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Application of Multivariate Analysis and Artificial Neural Networks for the Differentiation of Red Wines from the Canary Islands According to the Island of Origin

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Eleven metals (K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Sr, Li, and Rb) were determined in 83 red wines from the Canary Islands. The wines presented high concentrations of Na, and the concentrations of Cu and Zn were much lower than the maximum concentrations established by the International Office of Vine and Wine (OIV). Applying principal component analysis, the dimension space was reduced to five principal components that explain 76.4% of the total variance, and the wines tend to separate on the basis of the island of production. Linear discriminant analysis (LDA) allowed a reasonable classification of wines according to the island of production. When artificial neural networks (Kohonen self-organizing maps and back-propagation feed-forward as unsupervised and supervised techniques, respectively) were applied on the matrix of data constituted by the analyzed metals, the results improved in relation to those obtained by other multivariate methods observing a differentiation of wines according to island of production.

KEYWORDS: Red wines; metals; multivariate analysis; artificial neural networks

INTRODUCTION

In recent decades the quality of wines, and their production, in the Canary Islands have largely increased for both traditional and economic reasons. Since the introduction of the Denominations of Origin (DO) for Canary wines, their characterization has acquired special importance. Many papers have been published to characterize and differentiate wines according to their geographical origin using multivariate analysis. Artificial neural networks also have been recently introduced as a useful tool for the classification of wines (*1*−*5*). Moreover, the use of these methods would confirm the authenticity of the wines from a certain origin and also differentiate them from wines imported from other regions.

It is scientifically accepted that the mineral compositions of fruits and vegetables are a distorted reflection of the metal composition of the soil and environment in which the plants grow. The metal composition of wines is directly related to the metal content of grapes, and these are directly related to the metal contents of soils used for their cultivation. Therefore, mineral composition can be used as a criterion to distinguish the geographic origin of wines.

In previous papers we have reasonably characterized the Canary wines according to their type, vintage, and island of production by using conventional enological parameters, polyphenolic parameters, and volatile compounds (*6*). We have also used metal concentrations in wines to differentiate sweet wines using classical multivariate analysis (*7*) and artificial neural networks to differentiate sweet and dry wines (*5*). In this paper, we determined the concentrations of metals (K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Sr, Li, and Rb) in red wines produced in the Canary Islands and we have used multivariate techniques (factor analysis, discriminant analysis, and artificial neural network) to see whether the wines are grouped according to the island of production. This is a useful tool for the characterization and differentiation of wines according to the region of production contributing to its authentication.

MATERIALS AND METHODS

Samples. Eighty-three samples of red wines belonging to four islands were analyzed: Tenerife ($n = 47$), Gran Canaria ($n = 15$), Lanzarote ($n = 9$), and La Palma ($n = 12$). The grape for the production of wines was mainly Listán Negro, except in La Palma where Negramoll is commonly used. The wines were collected in the vintage corresponding to 1999 and were provided by the Certification Denomination of Origin Council, to ensure the geographic origin of the wines.

Reagents and Solutions. All chemicals were of analytical grade. Stock solutions of each metal (Na, K, Ca, Mg, Fe, Cu, Zn, Mn, Sr, Li, and Rb 1000±0.002 mg/L) were from Panreac (Barcelona, Spain). Working standard solutions were obtained by suitable dilution from stock solution. Lithium chloride 99% as ionic suppressor was obtained from Fluka (Buchs, Switzerland). Lanthanum chloride 99%, used as molecular suppressor, was from Riedel de Haën (Seelze, Germany). Nitric acid of suprapure quality was purchased from Merck (Darmstadt,

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Table 1. Instrumental Conditions for Determination of the Metals

metal	technique	λ (nm)	slit (nm)	lamp current (mA)	flame type
K	EAA	766.5	1	5	Air/C_2H_4
Na	EAA	589	0.5	5	Air/C_2H_4
Ca	EAA	422.7	0.5	8	C_2H_4/NO_2
Mg	EAA	285.2	0.5	4	C_2H_4/NO_2
Fe	EAA	248.3	0.2	5	Air/C_2H_4
Cu	EAA	324.7	0.5	4	Air/C_2H_4
Zn	EAA	213.9[a]	1.0	5	Air/C_2H_4
Mn	EAA	279.5[a]	0.2	5	Air/C_2H_4
Sr	EAA	460.7	0.2	10	C_2H_4/NO_2
Li	EEA	670.8	0.2	No	Air/C_2H_4
Rb	EEA	780.0	0.2	No	Air/C_2H_4

[a] Deuterium background correction.

Germany). Ultrapure water from a Milli-Q system (Millipore, Bedford, MA) with a conductivity of 18 MΩ was used throughout.

Apparatus. A CEM microwave oven, model MDS-81D, equipped with twelve Teflon vials, was used for wine sample digestion. A Varian Spectra AA-10Plus spectrophotometer equipped with a deuterium lamp background-correction system was used for metal determination involving atomic absorption spectrometry and atomic emission spectrometry.

Analytical Procedures. Metals Na, K, Fe, Cu, Zn, and Mn were determined from atomic absorption spectrometry using an air/acetylene flame, and Ca, Mg, and Sr were characterized by using an acetylene/nitrous oxide flame. Metals Li and Rb were measured from atomic emission spectrometry. The instrumental conditions for the determination are shown in **Table 1**. Major elements (Na, K, Ca, and Mg) were analyzed by dilution of the wine samples. For minor and trace elements (Fe, Cu, Zn, Mn, Sr, Li, and Rb), due to the matrix effect, the samples were previously treated with nitric acid in a microwave oven. A red wine (BCR E) from the Standards Measurement and Testing Program (Community Bureau of Reference, Brussels, EU), was routinely analyzed to perform quality control of the measurements. All results were the average of triplicate measurements.

Statistical Analysis. Mean values obtained for the variables studied in the different groups were compared by one-way ANOVA assuming that there were significant differences among them when the statistical comparison gave $p < 0.05$. The multivariate techniques applied can be divided into two groups: unsupervised and supervised.

1. Unsupervised Techniques. Principal components analysis (PCA) was used to summarize the information in a reduced number of components. This procedure permitted us to achieve a reduction of dimensionality and a data exploration investigating how many components (a linear combination of original features) were necessary to explain the greater part of variance with a minimum loss of information.

Kohonen self-organizing maps (SOMs) are the special type of neural networks which provide projection of multidimensional data into one- or two- (or in special cases three-) dimensional space. The method was designed specially for clustering, visualization, and abstraction (*8*). The Kohonen network can learn to recognize clusters of data and relate similar classes to one another. SOM has only two layers: the input layer and the output layer. The input layer is one-dimensional, whereas the output layer consists of radial units typically organized in two dimensions. The training process starts with a random set of radial centers in the output layer, and during training they are adjusted to cluster the training data. The algorithm is based on adjusting the winning neuron (neuron with the output nearest to the input) to be more like the input case. The topological ordering property is achieved by adjusting weights of neighborhood neurons to bring their output closer to the winning neuron's output and decreases with the topological distance. Usually the distance at which the changes take place decreases during the training process. Similarly, the learning rate is higher at the start and decreases during adaptation. When the network is trained, it can be used for visualization and for classification. The most similar samples are in the same cell or in neighborhood cells. The weights show the reason for clustering and similarity of objects.

2. Supervised Techniques. Linear discriminant analysis (LDA) is a supervised method used for classification purposes. LDA renders a number of orthogonal linear discriminant functions equal to the number of categories minus one. This method maximizes the variance between categories and minimizes the variance within categories (*9*). A basic problem in LDA is deciding which variables should be included in the analysis. This may be achieved with a stepwise LDA using Wilks' lambda (λ) as selection criterion (*10*). Results were validated using leave-one-out cross validation. In this test, a sample is removed from the dataset. The classification model is rebuilt and the removed sample is classified in this new model. All the samples of the data set are sequentially removed and reclassified, and then a percentage of good classification is given (*11*).

Back-Propagation Feed-Forward Artificial Neural Network (BP-ANN) (*12*). In the case of feed-forward ANN neurons are sorted in three or more layers: input, hidden(s), and output layers. Neurons are connected with all of the previous layer by weighted connections. In each neuron the sum of the weighted signals is calculated and when it overcomes a certain value, or threshold, it is processed by a so-called transfer function and sent to all neurons in the next layer. The work with ANN consists of two steps: adaptation (or learning, training) and prediction. During adaptation, the weight coefficients and threshold values are adjusted to fit the training data. Many algorithms have been developed, for example the quasi-Newton method, back-propagation, or delta−delta, and each of them has certain limitations. For our case, the back-propagation (BP) algorithm was the most suitable. BP is based on minimization of root-mean-square value (RMS, sum of squares of differences between target and calculated output values). Based on RMS changes the BP algorithm adjusts the weight coefficients and thresholds.

Software. Multivariate analyses were performed by means of the statistical software package STATGRAPHICS Plus for Windows 4.0 from Statistical Graphics Corporation and PARVUS 1.3. The software package Trajan 4.0E (Trajan Software Ltd., Durham, U.K.) was used for emultion of BP-ANNs and SOMs. All data were autoscaled before use.

RESULTS AND DISCUSSION

This section has been divided into two parts: the first is the characterization and correlation study; and the second is multivariate analysis using unsupervised and supervised techniques.

Characterization and Correlation Study. Table 2 shows the results for the metals analyzed in the red wines according to the island of production. The results of one-way ANOVA for comparison are also included in **Table 2**. K and Li were the metals with the highest and lowest contents, respectively, in the samples corresponding to all the islands considered. Some significant differences among the mean values obtained in the different islands were observed, which could be attributed to the metal content in the soil for cultivation, water used for irrigation, and the process for the production of wines. The wines produced in Lanzarote presented higher ($p < 0.05$) mean values of Na, Fe, and Li than the corresponding mean values found in the rest of the islands. However, they showed the lowest mean value of Rb ($p < 0.05$) and Zn. Potassium, Ca, and Cu presented few significant differences among the mean values according to the island of production. This could be due to the contents of these metals being influenced by other factors such as the use of fertilizers or wine treatments such as stabilization, clarification, or filtration (*13*). The wines from La Palma had the lowest ($p < 0.05$) mean values of Na, Li, Mg, and Mn and the highest ($p < 0.05$) mean value of Rb. The mean content in Zn was the highest ($p < 0.05$) in the wines from Gran Canaria, and the wines produced in Tenerife presented the lowest ($p < 0.05$) levels of Sr. In general, the levels observed in each of the metals analyzed fell into the normal intervals described in the

Table 2. Results (Mean, Standard Deviation, Minimum and Maximum Values, mg/L) of the Analyzed Metals According to the Island of Production

metal	Tenerife = 1 mean ± SD (min–max)	La Palma = 7 mean ± SD (min–max)	Lanzarote = 8 mean ± SD (min–max)	Gran Canaria = 9 mean ± SD (min–max)	significant differences ($p < 0.05$)
K	1099 ± 184	1158 ± 137	1243 ± 308	1236 ± 241	1–9
	828 – 1775	969 – 1453	816 – 1684	706 – 1741	
Na	70 ± 38	34 ± 20	168 ± 14	89 ± 71	1–7, 1–8, 7–8, 7–9, 8–9
	35 – 215	10 – 67	153 – 200	34 – 310	
Ca	76.0 ± 11.9	74.9 ± 7.4	69.2 ± 5.7	75.3 ± 13.7	no
	40.0 – 97.0	61.0 – 89.0	59.0 – 79.0	53.0 – 103.0	
Mg	85.3 ± 9.2	70.7 ± 3.6	89.6 ± 6.4	94.7 ± 10.9	1–7, 1–9, 7–8, 7–9
	70.0 – 121.0	64.0 – 77.0	82.0 – 99.0	72.0 – 115.0	
Fe	2.66 ± 0.92	2.75 ± 1.61	5.16 ± 1.07	3.65 ± 1.29	1–8, 1–9, 7–8, 7–9, 8–9
	1.2 – 4.6	1.5 – 7	3.4 – 6.7	2.1 – 7.2	
Cu	0.06 ± 0.09	0.14 ± 0.16	0.13 ± 0.13	0.12 ± 0.12	1–7
	0 – 0.4	0 – 0.4	0 – 0.4	0 – 0.5	
Zn	0.48 ± 0.33	0.32 ± 0.31	0.27 ± 0.16	0.75 ± 0.39	1–9, 7–9, 8–9
	0 – 1.5	0 – 1.1	0.1 – 0.6	0.2 – 1.7	
Mn	1.20 ± 0.46	0.40 ± 0.17	0.87 ± 0.10	0.79 ± 0.13	1–7, 1–8, 1–9, 7–8, 7–9
	0.3 – 2.4	0.2 – 0.8	0.7 – 1	0.6 – 1	
Sr	0.73 ± 0.21	1.27 ± 0.25	1.09 ± 0.26	1.33 ± 0.29	1–7, 1–8, 1–9, 8–9
	0.4 – 1.3	0.9 – 1.7	0.8 – 1.5	0.7 – 1.7	
Li[a]	7.5 ± 2.8	5.1 ± 1.6	27.8 ± 4.0	9.0 ± 4.5	1–7, 1–8, 7–8, 7–9, 8–9
	2.3 – 14.8	2.9 – 8.8	20.6 – 33.1	4.6 – 18.5	
Rb	2.54 ± 0.75	3.37 ± 0.89	0.22 ± 0.08	2.35 ± 1.37	1–7, 1–8, 7–8, 7–9, 8–9
	1.2 – 4.3	2.3 – 4.4	0.1 – 0.3	0.9 – 5.3	

[a] In μg/L.

literature, with the exception of Na (*14*), whose contents were very high, which could be due to the influence of the marine spray. The concentrations of Cu and Zn in the wines analyzed were much lower than the maximum threshold established by the International Office of Vine and Wine (OIV) of 1 and 5 mg/L for these metals, respectively (*15*). Neither the concentrations of Cu nor Fe represent any risk for cupric or ferric cases (*16*).

When the correlation matrix was obtained by plotting all the variables the correlations observed were rather weak. One can emphasize the correlations ($r > 0.6$) between the alkaline metals: Na−Li ($r = 0.693$); Na−Rb ($r = -0.619$); and Li−Rb ($r = -0.651$). Although Na can be associated with marine spray, the Rb and Li could be related to the soil composition. It is interesting to note that the significant correlations with Rb were always negative.

Multivariate Analysis. *Unsupervised Techniques.* Although some interesting information corresponding to the island of production is obtained by applying the univariate analysis on the metal contents of Canary wines, differentiation of the wines is quite difficult with a single direct observation. Thus, multivariate PCA was applied to all the samples of wines studied to obtain a more simplified view of the relationship among the metals considered. The first five PCs were chosen (76.4% of the total variance) because their eigenvalues were higher than 1 (**Table 3**). The first PC that explains the highest percentage of variance (28.5%) is mainly associated with Na and Li, and to a lesser degree with Fe and negatively with Rb. This agrees with the correlation study because all these parameters showed correlations with a relatively high degree of significance. The second PC, which explains 16.6% of the total variance, is negatively and positively related to Mn and Sr, respectively. These metals are usually associated with soil composition (*17*). The third PC selected, with 12.7% of the total variance explained, is related to Zn and Mg. The fourth and fifth PCs are closely associated with Ca and Cu, respectively. Most of the metals selected are mainly related to soil composition and marine spray, and some of them (such as Fe) may also be influenced by the technological processes. The scores plot for

Table 3. Weights of the Metals in the Principal Components, Eigenvalues, and Explained Variance

metal	PC1	PC2	PC3	PC4	PC5
K	0.4680	0.4130	0.1695	0.3300	0.1680
Na	0.8273	−0.2461	0.0054	0.1225	−0.1257
Ca	0.1395	0.3889	0.0322	0.6646	−0.5032
Mg	0.4735	0.1309	0.6711	−0.0142	−0.0575
Fe	0.7342	−0.0548	0.0119	−0.1985	0.3030
Cu	0.2267	0.4151	−0.3318	0.3281	0.6581
Zn	0.1350	0.3864	0.7305	−0.2601	0.0930
Mn	−0.2570	−0.6678	0.3604	0.2355	0.2661
Sr	0.3079	0.5737	−0.3017	−0.4771	−0.1920
Li	0.8553	−0.2232	−0.2122	0.0017	−0.0059
Rb	−0.7005	0.5271	0.1016	0.0420	0.1840
Eigenvalue	3.14	1.83	1.40	1.06	1.00
% variance	28.5	16.6	12.7	9.7	8.9
% cumulative variance	28.5	45.1	57.8	67.5	76.4

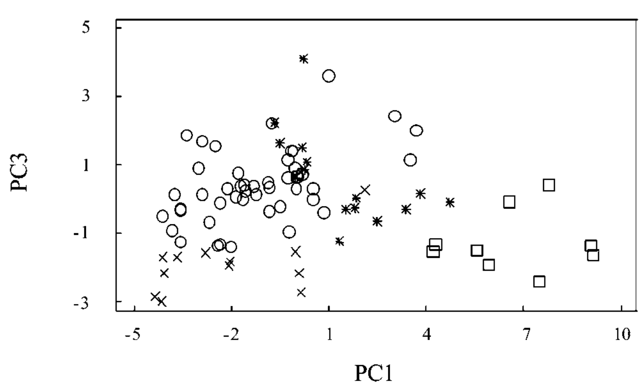

Figure 1. Scores of the wine samples on the axes representing the first and third principal components. Codification: □ = Lanzarote; × = La Palma, * = Gran Canaria, ○ = Tenerife.

all the samples of the representation of the first and third PCs are presented in **Figure 1**. It can be seen that the wines from Lanzarote, with the highest values on the PC1, are satisfactorily separated from the remainder of the wines. The wines from

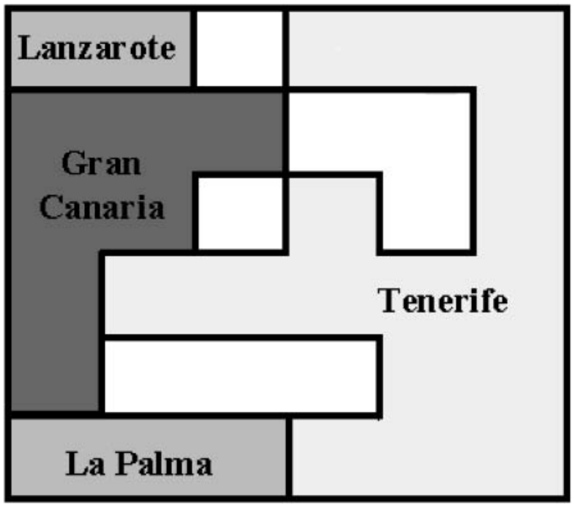

Figure 2. Distribution of wine samples in 6 × 6 Kohonen SOM.

La Palma are situated in the bottom left of the graph with values in the PC3 lower than the values observed in the wines produced in Gran Canaria and Tenerife. In this figure it can be seen that the wines from Tenerife and from Gran Canaria tend to separate.

Kohonen SOMs were tested with 11 neurons in the input layer (all 11 metal contents) and several architectures of the network were investigated. The one providing the best results was a 6 × 6 network. Learning rate was decreased from 0.5 to 0.01, and the neighborhoods affected by the winning neuron were decreased from 2 to 1. Total number of training cycles was 2000. The network with dimension 6 × 6 separated the wines perfectly on the basis of the island of production (**Figure 2**). Therefore, compared with the results obtained using PCA, the application of artificial neurons Kohonen self-organizing maps on the matrix of metal data improved the differentiation of Canary wines according to the island of production. These better results are due to the use of nonlinear algorithms in artificial neural networks against the linear combination of the variables in principal component analysis.

Supervised Techniques. Linear discriminant analysis (LDA) was applied to classify wines according to island of origin using the two following processes: (1) Stepwise LDA which selects the quantitative variables that enhance discrimination of the groups established by the dependent variable using Wilks' lambda as the criterion; and (2) introduction of all independent variables in order to maintain all the original information. In both cases validation of these results was performed using leave-one-out cross validation.

When the stepwise LDA was applied, eight variables (Li, Sr, Mg, Mn, Ca, K, Fe, and Zn) were selected and three statistically significant discriminant functions were obtained. This selection of variables is in accordance with the correlation study, as three of the four metals eliminated presented significant correlations with other metals such as Rb and Na with Li and Sr with Mn. In this way, 94.0% of recognition ability and 90.4% of prediction ability were obtained (**Table 4**). When all the variables (eleven) were introduced in the LDA, similar results were obtained: 95.2% of recognition ability and 89.1% of prediction ability. The results showed a prediction ability of 100% for Lanzarote, while several wines from other islands were interchanged. Therefore, La Palma and Lanzarote were the most specific islands because they did not include wines from any other island. In **Figure 3**, a scatter diagram of two first-discriminant functions derived from all the variables is represented. It is shown that the wines produced in Lanzarote and La Palma were differentiated from those produced in Tenerife or in Gran Canaria. Likewise, a tendency to separate the wines from Tenerife and Gran Canaria can be noticed.

Table 4. Recognition and Prediction Abilities Using Stepwise LDA and BP-ANN Techniques

	LDA (Li, Sr, Mg, Mn, Ca, K, Fe, Zn)		BP-ANN (Li, Sr, Mg, Mn)	
island	recognition ability (%)	prediction ability (%)	recognition ability (%)	prediction ability (%)
Tenerife	95.7	91.5	95.7	93.6
La Palma	100	91.7	100	100
Lanzarote	100	100	100	100
Gran Canaria	80.0	80.0	86.7	86.7
total	94.0	90.4	95.2%	94.0

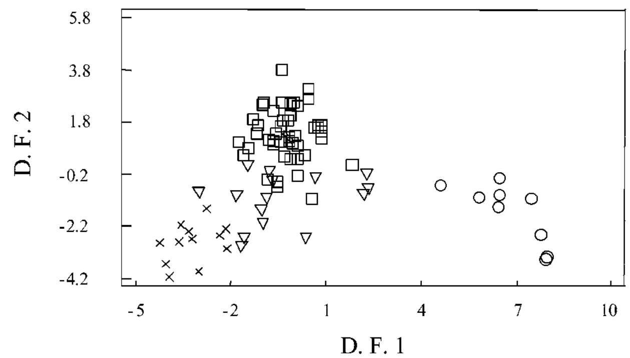

Figure 3. Scattered plot of the samples projected in the plane defined by the two first discriminant functions. Codification: ○ = Lanzarote; × = La Palma, ▽ = Gran Canaria, □ = Tenerife.

Artificial neural networks trained by back propagation were also applied. This method uses a nonlinear algorithm for classifying samples in the different categories. Samples were divided into two sets: the training set (80% of samples) and the test set (20% of samples). We tested several combinations of inputs taking into account the features selected according to the Wilks' lambda criterion. The architecture selected was chosen according to the lowest root-mean-squares (RMS) and best performance. The best results were obtained with a net of architecture 4 × 5 × 4 being the input layer formed by Li, Sr, Mg, and Mn, and the output layer by categories as neurons. These metals are often used in the literature to differentiate wines according to their geographical origin (*18*−*20*). The results obtained are shown in **Table 4**. For Lanzarote and La Palma, recognition and prediction abilities of 100% were obtained. So, good recognition and prediction abilities were obtained using both supervised techniques, LDA and BP-ANN.

CONCLUSIONS

Using artificial neural networks (Kohonen SOMs) on a data matrix formed by eleven metals (K, Na, Li, Rb, Ca, Mg, Sr, Fe, Cu, Zn, and Mn) on 83 samples of Canary red wines improves their grouping according to the island of production in relation to results from principal component analysis (PCA).

In contrast, in the case of a supervised technique, similar results were obtained using LDA (Li, Sr, Mg, Mn, Ca, K, Fe, and Zn) and BP-ANN (Li, Sr, Mg, and Mn) to classify wines according to their geographical origin.

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