

DISCRIMINATION OF WINES FROM THE MERCOSUL COUNTRIES ACCORDING TO THEIR MINERAL COMPOSITION

DISCRIMINATION DE VINS DES PAYS DU MERCOSUL D'APRÈS LEUR COMPOSITION MINÉRALE

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Abstract : The chemical and sensory characteristics of wines are related to the natural factors of their viticultural areas. The existing soil and climate diversity of the Mercosul countries is favorable to the elaboration of wines with different chemical composition. The mineral elements have already been studied to characterize wines from several viticultural regions all over the world. But the discrimination of wines from the Mercosul countries according to their mineral composition has not been done yet. The objective of this work was to characterize wines from Argentina, Brazil and Uruguay according to their mineral composition. Thirty-one wines were analyzed: 11 were from Argentina, 10 from Brazil and 10 from Uruguay; in relation to the type of wine, 10 were white, 11 rosé and 11 red ones. The analyses were made through the atomic absorption spectrophotometry; flame emission spectrophotometry; and colorimetry. The principal component analysis showed that the axes 1, 2 and 3 explained 38.6%, 28.2% and 10.4% of the total variation. The principal component analysis made it possible to discriminate the wines from these three countries apart. The mineral elements which showed the highest discriminant effect were Li, Mg, P, K, Rb, Na, Mn and Fe. The Argentinian wines showed higher contents of minerals, specially the Li, Na, Mg and P; the Brazilian ones had higher levels of Rb and Mn; the Uruguayan wines showed an intermediary composition.

Résumé : L'objectif du travail a été de caractériser les vins provenant de l'Argentine, du Brésil et de l'Uruguay d'après leur composition minérale. Les analyses ont été faites par la spectrophotométrie d'absorption atomique, la spectrophotométrie d'émission de flamme et la colorimétrie. L'analyse en composantes principales a permis la discrimination des vins de ces trois pays. Les éléments minéraux qui ont montré l'effet discriminant le plus élevé ont été : Li, Mg, P, K, Rb, Na, Mn et Fe. Les vins de l'Argentine ont montré les taux les plus élevés en minéraux, spécialement Li, Na, Mg et P; ceux du Brésil, les concentrations les plus élevées en Rb et Mn; les vins de l'Uruguay ont une composition minérale intermédiaire.

Key words : geographic origin, mineral composition, principal component analysis

Mots clés : origine géographique, composition minérale, analyse en composantes principales

INTRODUCTION

Among the Mercosul countries, Argentina is the one in which the viticultural segment has an important economic participation. The climate and soil of the grape growing areas of this country are characterized by the dryness, where the annual rainfall is lower than 180 mm (DIAZ, 1992). In Brazil, the most important viticultural region is located in the State of Rio Grande do Sul. This region has mountainous topography with differences in height which exceed 500 m; the annual average rainfall is 1704 mm (MIELE *et al.*, 1992); and

the soils are low deep, clay type and acid. In Uruguay, the viticultural areas have an annual average rainfall of 1600 mm; the soils are generally acid, not very deep and their texture varies from median to heavy (ZUNINO, 1992).

The diversity of the natural resources of these countries induces to wines with different chemical composition and sensory characteristics. These differences are also due to the agronomical aspects of grape production, to the cultivars grown and to the wine making techniques.

The mineral elements have already been studied to characterize wines from several regions in France (LACASTA, 1982 ; MEDINA and VAN ZELLER, 1984), three appellations of Rioja (GONZALES-LARRAINA *et al.*, 1987), Galician wines from other regions in Spain (HERRERO-LATORRE and MEDINA, 1990), and also to recognize the differences of wines from the Veneto region in Italy (SCARPONI *et al.*, 1982).

In Brazil, considering mineral elements and volatile compounds, white wines were discriminated from four productive regions of the Serra Gaúcha, State of Rio Grande do Sul (RIZZON *et al.*, 1987). MIELE *et al.* (1996) used the mineral elements and other chemical compounds to differentiate Cabernet Sauvignon wines of three viticultural regions. But the distinction of wines from the Mercosul countries using their mineral composition has not been done yet.

The wine trading among the Mercosul countries, and even with those belonging to other economic blocs, have a tendency to become more intense. In this way, the wine characterization according to its geographic regions is demanded. Regarding this situation, this work has been done with the objective of discriminating wines from Argentina, Brazil and Uruguay according to their mineral composition

MATERIAL AND METHODS

Thirty-one wines were analyzed : eleven were from Argentina, ten from Brazil and ten from Uruguay ; ten were white wines, eleven, rosé and ten, red ones.

The analysis of K, Na, Li and Rb was performed through flame emission spectrophotometry ; Ca, Mg, Mn, Fe, Cu and Zn with atomic absorption spectrophotometry (PERKIN-ELMER, 1976). For the Ca determination, the samples were prepared by adding a lanthanum oxide solution in order to avoid the specific interferences of other elements. For the analysis of Li and Rb the standard curves were prepared with a solution of 1.0 g/l of K to avoid the interference of this cation. The P was determined by the colorimetric method employing the ammonium molybdate.

Data were submitted to the multivariate analysis, principal component analysis (APC), according to FOUCAIT (1982) and ROSIER (1992).

RESULTS AND DISCUSSION

The minimum, maximum and mean values of the mineral elements in the wines from Argentina, Brazil and Uruguay are indicated in table I.

The results showed that the composition of the Brazilian wines was similar to those obtained by RIZZON and SALVADOR (1987). Argentinian wines

TABLE I

The minimum, maximum and mean values of the mineral elements in the wines from Argentina, Brazil and Uruguay

Tableau I — Valeurs minimales, maximales et moyennes des éléments des vins de l'Argentine, du Brésil et de l'Uruguay

Mineral element (mg/l)	Argentina			Brazil			Uruguay		
	Minimum	Maximum	Mean ± standard deviation	Minimum	Maximum	Mean ± standard deviation	Minimum	Maximum	Mean ± standard deviation
K	952.0	1704	1319 ± 259	481	1299	819 ± 299	585	1917	1140 ± 406
Na	80.0	198.0	134.8 ± 10.0	8.0	53.0	22.7 ± 15.7	31.0	168.0	89.3 ± 51.1
Ca	65.0	97.0	78.8 ± 11.5	58.0	111.0	84.0 ± 15.5	53.0	108.0	81.8 ± 17.3
Mg	75.0	122.0	95.4 ± 16.0	48.0	92.0	67.9 ± 13.8	46.0	104.0	76.3 ± 17.8
Mn	1.0	1.8	1.3 ± 0.3	1.5	3.4	2.2 ± 0.6	0.6	2.5	1.7 ± 0.6
Cu	0.1	1.1	0.5 ± 0.4	0.1	3.0	0.6 ± 0.9	0.2	3.0	1.1 ± 1.0
Fe	3.6	8.1	5.0 ± 1.5	1.3	6.6	2.9 ± 1.7	2.3	10.1	5.2 ± 2.2
Zn	0.4	1.1	0.6 ± 0.3	0.3	0.6	0.5 ± 0.1	0.3	2.0	1.2 ± 0.6
Li*	139.1	250.8	193.6 ± 0.4	0.5	9.1	5.0 ± 3.2	4.1	31.4	23.0 ± 7.7
Rb	0.3	0.7	0.5 ± 0.2	3.2	7.6	4.8 ± 1.5	0.9	5.2	2.8 ± 1.3
P	73.0	165.6	110.3 ± 27.5	33.0	119.0	63.1 ± 5.5	31.0	158.0	97.0 ± 42.1

*µg/l

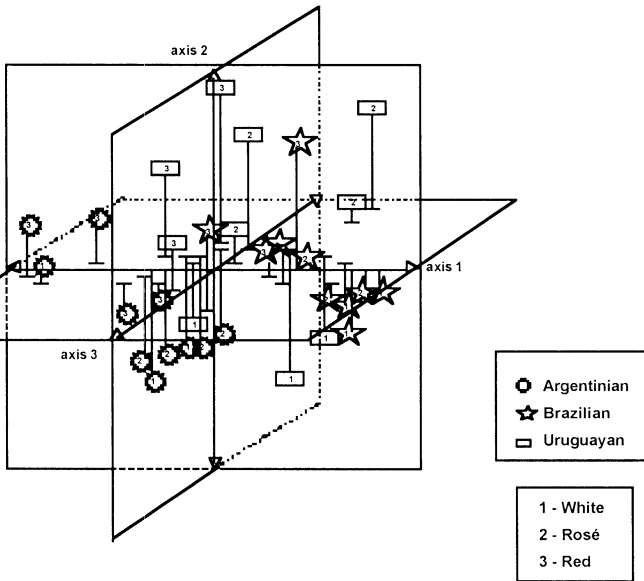


Fig. 1 — Projection of wines from Argentina, Brazil and Uruguay on the planes formed by the axes 1, 2 and 3

Fig. 1 — Projections des vins de l'Argentine, du Brésil et de l'Uruguay sur les plans formés par les axes 1, 2 et 3

that the axes 1, 2 and 3 explain 38.6 p. cent, 28.2 p. cent and 10.4 p. cent, respectively, that is, 77.2 p. cent of the total variation. Figure 1 shows the graphic representation of the wine projection on the plane represented by the axes 1, 2 and 3.

Axis 1 separates the wines according to the country. The Argentinian wines showed more significant differences in relation to the Brazilian ones, while the Uruguayan wines had intermediary composition. Taking into account this discriminating characteristic it is possible to say that axis 1 represents the geographic origin.

Axis 2 separates the wines according to the type, white, red or rosé, but the discrimination was not so evident, because some rosé wines were similar to the white wines and some to the red ones. Rosé wines from Argentina and Brazil looked like white wines, placing them in the middle or in the lower part of the graphic ; but rosé wines from Uruguay showed similarity with the red wines (higher position of the graphic) (figure 1).

The graphic representation of the mineral elements on the factorial plane formed by the axes 1, 2 and 3 is indicated in figure 2.

The best correlations were found with Li, Mg, P, K, Rb, Na and Fe, which form the axis 1 (table II).

The highest content of Li was detected in the Argentinian wines, having a strong influence in the

TABLE II

Correlations of the mineral elements with the three principal axes

Tableau II — Corrélations des éléments minéraux par rapport aux trois axes principaux

Variable	Coefficient of corrélation (r)		
	Axis 1	Axis 2	Axis 3
K	<i>-0.7413</i>	0.3857	0.2663
Na	<i>0.7042</i>	0.4941	0.1857
Ca	0.1414	<i>0,5704</i>	0.3119
Mg	<i>-0.8420</i>	0.3046	0.2202
Mn	0.4035	<i>0.7559</i>	0.3206
Cu	0.0707	<i>0.6667</i>	<i>-0.5040</i>
Fe	<i>-0.6374</i>	0.4034	0.2078
Zn	0.1622	<i>0.6894</i>	<i>-0.6377</i>
Li	<i>-0.8443</i>	0.3081	0.1025
Rb	<i>-0.7152</i>	<i>0.6065</i>	0.2166
P	<i>-0.8060</i>	0.4214	0.1847

Important correlations are in italic

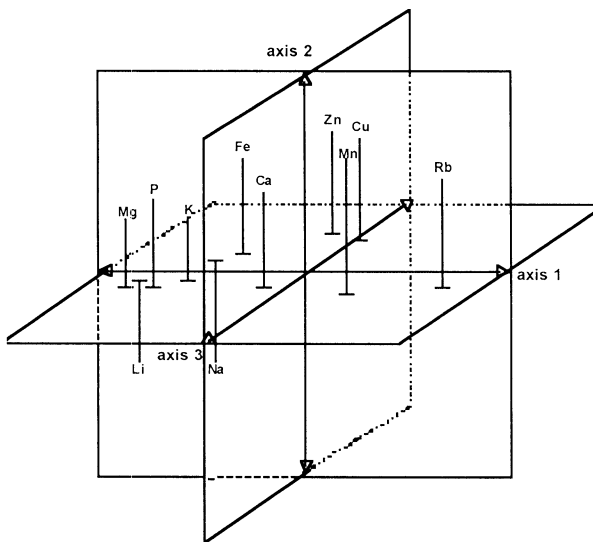


Fig. 2 — Mineral elements projection of wines from Argentina, Brazil and Uruguay on the planes formed by the axes 1, 2 and 3

Fig. 2 — Projection des éléments minéraux des vins de l'Argentine, du Brésil et de l'Uruguay sur les plans formés par les axes 1, 2 et 3

had Na contents higher than those found in the literature (PANDOLFI *et al.*, 1987 ; O.I.V., 1989). However, there is no information on the mineral composition of the Uruguayan wines.

The values of the mineral elements analyzed and submitted to the principal component analysis showed

wine discrimination of the three countries. The Brazilian wines were characterized by lower contents of Li as the values have always been lower than 10 µg/l. Li, as well as Rb, was already pointed out as an element to separate red wines of three different regions of France (MEDINA and VAN ZELLER, 1984). It is an alkaline metal found in small amounts in the soil. However, its content increases in the soils of granite origin (HERRERO-LATORRE and MEDINA, 1990). But in wine, Li appears in little concentrations (VOULGA-ROPOULOS and SOULIS, 1987) which usually do not exceed 50 µg/l (MEDINA and SUDRAUD, 1979). The other factors which might contribute to increase the content of Li in the Argentinian wines could be related to the type of soil, its dryness and the composition of the water used in irrigation. It was also shown that the content of Li in the wine is influenced by the time of maceration (RIZZON, 1985), by the utilization of enological products (MANFROI *et al.*, 1994), by the time of wine aging in the bottle (MEDINA and SUDRAUD, 1979) and by the use of inadequate material (GONZALES-LARRAINA *et al.*, 1987).

Mg and P were the other minerals showing an important influence in the formation of axis 1. The Argentinian wines were outstanding by showing higher concentrations of these two minerals, followed by the Uruguayan and Brazilian ones. The low contents of Mg in Brazilian wines were already registered (RIZZON and SALVADOR, 1987), which was probably due to the low content of this element in the soil. The low pH level of the Brazilian soils may release Al which competes with the absorption of Mg and P. The contents of these two minerals in the red wines could be related to the grape maturation or even to the maceration and pressing conditions.

K, Rb and Na have also had an outstanding participation in the formation of axis 1. Quantitatively, K is the most important cation in grapes and wines. The grapevine roots are able to absorb primarily the K in relation to other available cations. On the other hand, the rainfall and sunlight show a relationship with plant transpiration, which regulates the metallic ions absorption (GONZALES-LARRAINA *et al.*, 1987). Therefore, a dry region would be responsible for a poor development of the plant and thus for a reduced absorption of K and other cations. This would happen to the Argentinian wines if there was no effect of irrigation. However, these wines had higher contents of K, followed by the Uruguayan and Brazilian ones. On the other hand, the final concentration of K is influenced by the ionic balance in the wine.

The Rb was found in higher contents in Brazilian wines. This probably could be related to the soil. The

Argentinian wines showed higher contents of Na, which was maybe due to the climatic and soil conditions of this country, since the vineyards are cultivated in desert and irrigated regions. The water used in irrigation has high contents of salt and also contributes to increase the proportion of Na in the wine (O.I.V., 1989). The Na is naturally found in low concentrations in wines, usually less than 50 mg/l. However, vineyards which are located next to the sea produce wines with higher Na contents. Except to the white wines, the differences between the Uruguayan and Argentinian wines are easily observed through the axis 2.

The Fe was another mineral which took part in the formation of axis 1. In general, the concentration of Fe was low since only one single wine showed a value higher than 10 mg/l. Considering that the concentration of Fe in grapes is low, a high content of Fe could probably be due to the liberation of this mineral to the wine by equipments and recipients used.

The most important variables responsible for the formation of axis 2 were Mn, Zn, Cu, Rb and Ca. These minerals, except for the Ca, are naturally found in small quantities in wines and they are originated from the soil. A probably increase in their amounts may be related to the sprays of fungicides applied to the vineyards and to the liberation by equipments, recipients and enological products used. The higher content of Mn found in Brazilian wines could be related to the concentration of this element in the soil or to the grapevine phytopathological programs.

CONCLUSION

The principal component analysis permitted discriminate wines from Argentina, Brazil and Uruguay, forming with Paraguay the Mercosul economic block, according to their mineral composition. The elements showing higher discriminating effect were Li, Mg, P, K, Rb, Na and Fe. The characteristics of these wines were transmitted mainly by their geographic origin and possibly by the enological processes used in these countries.

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