

Characterization of “Ribera del Guadiana” and “Mérida” Spanish red wines by chemometric techniques based on their mineral contents

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Summary

The elemental composition of red wines from two important wine-producing Spanish regions (“Ribera del Guadiana” and “Mérida”) was used in a multivariate statistical analysis to discriminate the wines according to their geographical origin. A total of 19 elements were analysed by inductively coupled plasma atomic emission spectrometry. By using the element concentrations as chemical descriptors, both classes of certified red wines were perfectly discriminated, when applying pattern recognition techniques such as principal component analysis and linear discriminant analysis. Specifically, linear discriminant analysis using As, Cd, Cu, Li, Pb and Sr led to 97% and 88% recognition ability, respectively, for “Ribera del Guadiana” and “Mérida” red wines.

Keywords

red wine; mineral content; multivariate analysis; Spain

Wine is a widely consumed beverage across the world and presents an obvious commercial worth [1]. Constituting a complex product, wine contains not only water, saccharides and alcohol, but also a great variety of inorganic and organic substances. In fact, wine composition depends on many and diverse factors such as grape variety, edafoclimatic conditions and enological practices [2]. These factors are especially important for quality wines from specific regions, such as “denomination of origin” (DO) Spanish wines. These wines are produced using particular varieties of grape and they are cultivated in specific geographical regions under controlled growing and production conditions. They are also subjected to Regulatory Councils, which try to prevent frauds by guaranteeing the origin and quality of wines [1, 3]. Determination of wine authenticity based on non-subjective techniques is a way to avoid damage to the image of the product and economic injury to the producers [4]: labelled wines with the same DO should have a similar and typical composition that provides

them with particular characteristics that identify them from other DO [3].

The classification of product brands and quality of origin is an area for the application of chemometric classification procedures [5–8]. Some of the most used multivariate analysis techniques for this purpose are principal components analysis, discriminant analysis, cluster analysis, soft independent modelling class analogy (SIMCA) and *K*-nearest neighbours analysis (KNN) [9]. The application of such techniques for the classification of wines and other alcoholic beverages has widely increased in recent years. The studies started in 1979, when KWAN et al. determined the concentration of 17 different elements in Pinot noir wines from France and USA [10], allowing the analysed wines to be classified on the basis of their Ba and Ca content. Till that moment, mineral content of wines had been extensively studied due to its organoleptic, hygienic and dietetic characteristics, as well as toxicological implications [11]. Nevertheless, from a new perspective, elemental analysis

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allowed the characterization and the geographical differentiation of wines when reliable chemical analyses techniques in combination with modern chemometrical methods were used [12].

When considering that mineral content of wines depends on several factors including type of grape, area of production, soil characteristics and environmental conditions, its determination can be of great interest because it allows the definition of a “fingerprint” for each of them [13], establishing a link between the wine samples and their geographical origin [14]. In this sense, modelling techniques allow not only to establish the characterization of wines, but also to establish the contribution of each variable to the model and its capacity to discriminate between categories [15]. Different statistical methods must be applied to visualize data trends, to establish criteria for quality and to retrieve information on variables that influence similarities and differences with respect to the wines being tested [1, 12, 16, 17].

With the rapidly increasing progress of multielement techniques in element analysis, these were increasingly applied also to the problem of fingerprinting of wines. In particular, inductively coupled plasma (ICP) excelled by true multielement capabilities together with extremely low detection limits [18]. When using the obtained results, the use of multivariate statistical techniques facilitates the differentiation of wines, clarifying the interpretation of the chemical data and highlighting those variables that best explain the differences between the types of wine [19]. As previously indicated, the capability of such multivariate analysis techniques for wine classification has been widely used in recent years. Several authors published works applying different multivariate techniques using the mineral content in the differentiation and classification of wines according to their geographical origin [20]. This differentiation can be carried out by using major, trace and ultratrace elements [21], with major being most widely used. LARRECHI et al. [22] used these elements to differentiate wines from four wine-growing areas in Catalonia (Spain). DANZER et al. [23] differentiated wines from 6 different regions of Germany according to their contents of 16 elements and, similarly, MARISA et al. [24] classified Portuguese wines. CASTIÑEIRA et al. [25] studied German wines from 4 areas, analysing contents of 13 metals and rendering Li, Zn, Mg and Sr as the most important for the wine classification. In Spain, GONZÁLEZ-LARRAINA et al. [26] found that Mn, Li, K and Fe were the most important elements for such classification in the area of Rioja. HERRERO-LATORRE and MEDINA [27] used con-

tents of metals to differentiate wines from Galicia and those from other Spanish regions, and even within the same region. The chemometric analysis of 48 trace elements in English and Spanish wines facilitated the differentiation of their origins and also unequivocal identification of the Spanish wines from different regions [28]. ORTEGA-HERAS et al. [29] used K, Na, Ca, Mg, Fe, Cu and Zn to discriminate among Spanish red wines from “Ribera del Duero”, “Rioja”, “Valdepeñas” and “La Mancha”. FRÍAS et al. [30] differentiated sweet wines of the Canary Islands by Na and Mg contents. In general, Mn, K, Li, Mg, Ca, Na, Fe and Sr are some of the most cited elements for their capacity to discriminate wines according to their geographical origin. These elements are also the most abundant in wines, and thus among the most analysed [31].

In the present paper, the contents of 19 elements (Al, As, B, Ba, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Zn and V) were determined in samples of red wines of two DO by using inductively coupled plasma emission spectrometry (ICP-AES). These elements (ultratrace, trace and major components) were selected according to their relevance for wine characterization in previous studies. A chemometric analysis of the obtained data was undertaken for classification and discrimination between red wine samples from the DO “Ribera del Guadiana” (Extremadura) and “Méntrida” (Toledo) in Spain. The relationship between the concentrations of the different considered elements could be an adequate tool in differentiating these red wines from those produced in different geographical areas, and in establishing criteria of genuineness to assure the origin of the wines produced in these Spanish regions.

MATERIALS AND METHODS

Sample collection and treatment

Red wine samples were obtained from both DO, “Ribera del Guadiana” ($n = 37$) and “Méntrida” ($n = 25$), in triplicate for each wine. Each sample was identified with a code referring to its origin class together with the sample number. All the wines were of unsuspecting origin and were made with the traditional varieties of these Spanish producing regions during the period of 1994–2007. Samples were collected in 750 ml glass bottles and stored at 2–4 °C until analysis.

Once opened, three different samples of every bottle of wine were digested according to the following procedure: 50 ml of wine were transferred to a borosilicate glass tube and 5 ml of acid mix-

ture (nitric:perchloric:sulphuric, 8:8:1) were added to the tubes in order to facilitate mineralization of the samples. This was performed using a digestion apparatus (Selecta, Barcelona, Spain), thus guarantying optimum boiling characteristics without a boiling delay [32]. The temperature was programmed to increase from the room temperature to 370 °C during 5.5 h. Following mineralization, 500 µl of HCl and 5 ml of milliQ water (Millipore, Madrid, Spain) were added to the tubes and the mixture was submitted to ultrasound for 30 s, in order to re-dissolve the mineralized matrix. The resultant solution was filtered, transferred to a polystyrene container and brought to a final volume of 50 ml with milliQ water. Blank samples were prepared in an identical way, but omitting the sample. The average of blank signals was subtracted from analytical signals of the digested samples before interpolation in calibration graphs. The general wet ashing technique was used because by mineralization of samples, loss of volatiles is prevented [12]. With every group of samples, a red wine of known mineral composition (previously analysed) was also analysed for checking any instrument drift. Daily variations between 4% and 28% were observed, most of them being lower than 10%.

Analytical procedure

Elemental analysis were carried out on a Perkin-Elmer Optima 3 radial vision inductively coupled plasma atomic emission spectrometer (PerkinElmer, Madrid, Spain). Tab. 1 shows the analytical lines for each element, as well as the instrumental conditions. The settings were optimized daily.

The element quantification was carried out using the external standard method. The quantification limits were established at 1 µg·l⁻¹ (As, Cd, Co, Cu, Ni, Pb, V) or 5 µg·l⁻¹ (Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, Sr, Zn). In order to validate the method for determining the concentration of elements in wines, a synthetic slightly alcoholic sample (2% ethanol) was prepared with appropriate dilutions to cover the concentration range of each element in the wines. Standards were obtained from Scharlau (Barcelona, Spain). Since wines contain usually 10–12% alcohol, a synthetic sample containing 2% alcohol resembled real samples with sufficient fidelity [33].

Data analysis

Using element contents found in red wine samples as chemical descriptors, statistical methods were applied to establish differences between both DO red wine samples for classification and

authentication purposes [14]. In this sense, there are different display methods for visualizing data trends, but when considering that the present research starts from the a priori knowledge of class membership of the samples to be processed, typical supervised learning pattern recognition methods had to be applied.

Each wine sample (object) was considered as an assembly of 19 chemical descriptors represented by the chemical data. These variables, called “features”, formed a “data vector” which represented a wine sample. The effect of differing measurement magnitudes and units was compensated by normalizing measurements. Subtracting the variable average and dividing by the variable standard deviation the result is a variable with zero mean and a unit standard deviation [34].

Pattern recognition methods were applied to the data matrix, composed of 19 columns (the analysed elements) and 62 rows (37 from “Ribera del Guadiana”, 25 from “Mérida”). Principal component analysis (PCA) [35] was employed

Tab. 1. Analytical lines for the elements and the instrumental conditions in ICP-AES.

Operating power	1 500 W
Nebulizer type	Meinhard
Carrier air flow	1.0 l·min ⁻¹
Coolant air flow	15.0 l·min ⁻¹
Detection wavelength [nm]	
Al	396.153
As	188.979
B	208.957
Ba	455.403
Ca	317.933
Cd	228.802
Co	231.160
Cu	324.752
Fe	259.939
K	766.490
Li	670.784
Mg	285.213
Mn	257.610
Na	589.592
Ni	231.604
Pb	220.353
Sr	407.771
V	292.402
Zn	206.200

as a visualisation technique, in order to achieve a reduction of dimensionality, i.e. to fit a j -dimensional subspace to the original p -variate ($p > j$) space of objects and permit a primary evaluation of the between-category similarity but retaining the maximum amount of variability [36, 37] with a minimal loss of information [4, 17, 30]. This analysis was carried out by means of the multi-variant statistical software package Unscrambler 9.2 (CAMO Software, Oslo, Norway).

Similarly, the package PASW Statistics 18 (Predictive Analytics Software, previously named SPSS, from IBM, Madrid, Spain) was used for the linear discriminant analysis (LDA), with the aim to obtain classification rules [38]. LDA maximizes the variance between categories and minimizes the variance within categories [39], so it is valuable in exploring data structure [17, 30]. This method renders a number of orthogonal linear discriminant functions, equal to number of categories minus 1. A basic problem in LDA is to decide which variables should be included in the analysis. This may be achieved with a stepwise LDA using Wilks' Lambda as selection criterion and an F -statistic to determine the significance of the changes in lamb-

da when a new variable is tested [30]. The prediction ability was made by a full cross-validation method (leave-one-out option of PASW software).

RESULTS AND DISCUSSION

The corresponding descriptive basic statistics of the concentrations of the 19 selected elements for the "Ribera del Guadiana" and "Mérida" red wines are presented in Tab. 2. The determined levels were similar to those found by other authors in DO red wine from other regions of Spain, for instance Galicia [40, 41] or the Canary Islands [14, 30]. Moreover, they are also quite similar to red wine samples from other countries, as for example Italy [42], Portugal [43], Greece [44] or Argentina [45]. As can be seen, by considering the median value for instance, the metal contents of "Ribera del Guadiana" wines were higher than those of "Mérida", with the exception of Sr. Moreover, it must be emphasized that K and Mg were the elements found in highest concentrations in all analysed samples (average concentrations of $918.6 \text{ mg}\cdot\text{l}^{-1}$ and $83.81 \text{ mg}\cdot\text{l}^{-1}$, respectively),

Tab. 2. Results on mineral concentrations determined for "Ribera del Guadiana" and "Mérida" red wines.

Element	"Ribera del Guadiana"					"Mérida"				
	Mean	SD	Min	Max	% $n < \text{DL}$	Mean	SD	Min	Max	% $n < \text{DL}$
Al	0.423	0.2052	0.075	1.13	0	0.611	1.6370	0.202	0.3654	0
As	0.060	0.0304	N.D.	0.132	2.7	0.047	0.0273	N.D.	0.113	8
B	1.499	16.825	0.226	7.914	0	0.800	0.6695	0.192	2.363	0
Ba	0.263	0.0929	0.065	0.489	0	0.217	0.0580	0.131	0.353	0
Ca	54.96	13.195	23.86	99.24	0	55.84	7.2605	44.86	71.44	0
Cd	0.002	0.001	N.D.	0.005	0.9	0.017	0.0062	N.D.	0.028	6.7
Co	0.010	0.0033	N.D.	0.017	4.5	0.010	0.0025	N.D.	0.014	4
Cu	0.113	0.1446	N.D.	0.865	0.9	0.058	0.0299	0.024	0.132	0
Fe	3.122	11.746	0.97	5.762	0	3.098	1.0310	1.083	4.803	0
K	918.6	226.47	430.5	1373	0	977.7	184.40	642.7	1329	0
Li	0.048	0.0213	0.03	0.135	0	0.069	0.0267	0.041	0.134	0
Mg	83.81	12.057	55.12	105.9	0	90.3	13.045	65.77	123.5	0
Mn	0.979	0.2801	0.382	1.776	0	1.465	0.4706	0.519	2.449	0
Na	12.50	50.264	5.976	31.17	0	18.57	9.0643	8.024	50.95	0
Ni	0.038	0.0375	0.019	0.254	0	0.029	0.0111	0.013	0.054	0
Pb	0.047	0.0139	0.026	0.084	0	0.043	0.0183	N.D.	0.079	6.7
Sr	0.379	0.1044	N.D.	0.596	7.2	0.981	0.3434	0.580	2.090	0
V	0.044	0.0158	0.031	0.100	0	0.051	0.0304	N.D.	0.152	1.3
Zn	0.309	0.1529	0.052	0.748	0	0.547	0.2084	0.238	1.016	0

Values are expressed in $\text{mg}\cdot\text{l}^{-1}$. SD – standard deviation, % $n < \text{DL}$ – % of samples under detection limit (DL).

while lowest concentrations were obtained for Cd, Co and Ni. It is interesting to indicate that Cd is a toxic element, with no physiological functions. Cadmium levels in wines may be of anthropogenic origin due to residues of agrochemical products, or directly related to environmental contamination in those places where industrial complexes exist close to vineyards [45]. Nevertheless, in general, Cd concentration in wines has been found to be quite low, with no toxicological importance. However, when the consumption of large quantities of wine causes the dietary intake of Cd to reach the maximum allowable levels, it may be physiologically significant [45].

Principal components are orthogonal, and each principal component is a linear combination of the original variables. As can be seen in Tab. 3, the first two and three eigenvectors represented 36.5% and 47.3%, respectively, of the total variability of the data. Thus, by reducing the number of features from 17 original variables (manifest variables) to two or three principal components (latent variables), the preserved information is enough to permit primary examination of the samples according to their origin in a 2D- or 3D-plot [4]. The variables with the higher scores (positive or negative) are those which contribute most to explanation of the meaning of each principal component [30]. From the coefficients (loadings) of features in the first and second principal components (see Fig. 1), Zn, Mg, Mn, Sr, Cd and Li were the dominant features in the first component, which represented 23.3% of the total variability. Pb, Cu and Ni contributed most to the second principal component, representing 13.2% of the total data variability. In this sense, Li, Mn and Sr were the features that mainly represented the effect related to the soil where the grapes were grown. Similarly, Mg levels in wines may be influenced not only by soil composition but also by pH, the time and

Tab. 3. Percentage of total variance explained by the principal components.

Principal component	Percent variance	Cumulative percentage of variance
1	23.32	23.32
2	13.18	36.5
3	10.81	47.3
4	7.98	55.28
5	7.5	62.78
6	6.29	69.07

the temperature of storage, the rate of pressing and the use of fining agents [4, 29, 30, 41, 42]. In particular, Mg and Mn concentrations are rather mobile elements in soils, and important micronutrients for plants and grape berries [46, 47] and they are both very frequently quantified and cited for wine authentication [48]. With respect to Zn, plants absorb this metal from the ground in small quantities [49]. The Zn content of wines increases by usage of Zn containers during processing and ageing stages, as well as of zinc-containing pesticides. It must be said that, among all the other considered elements, V was present at zero values for both PC's and accordingly it lacked any featuring efficiency.

When a 2D-plot of the red wine samples was drawn in the space defined by the first two eigenvectors (Fig. 2), an interesting separation of red wines into two groups was observed. These two groups were formed up mainly by the group of samples of "Ribera del Guadiana" wines in one case (to the left of the graph) and samples of "Mérida" wines in the other (to the right). The slight overlapping between the two categories observed can be explained on the basis of the natural composition of both wines [4]. This result could

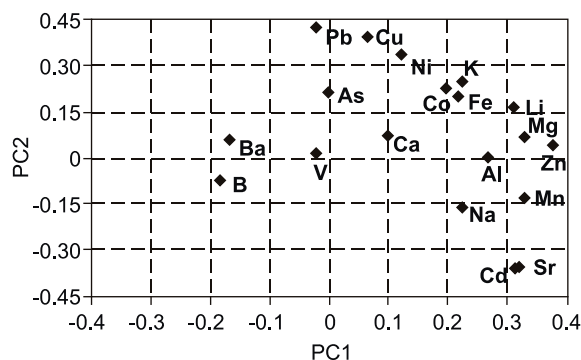


Fig. 1. Loading plot for the two first principal components.

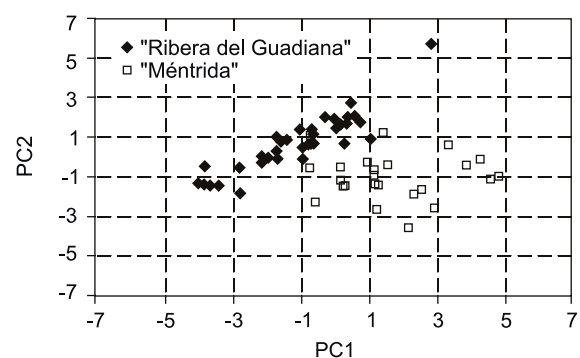


Fig. 2. Eigenvector projection of red wine samples according to the first two principal components.

be expected if it is taken into account that all the red wines studied had been produced with similar grape varieties and in very close areas. The latent structure of the first two principal components seems to describe adequately the origin and different characteristics of red wine samples from the two Spanish DO studied.

In the second step of data analysis, LDA was applied to the complete data set (62 objects, 19 variables divided between both DO) after autoscaling to eliminate the effect of different sizes of individual variables. The classification of cases was made according to a Bayesian estimation of the a posteriori probability of class membership derived from Mahalanobis distance [1]. LDA is a method for seeking subsets of variables most useful for discrimination among categories [30, 50]. The number of canonical variates is either the number of variables or the number of classes less one, whichever is smaller.

In the present case, for 19 descriptors and two classes, $2 - 1 = 1$ canonical variate or discriminant function was obtained. After applying standard LDA and according to the Wilks' Lambda values of each variable in the model (Tab. 4), the selected most discriminating variables were As, Cd, Cu,

Li, Pb and Sr, with $p < 0.05$. These results partially agree with the conclusions obtained by PCA, where Cd, Li and Sr were some of the dominant features in principal component 1, and Pb in principal component 2. Feature selection provided one result analogous to that published by LATORRE et al. [20] and REBOLO et al. [4], where wines from Galicia could be distinguished by Li as a key feature. Similarly, Li (together with Rb) was an effective feature for the classification of French wines of Médoc and Saint-Emilion origins [51].

As can be seen in Tab. 5, LDA achieved a value of 97.6% of correct classification for "Ribera del Guadiana" wines, and 88.3% for "Mérida" wines, with a significant squared Mahalanobis distance (38.095). All samples were correctly classified according to their origin, except for one red wine from "Mérida". A high level of correct assignment of red wines from "Ribera del Guadiana" was achieved. A slightly less successful result was obtained for the other considered DO. This fact indicates that the pattern recognition procedure was more sensitive for "Ribera del Guadiana" red wines, the probability of those wines being classified as "Mérida" was low. However, a minor level of hits in classification of "Mérida"

Tab. 4. Summary of the LDA.

Element	Wilk's Lambda	Partial Lambda	F-remove (1.42)	p-level	Toler.	1-Toler. (R-sqr)
Al	0.095541	0.099433	0.02381	0.878103	0.284808	0.715192
As	0.106763	0.894382	4.95980	0.031359	0.502492	0.497508
B	0.098937	0.965124	1.51773	0.224817	0.464463	0.535537
Ba	0.09838	0.970589	1.27271	0.265663	0.494861	0.505139
Ca	0.096333	0.991212	0.37235	0.545014	0.60503	0.394970
Cd	0.125672	0.759812	13.27683	0.000733	0.708023	0.291977
Co	0.100098	0.953936	2.02811	0.161800	0.436992	0.563008
Cu	0.108409	0.880802	5.68384	0.021717	0.507294	0.492706
Fe	0.09793	0.975054	1.07455	0.305852	0.383358	0.616642
K	0.095487	0.999996	0.00017	0.989805	0.638383	0.361617
Li	0.108595	0.879292	5.76572	0.020847	0.523406	0.476594
Mg	0.100059	0.954304	2.01114	0.163526	0.393341	0.606659
Mn	0.096561	0.988879	0.47234	0.495690	0.402228	0.597772
Na	0.096603	0.988444	0.49103	0.487334	0.353955	0.646045
Ni	0.095528	0.999573	0.01792	0.894136	0.773364	0.226636
Pb	0.106307	0.898223	4.7591	0.034793	0.563958	0.436043
Sr	0.140044	0.681835	19.59846	0.000067	0.515380	0.48462
V	0.100514	0.949983	2.21131	0.144471	0.756448	0.243552
Zn	0.098168	0.972691	1.17917	0.283719	0.367785	0.632215

Wilks' Lambda: 0.09549 approx. $F(19,42) = 20.940$.

Tab. 5. Classification of red wines by LDA.

Wine	Recognition ability [%]	Prediction ability [%]	Mahalanobis distance
"Ribera del Guadiana"	97.6	95.0	38 095
"Méntrida"	88.3	85.1	

da" red wines suggests that there exists a certain probability that one of them might be considered as genuine "Ribera del Guadiana". This result coincides with those obtained by PCA, where some samples from "Méntrida" origin were grouped into "Ribera del Guadiana" wines (Fig. 2)

CONCLUSIONS

In this work, the mineral composition of bottled red wines from two Spanish DO, "Ribera del Guadiana" and "Méntrida" was studied in order to differentiate between wine samples of different origin. Using multidimensional chemometric techniques applied to a chemical dataset, the mineral content provides a suitable method to differentiate two classes of Spanish red wines, both with DO designation. Feature selection procedures indicated that the most discriminating variables for this purpose were As, Cd, Cu, Li, Pb and Sr, whereas other quantified elements with no extra discriminating information only introduced noise in the pattern recognition process. Although the potential of pattern recognition techniques in the classification of the considered wines has been demonstrated, it should be noted that the results are based on a limited number of samples. A broader study with an extended training set, which will include further possible sources of variation, will be necessary to elaborate an optimized authenticity test.

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