± 1.2	450 ± 130	1.4 ± 0.7	2.0 ± 1.8	10600 ± 1400	0.2 ± 0.2	440 ± 90	8 ± 7	22 ± 20	1.3 ± 1.2	3 ± 2	2.5 ± 0.7	1.9 ± 0.6
	median	2.1	1.7	400	1.3	1.7	11100	0.03	400	5.1	20	1.0	2.4	2.4	1.8

NOTE: concentration in mg kg^{-1} dry weight. n= number of samples aluminium. So, this information evidences that the mineral profile could be important as a basis of the kaki fruit PDO authentication. We also performed a two-way ANOVA including the production year, in this case samples from Alicante and Castellon had not considered because we did not harvested samples in 2010 (see Table 2). As can be seen in Table 2 from the two-way ANOVA there were differences between harvest areas for all the hand Cu, Li, K, Mg, Mn, Na, Ni, Sr, Ti and Zn did not present differences among production year.

Table 2. Two way ANOVA evaluation of the comparability of the mineral profile of kaki samples produced inside and outside the PDO and the production year

Element	F_A	F_B	Element	F_A	F_B
Al	47.16	9.78	**Mg**	14.47	0.86
Ba	55.2	11.4	**Mn**	19.02	2.74
Ca	28.01	4.98	**Na**	15.26	1.75
Cu	11.94	0.86	**Ni**	5.35	0.67
Fe	26.38	4.25	**Sr**	16.86	2.21
Li	19.04	2.47	**Ti**	10.81	0.53
K	10.60	0.42	**Zn**	47.16	9.78

NOTE: F_A is calculated Fisher's F to different origin, F value critic is 2.14. F_B is calculated Fisher's F to different production year, F value critic is 2.75.

3.2.2. Multivariate analysis

In this study, the concentration of 14 elements was used to evaluate the fruits coming from PDO "Kaki Ribera del Xúquer" produced in a restricted area near Valencia and to discriminate between different regions of kaki fruit production close to the zone covered by the PDO label. In this sense, mineral content of the edible part of the samples was used as chemical descriptor for building the statistical methods, in order to establish differences between PDO kaki fruit and the other ones. As it has been indicated, PCA, HCA, LDA and CART models were employed for chemometric treatment. Results obtained from this chemometric models were compared between them, in order to look for the best discrimination processing tool.

Principal component analysis

Principal component analysis is an unsupervised technique that allows visualising the information of the data set in a few principal components retaining the maximum possible variability within that set.

From the loadings of original variables in the two first considered principal components (see Table 3).

Table 3. Loadings of the variables for the two first Principal Components established from the mineral profile of kaki samples produced in different parts of Spain during the period 2010-2011

Variable	PC1	PC2	Variable	PC1	PC2
Al	-0.131	-0.312	**Mg**	0.620	0.579
Ba	0.543	-0.531	**Mn**	0.277	-0.011
Ca	0.590	-0.128	**Na**	0.095	0.444
Cu	0.731	-0.288	**Ni**	0.692	-0.104
Fe	-0.020	-0.284	**Sr**	0.609	-0.342
K	0.284	0.856	**Ti**	0.480	0.455
Li	0.390	0.061	**Zn**	0.703	-0.108

Principal component 1 (PC1) represents 24.80 % of the total variance. Cu, Ni, Mg and Sr were identified as the dominant variables in the PC1 while Fe and Na show the lowest values. PC2 explains 15.54 % of the total variance. Revising loadings, K, Mg and Ba result as the most dominant variables in PC2, while Li and Mn show the lowest dominant values. PC1 and PC2 account for 40.34 % of the total variance, and it allows differentiating two groups by harvest years, 2010 and 2011 (see Figure 2). However, it is really difficult to discriminate between samples produced in different areas during the two evaluated years, neither within each of the considered harvest years. The values of total variance explained are very similar than to values reported in bananas from Tenerife and Ecuador (24) and different banana flours (25).

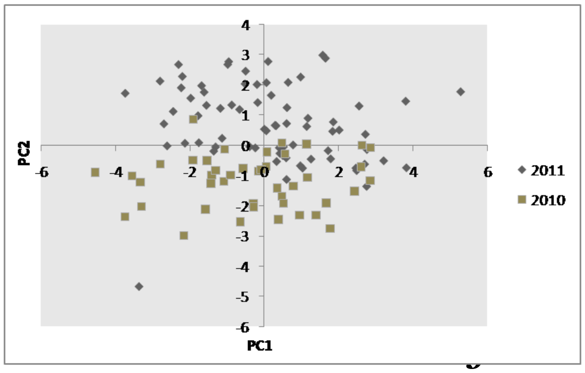

Figure 2. Principal components analysis (PC1 vs. PC2) of the mineral profile of kaki samples produced in different parts of Spain.

Hierarchical cluster analysis

Hierarchical cluster analysis is an unsupervised technique that uses the information obtained from the measuredmineral elements, to determine if there are cluster association between investigated samples with the same origin. Based on the previous results obtained by PCA analysis, HCA was applied to the whole sample population and was separately used in order to evaluate samples produced in 2010 and 2011. As it can be seen in Figure 3, seven clusters were obtained from the 162 samples considered. However, clusters A1 and A2 concerns both the Alicante samples and because of their vicinity they were cumulated in a single cluster A. Cluster B contains two samples from PDO, one sample from Ribera and another sample from Valencia. Cluster C includes samples of four different origins (PDO (8), Castellón (1), Ribera (4) and Valencia (2)). Cluster D contains a single sample from PDO. Cluster E contains the main part of samples produced from the PDO (65 samples) which are accompanied by 25 samples from different origins (Alicante (1), Andalucía (7), Castellón (7), Ribera (2) and Valencia (8), thus providing also a bad classification of kaki fruit from their origin. Cluster F contains 49 samples (PDO (36), Andalucía (4), Castellón (2), Ribera (2) and Valencia (5)). So it can be concluded that the mineral composition of kaki fruits produced in different parts of Spain during the period 2010-2011 cannot be described correctly by HCA in order to authenticate their origin.

The HCA of the mineral profile of samples corresponding to 2010 and 2011 harvest provided five and seven clusters respectively. However, the distribution of the 56 samples collected in 2010 between the five clusters was arbitrary, and as an example 38 samples of the PDO were classified in all clusters. Similar results were found applying HCA to samples collected in 2011. Only one of the clusters correctly classified Alicante samples. The remaining clusters contained samples of the other origins. Therefore, it can be concluded that HCA is an unsuitable tool to do the authentication of kaki fruits from their mineral profile. Compared with other authors, Foster et al., 2002 (24) differentiated between Tenerife and Ecuador bananas by HCA, this may be due to the large distance between the two origins, because they belong to different continents with very different characteristics. According to the investigated kaki fruits, all samples belong to the same country and all regions analyzed show very similar characteristics in both climatic and soil conditions.

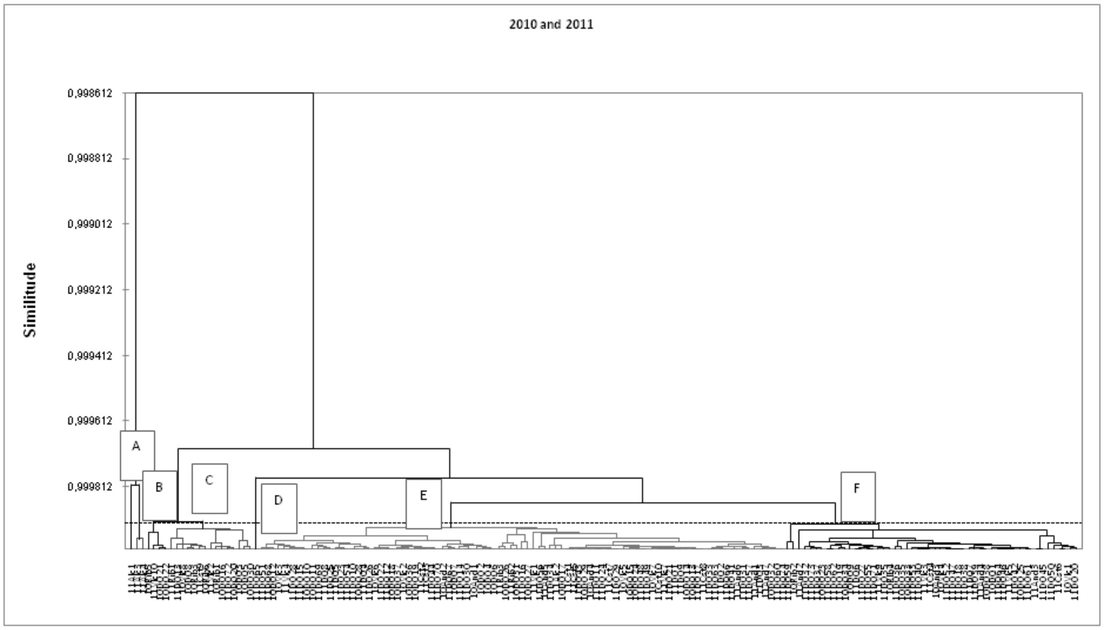

Figure 3. Cluster classification of kaki fruit samples obtained from their mineral profile

Linear discriminate analysis

Linear discriminate analysis is a supervised technique for classifying a set of observations into predefined classes. LDA maximises the variance between categories, minimises the variance within categories, and suppresses the correlation among variables.

LDA was performed by separating the samples in 6 classes: Alicante, Andalucía, Castellón, PDO Kaki Ribera del Xúquer, Ribera (outside the PDO) and Valencia. The kaki samples were divided in two groups: a training set consisting in 108 samples (2 from Alicante, 8 from Andalucía, 6 from Castellón, 78 from PDO, 6 from Ribera outside PDO and 8 from Valencia) and another set for validation containing 54 samples (2 from Alicante, 4 from Andalucía, 4 from Castellón, 36 from PDO, 3 from Ribera outside the PDO and 5 from Valencia). The division into two groups was made randomly. Results were satisfactory, obtaining a classification rate for calibration of 100 % and 67 % for validation (see Table 4) for the validation set.

In Table 4 it is also included the confusion matrix for the validation samples. For the 2010 harvest, a total of 56 samples were divided into 2 sets; one for calibration, containing 36 samples (3 from Andalucía, 23 from PDO, 7 from Ribera and 3 from Valencia), and another set for validation, containing 20 samples (1 from Andalucía, 16 from PDO, 3 from Ribera and 0 from Valencia). In this case a correct classification rate of 85 % was obtained for validation.

Table 4. LDA confusion matrix of validation set for the classification of kaki fruit samples from their mineral profile

	Assigned group **Original group**	**Alic**	**And**	**Cast**	**PDO**	**Rib**	**Val**	**Total**	**% Correct**
All samples (harvest 2010 and 2011)	Alic	2	0	0	0	0	0	2	100%
	And	0	3	0	1	0	0	4	75%
	Cast	0	0	2	1	0	1	4	50%
	PDO	0	1	2	25	5	3	36	**69%**
	Rib	0	0	0	2	1	0	3	33%
	Val	0	0	1	1	0	3	5	60%
	Total	2	4	5	30	6	7	54	67%

	Assigned group **Original group**	**And**	**PDO**	**Rib**	**Val**	**Total**	**% Correct**
Samples of the 2010 harvest	And	1	0	0	0	1	100%
	PDO	1	14	1	0	16	**87%**
	Rib	0	1	2	0	3	67%
	Val	0	0	0	0	0	0%
	Total	2	15	3	0	20	85%

	Assigned group **Original group**	**Alic**	**And**	**Cast**	**PDO**	**Rib**	**Val**	**Total**	**% Correct**
Samples of the 2011 harvest	Alic	2	0	0	0	0	0	2	100%
	And	0	2	0	1	0	0	3	67%
	Cast	0	0	3	1	0	1	5	60%
	PDO	0	2	5	17	1	0	25	**65%**
	Rib	0	0	0	0	1	0	1	100%
	Val	0	0	0	1	0	3	4	75%
	Total	2	4	8	20	2	4	40	68%

In the case of the 2011 harvest, a total of 106 samples were divided into a set of calibration, containing 66 samples (2 from Alicante, 4 from Andalucía, 5 from Castellón, 47 from PDO, 2 from Ribera and 6 from Valencia), and a set of validation with 40 samples (2 from Alicante, 3 from Andalucía, 5 from Castellón, 25 from PDO, one from Ribera and 4 from Valencia). As it can be seen in Table 3 a correct classification rate of 68 % was obtained.

So, as it can be seen, the capability of LDA for a correct classification of kaki fruit samples from their mineral profile is quite good and does not depends dramatically on the harvest. So, it is possible authentication of Kaki Ribera del Xúquer at a 69 % correct level; being those samples produced in the same area, but outside the protected label, the most critical group to obtain a correct differentiation. Other authors obtained a correct classification of 100 % in bananas and cherries (20,25) but they do not explained if it corresponds to classification set or validation set, in this case we could think that they have not performed external validation sets, so their data are comparable with ours.

Classification analysis regression trees

CART technique was applied to the samples collected during the two harvests (2010 and 2011) in order to check the capability of classification of determined concentration of mineral elements in kaki fruits.

This technique divides the data into sub-groups (nodes) that are more homogeneous with respect to the response of the initial data set. When performing the CART data with both harvests, we obtain a separation of 79 % for the PDO, with 4 nodes (see Figure 4), been characterised these samples by low concentrations for calcium and nickel and high concentrations for sodium and strontium. This separation is not pure, and does not let us to separate completely the PDO samples from other ones produced in the Ribera (7), Valencia (2), Andalucía (5) and Castellón (2).

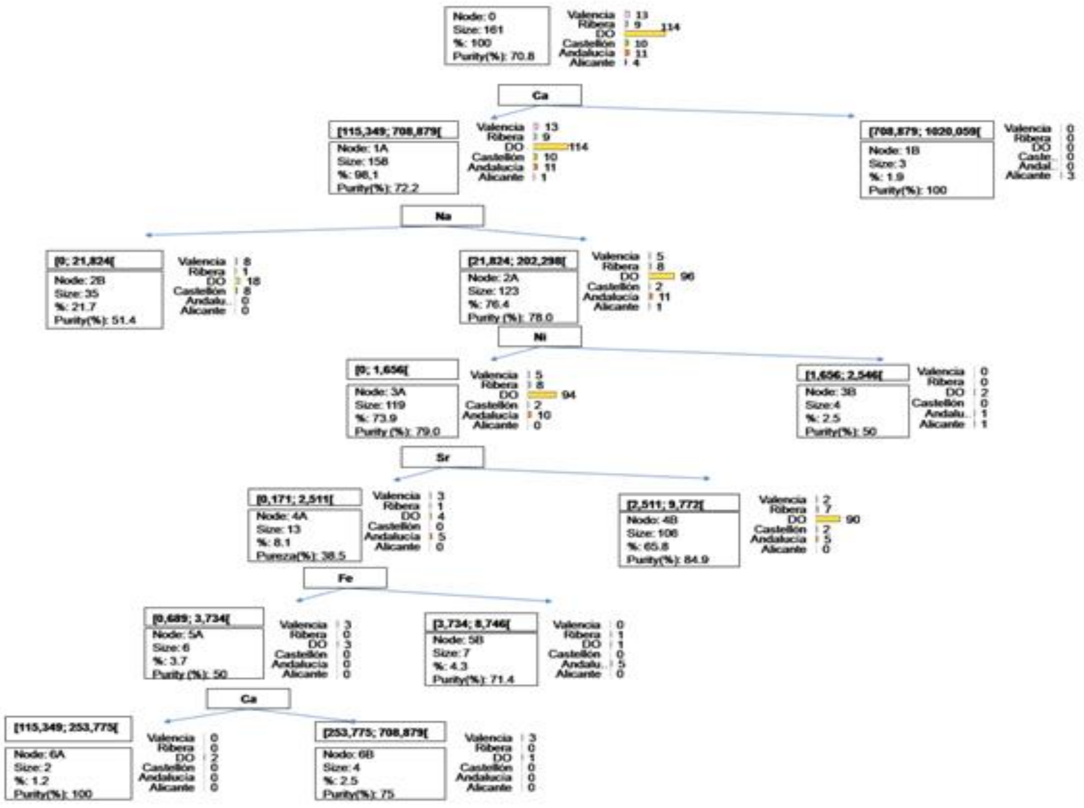

Figure 4. Classification analysis regression trees for kaki fruit samples collected in 2010 and 2011 harvests

On the other hand, CART analysis of samples collected in the 2010 harvest provided a correct classification of 84 % of samples produced inside the PDO with two nodes corresponding to low concentrations of Ca and Li. However once again, the separation was not complete. It was the same for samples produced in 2011, for which the separation was 85 % with 5 nodes corresponding to low concentrations of Ca and Ni, and high concentrations of Zn and Sr.

So, it can be concluded that CART provided coherent results with those suggested by LDA.

Conclusions

Mineral profile of kaki fruit samples from different origin produced in Spain cannot be clearly discriminate by their production area. Because of that, kaki fruits produced inside the PDO "Kaki Ribera del Xúquer" cannot be totally authenticate, being obtained uncorrected classification of other samples produced in Alicante, Andalucía, Castellón, Ribera outside PDO and Valencia by using HCA, PCA and CART chemometric treatment. LDA provided satisfactory results to the authentication of PDO "Kaki Ribera del Xúquer", obtaining a classification rate of 100 % for samples of the calibration set and 67 % for validation set. Although, additional data must be required for a complete description of the fruit PDO and new efforts are in due course to use improved chemometric tools for data treatment.

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