Ciência Téc. Vitiv. 18 (1), 15-27. 2003

MULTI-ELEMENT COMPOSITION AND $^{87}Sr/^{86}Sr$ OF WINES AND THEIR POTENTIALITIES AS FINGERPRINTS OF WINE PROVENANCE

COMPOSIÇÃO MULTI-ELEMENTAR E RAZÃO ISOTÓPICA DE ESTRÔNCIO COMO MARCADORES DA REGIÃO DE PROVENIÊNCIA DE VINHOS

C. Marisa R. Almeida, M. Teresa S. D. Vasconcelos[1]

Departamento de Química, Faculdade de Ciências, Universidade do Porto. Rua do Campo Alegre, 687. 4169-007 PORTO. Portugal.

[1]mtvascon@fc.up.pt

(Manuscrito recebido em 02.05.03. Aceite para publicação em 10.06.03.)

SUMMARY

The potentialities of both multi-element composition and the ratio $^{87}Sr/^{86}Sr$ as tracers of wine provenance were evaluated, by studying the relative influence of the provenance soil and vinification process on these two parameters. With this purpose, two wines were selected: one red table wine and one red fortified wine, both from the Douro wine-district, Portugal. The values of the $^{87}Sr/^{86}Sr$ ratio were also determined in ten wines of different regions of origin.

Both vinification processes changed the multi-element composition of the wines. Nevertheless, significant and linear correlations were obtained between the patterns of the wines and that of the respective musts prepared in the laboratory (without contact with the vinification system), as well as between those of the wine and of the provenance soil. Regarding $^{87}Sr/^{86}Sr$, statistically identical values were found in the wines, respective musts and provenance soil. In addition, significant differences in the $^{87}Sr/^{86}Sr$ ratios were found in wines from different regions of origin.

Therefore, the multi-element composition together with the $^{87}Sr/^{86}Sr$ ratio showed to be suitable to act as fingerprints of the origin of a wine. A database of these parameters in different wines will be very useful for discriminating wines by regions in order to detect/prevent wine fraud.

Keywords: wine, multi-element composition, $^{87}Sr/^{86}Sr$, fingerprints of provenance

Palavras-chave: vinho, composição multi-elementar, $^{87}Sr/^{86}Sr$, marcadores de proveniência

INTRODUCTION

Prestige wines are among the most imitated and falsified items. It is important to study in detail such wines in order to identify specific characterisations, which can be used as proper fingerprints of the wine origin for preventing adulterations.

Some previous studies (Greenough *et al.*, 1997; Baxter *et al.*, 1997) have indicated that the multi-element composition of a wine can be used to obtained information about its origin, making up a way for laying down a wine fingerprint that is able to secure the authenticity of the wine.

The ability for discriminating wines by regions through their elemental patterns suggests that elements are mainly regulated by their movement from rock to soil and from soil to grape. However, several factors, like environmental contamination, agricultural practices, climatic changes and winemaking processes, may change markedly the multi-element composition of the wine and may endanger the relationship between wine and soil compositions.

As concerns winemaking processing, there is already some information in the literature indicating that it has some influence on the multi-elemental pattern of a wine (Eschnauer *et al.*, 1989; Teissedre *et al.*, 1993; Angelova *et al.*, 1999; Jakubowski *et al.*, 1999; Kristl *et al.*, 2002; Almeida and Vasconcelos, 2003a). As the vinification process can influence the concentration of several elements in the wine, and different winemaking processes have been used, element fingerprints of the wines should be relic of soil signatures that survived metabolic and winery processing. Otherwise, the utilization of the multi-element pattern as fingerprint of wine origin has to be confined to high quality wines, which are produced from specific vine varieties and whose influence of the vinification processes on the wine patterns had been previously studied and permanently controlled.

Another potential fingerprint of wine provenance, that only recently was explored (Horn *et al.*, 1998), is the strontium isotope ratio $^{87}Sr/^{86}Sr$. The alkali-earth metal strontium is one of the few elements that show variable isotopic composition in the nature. This element has four stable naturally occurring isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. Only ^{87}Sr is radiogenic, and gradually increases in minerals due to the radioactive decay of ^{87}Rb isotope. Differences in the absolute proportion of ^{87}Sr vary with geological ages and consequently with geographical locations. This variation may be explored in order to determine the origin of a wine, since elements are taken up by the roots of plants, passing to the grapes with the same isotopic proportions in which they occur in the soil. Thus, the $^{87}Sr/^{86}Sr$ ratio can be used as a tracer of wine origin if a significant correlation between this ratio in the soil and in the wine is observed. The results published by Horn *et al.* (1998) for German wines are promissory but the ratio $^{87}Sr/^{86}Sr$ has to be determined in much more wines to consolidate the use of this parameter as a suitable tool for establishing wine provenance.

This paper summarises the results obtained recently in a project whose major aim was the evaluation of the potentialities of both multi-element composition and $^{87}Sr/^{86}Sr$ isotope ratio to be used as fingerprints of wine provenance (Almeida and Vasconcelos, 2001 and 2003b; Almeida, 2003). We were prompted to follow, from the vineyard to the final product, the production of two different wines, in order to investigate the relative influence of the soil composition and the vinification process on both the multi-elemental pattern and the $^{87}Sr/^{86}Sr$ ratio of the wine. Both selected wines were from the Douro wine-district – Northeast of Portugal. However, the grapes used to produce those wines (a monovarietal red table wine and a polyvarietal red fortified wine) were from two distinct vineyards (an old one with sixty to seventy years and a young one with less than ten years raised in a forest-soil) and the wines were produced in different wineries accordingly to very distinct procedures.

In addition, the $^{87}Sr/^{86}Sr$ ratio was determined in ten wines, eight from five different Portuguese regions and two from a French region. The results were compared in order to determine whether $^{87}Sr/^{86}Sr$ would be significantly different in wines of different origins.

METHODS

The multi-element compositions (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hf, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sr, Ti, Th, Tl, U, V, W, Y, Zn, Zr and the REEs La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) of soil, musts (prepared in the laboratory by smashing grape berries), samples collected in the different steps of each winemaking process and final wine products were measured, using inductively coupled plasma mass spectrometry (ICP-MS), after suitable pre-treatment of the samples (by UV-irradiation for liquid samples and high-pressure microwave digestion for soil) (Almeida and Vasconcelos, 2002 and 2003b).

The ratio $^{87}Sr/^{86}Sr$ was determined in wines, musts (prepared in the laboratory) and provenance soil also using ICP-MS, after elimination of the interferent rubidium from the samples by a cation-exchange chromatographic separation procedure (Almeida and Vasconcelos, 2001).

RESULTS AND DISCUSSION

Relative Influence of the Soil Multi-Elemental Pattern and Vinification Process on the Wine Multi-Element Composition

In this work it were determined the multi-element compositions of the two selected Portuguese wines of the Douro wine-district and their precursors: respective musts prepared in the laboratory; samples collected throughout the vinification processes (see Fig. 1, A - fortified and B - table wines); and respective provenance soil.

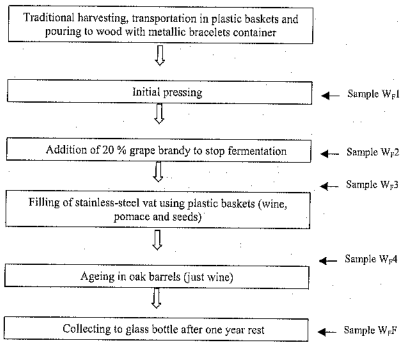

Fig. 1A

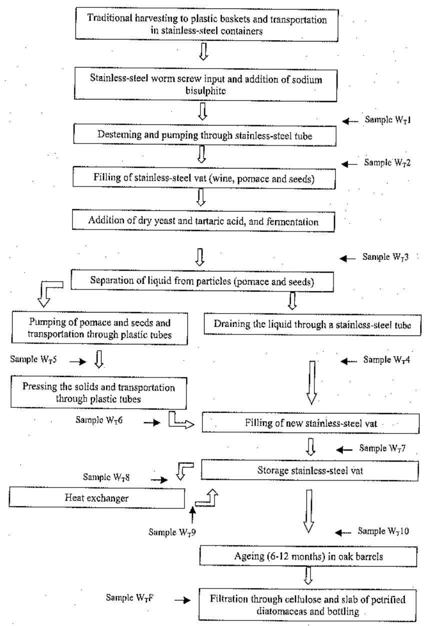

Fig. 1B

Fig. 1 - Schematics of the vinification processes with indication of the points were samples were collected: (A) red fortified wine produced from grapes of an old vineyard (W_F1 to W_F4 and W_FF); (B) red table wine produced from grapes (named "Touriga Nacional") of a young vineyard (W_T1 to W_T10 and W_TF) (Almeida and Vasconcelos, 2003b).

Esquema dos processos de vinificação com indicação dos pontos onde foram recolhidas as amostras: (A) vinho tinto licoroso produzido com uvas de uma vinha antiga (W_F1 até W_F4 e W_FF); (B) vinho de mesa tinto produzido com uvas (casta Touriga Nacional) de uma vinha nova (W_T1 até W_T10 e W_TF) (Almeida e Vasconcelos, 2003b).

In Table I are presented the concentration values of the elements determined in the two produced wines. The concentrations of most of the measured elements fell within the range of those found in other wines of different characteristics

TABLE I

Total concentrations[a] of the multiple elements measured in two wines: a red fortified wine produced with grapes from an old vineyard and a red table wine produced with grapes from an young vineyard (Almeida and Vasconcelos, 2003b).

Valores das concentrações totais de múltiplos elementos medidos nos dois vinhos: um vinho tinto licoroso produzido com uvas de uma vinha antiga e um vinho de mesa tinto produzido com uvas de uma vinha nova (Almeida e Vasconcelos, 2003b).

Element	Fortified wine	Table wine
	Concentration (μg L^{-1})	
La	0.35 (0.01)	0.19 (0.02)
Ce	0.30 (0.01)	0.31 (0.03)
Pr	0.07 (0.01)	< LOD[b]
Nd	0.35 (0.03)	0.20 (0.03)
Sm	0.06 (0.02)	< LOD[b]
Gd	0.06 (0.01)	< LOD[b]
Dy	0.05 (0.01)	< LOD[b]
W	0.13 (0.04)	0.06 (0.02)
Cd	0.51(0.09)	0.26 (0.03)
Sb	1.1 (0.2)	0.30 (0.05)
Tl	< LOD[b]	0.37 (0.03)
Zr	< LOD[b]	0.65 (0.05)
Mo	< LOD[b]	0.73 (0.03)
Ga	1.0 (0.1)	0.78 (0.05)
V	0.47 (0.05)	3.65 (0.03)
Be	3.7 (0.7)	2.9 (0.2)
Y	6.1 (0.6)	3.25 (0.08)
Co	9.5 (0.1)	5.4 (0.2)
Cs	5.3 (0.1)	17.4 (0.4)
Pb	14.0 (0.4)	10.5 (0.2)
Li	13.0 (0.7)	32 (1)
Cr	28 (1)	24.6 (0.5)
Ni	22.4 (0.7)	33.2 (0.6)
Cu	70 (1)	15.7 (0.4)
Al	170 (18)	268 (6)
Ti	247 (62)	244.0 (0.6)
Ba	177 (4)	293 (4)
Sc	459 (25)	328 (12)
Zn[c]	1.03 (0.02)	0.428 (0.003)
Sr[c]	1.56 80.01)	1.45 (0.02)
Fe[c]	2.11 (0.09)	1.301 (0.001)
Rb[c]	2.0 (0.1)	2.91 (0.08)
B[c]	5.6 (0.4)	2.81 (0.04)
Ca[c]	61 (5)	60 (2)

a: Mean and standard deviation (in brackets), n = 3;
b: Below the limit of detection;
c: Concentration in mg L^{-1}.

and origins as reported by Greenough *et al.* (1997). As concerns the elements considered of special interest due to either their toxicity in case of excess, like Cd, Cr, Ni, Pb or even Cu, or the effect they seem to have on the organoleptic properties of wine, like Al, Fe, Zn and Cu, relatively low concentrations (much lower than the legal threshold limit values when available) were found.

The results obtained in the musts, prepared in the laboratory, and in the different samples collected during and at the end of the vinification processes are illustrated in Fig. 2 (A - fortified and B - table wines) for Co, La, Al and Fe.

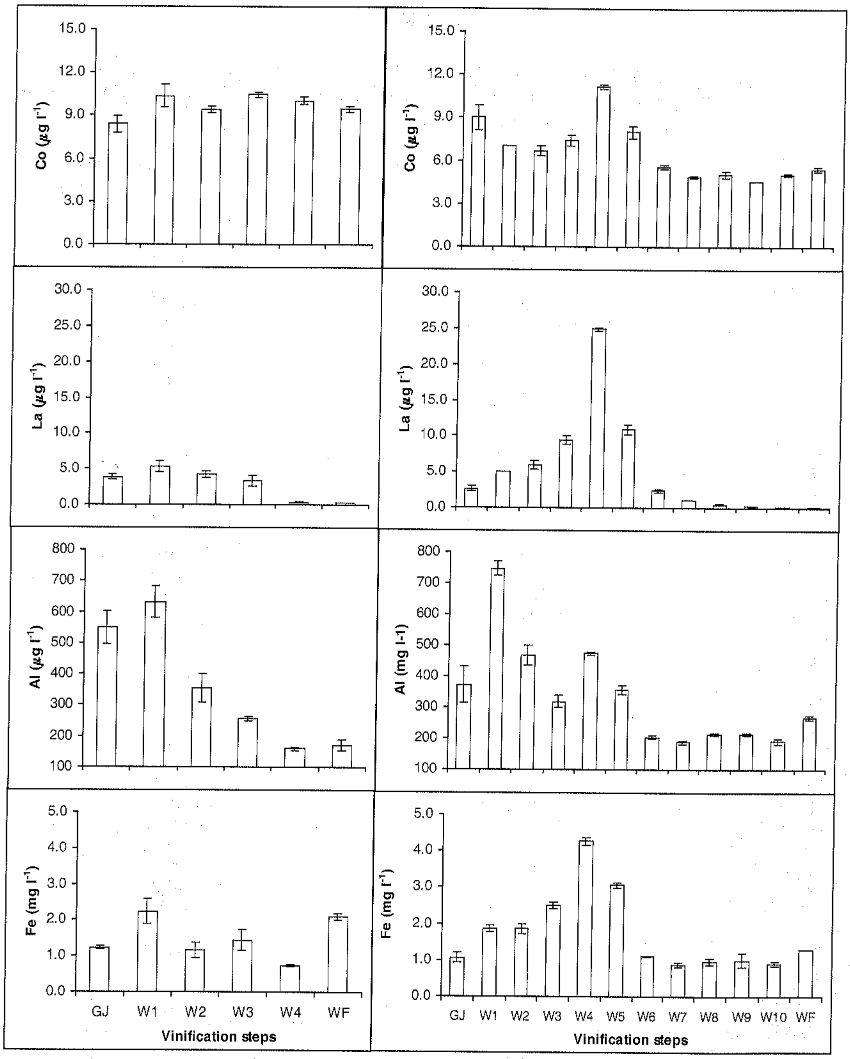

Fig. 2 - Total concentration of Co, La, Al and Fe (in µg L^{-1} and mg L^{-1}) (mean and standard deviation, n = 3) observed in the musts (GJ_F and GJ_T for the fortified and table wine, respectively), in the samples collected throughout the vinification processes (from W_F1 to W_F4 for the fortified and from W_T1 to W_T10 for the table wines) and in the final products (W_FF and W_TF). (A) red fortified wine produced with grapes from an old vineyard; (B) red table wine produced with grapes from an young vineyard (Almeida and Vasconcelos, 2003b).
Concentrações totais de Co, La, Al e Fe (em µg L^{-1} e mg L^{-1}) (média e desvio padrão, n =3) observadas nos mostos (GJ_F e GJ_T para o vinho licoroso e de mesa, respectivamente), nas amostras recolhidas ao longo dos processos de vinificação (de W_F1 a W_F4 para o vinho licoroso e de W_T1 a W_T10 para o vinho de mesa) e no produto final (W_FF e W_TF). (A) vinho tinto licoroso produzido com uvas de uma vinha antiga (W_F1 até W_F4 e W_FF); (B) vinho de mesa tinto produzido com uvas (casta Touriga Nacional) de uma vinha nova (W_T1 até W_T10 e W_TF) (Almeida e Vasconcelos, 2003b).

It was observed that both vinification processes influenced the multi-element composition of the produced wines. Most of the elements displayed similar or even lower concentration in the produced wine compared to that observed in must (in which contact with the winemaking system did not occur), probably as a result of precipitation or co-precipitation with suspended particles during fermentation and/or wine ageing. Just for the fortified wine a 20 % dilution of the wine with grape brandy constitutes a relevant additional factor. Evidence of effective contamination of intermediary products induced by the vinification system was only observed for a few elements: Cd, Cr, Cu, Fe, Ni, Pb, V and Zn in the fortified wine and Al, Cr, Fe, Ni, Pb and V in the table wine. Even so, only the levels of Cd, Cr, Fe, Pb and Zn in the fortified wine and of Cr, Ni, Pb and V in the table wine were higher in the wine than in the must.

In spite of the elemental concentration variations observed throughout the vinification of both wines, statistically significant and even linear correlations were observed between the concentrations of a large number of the elements ($n = 31$) determined in common in the final product and in the respective must (see Table II). Therefore, these concentration variations seem not to be a preventive of the usefulness of wine multi-element composition as fingerprint of wine origin.

The average concentration values of the elements determined in the schistous soil (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hf, Li, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V, Zn, Zr and the REEs La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) of the two selected Douro wine-district vineyards, fell within typical contents of uncontaminated soils (Forstner, 1995). This is compatible with the fact of both studied vineyards being located in an agricultural area, which is far from industrial and urban areas and heavy traffic roads.

For the set of elements determined in common, significant correlations (see Table II) between their mean concentrations in soil and produced wine were found when only Al, Fe and Ca (the three more abundant elements in the soil) were excluded. The median of the multi-element concentrations of the two vineyards soil was also linearly correlated with that of the median of the two wines ($R = 0.994$, $n = 19$, $P < 0.01$).

It is worth mentioning that when the median of the determined multi-element composition of the soil of the two vineyards was compared with that of a previously studied French red table wine, from the region of Bordeaux, no significant correlation was obtained even when Al, Fe and Ca were not included. Significant correlation was not observed either between the multi-element composition of the studied wines and that of the French wine. These results

TABLE II

Pearson's correlations obtained for average multi-element concentrations in the different types of samples (Almeida and Vasconcelos, 2003b).

Correlações de Pearson's obtidas para as concentrações multi-elementares em diferentes tipos de amostras (Almeida e Vasconcelos, 2003b).

	Soil	Must	Wine
		Old vineyard / Fortified wine	
Soil	1		
Must	0.282 / 0.986^{a,b} n = 29^{c}	1	
Wine	0.238 /0.994^{a,b} n = 24^{d}	0.997^{a} n = 31^{e}	1
		Young vineyard / Table wine	
Soil	1		
Must	0.225 / 0.904^{a,b} n = 27^{f}	1	
Wine	0.193 / 0.986^{a,b} n = 20^{g}	0.979^{a} n = 31^{h}	1

a: Correlation significant at $P < 0.01$;
b: Al, Ca and Fe excluded;
c: Ba, Be, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Pb, Rb, Sr, Th, U, V, W Zn, Zr and La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er;
d: Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Pb, Rb, Sr, V, W, Zn, and La, Ce, Pr, Nd, Sm, Gd and Dy;
e: Al, B, Ba, Be, Ca, Co, Cr, Cs, Cu, Fe, Ga, Li, Mn, Ni, Pb, Rb, Sb, Sc, Sr, Ti, V, W, Y, Zn and, La, Ce, Pr, Nd, Sm, Gd and Dy;
f: Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Pb, Rb, Sr, Th, U, V, Zn, Zr and La, Ce, Pr, Nd, Sm, Eu, Gd and Dy;
g: Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Pb, Rb, Sr, V, Zn, Zr and La, Ce, and Nd;
h: Al, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sr, Ti, Tl, V, W, Y, Zn, Zr and La, Ce and Nd.

are understandable, as the composition of the wine seems to depend markedly of the vineyard soil elemental pattern.

The results of this study are compatible with those of a very recent work of Taylor *et al.* (2003). These authors reported the discrimination of wines from two Canadian regions through their multi-element composition, concluding that their composition was strongly influence by the soil chemistry.

Suitability of $^{87}Sr/^{86}Sr$ as Tracer of Wine Provenance

1 – Does the vinification process influence $^{87}Sr/^{86}Sr$ of the wines?

For the two Douro wine-district wines selected (a fortified and a red table wines), the mean and the standard deviation of $^{87}Sr/^{86}Sr$ determined in the final products, musts prepared in the laboratory and provenance soil are presented in Fig. 3. The values of $^{87}Sr/^{86}Sr$ were similar in the wines and respective musts. Therefore, the two winemaking systems tested did not significantly

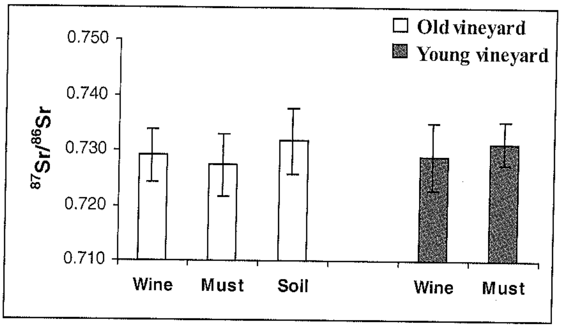

Fig. 3 - $^{87}Sr/^{86}Sr$ (mean and standard deviation, n = 3) obtained in the wines, musts prepared in the laboratory and provenance soil (Almeida, 2003).

$^{87}Sr/^{86}Sr$ (media e desvio padrão, n =3) obtida nos vinhos, nos mostos preparados no laboratório e no solo de proveniência (Almeida, 2003).

change the value of the $^{87}Sr/^{86}Sr$ ratio, which is compatible with no significant strontium anthropogenic contamination.

In addition, a statistical comparison through t-paired test between $^{87}Sr/^{86}Sr$ in wines and soil indicated that they did not differ significantly. Therefore, it seems that the element is being taken up by the roots of plants, passing to the grapes with the same isotopic proportions present in the soil and that the $^{87}Sr/^{86}Sr$ ratio of the wine reflects that of the soil in which the vine is grown.

These results indicate that $^{87}Sr/^{86}Sr$ can be used as a tracer of the provenance of the studied wines

2 - $^{87}Sr/^{86}Sr$ in wines of different regions

The $^{87}Sr/^{86}Sr$ ratio was determined in ten samples of different table (T_1-T_6) and fortified (F_1-F_4) wines. Eight samples were from five different Portuguese regions, Douro (R_1), Dão (R_2), Bairrada (R_3), Borba (R_4) and Madeira (R_5), and two were from one French region, Bordeaux (R_6). Results are presented in Fig. 4.

Some statistically significant differences were found between wines of different regions. For example, the T_5R_6 and T_6R_6 wines, both from the Bordeaux region, displayed the lowest $^{87}Sr/^{86}Sr$, which were significantly different from those observed for all the Portuguese wines. In addition, wines from northeast of Portugal (Douro and Dão regions) displayed statistically higher $^{87}Sr/^{86}Sr$ than all the other Portuguese wines tested (from the centre/southern of Portugal and from Madeira Island). These results demonstrated that it was possible to distinguish some wines of different regions through their strontium isotopic

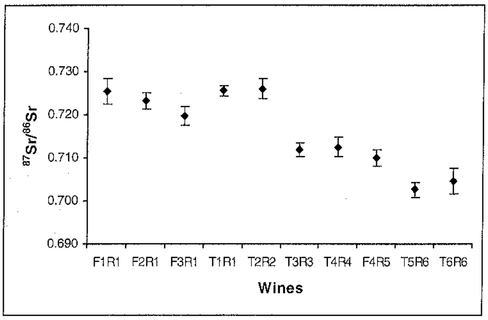

Fig. 4 - $^{87}Sr/^{86}Sr$ (mean and standard deviation, n = 3) obtained for ten samples of different table (T_1-T_6) and fortified (F_1-F_4) wines, from five Portuguese regions, Douro (R_1), Dão (R_2), Bairrada (R_3), Borba (R_4) and Madeira (R_5), and one French region, Bordeaux (R_6) (Almeida and Vasconcelos, 2001).

$^{87}Sr/^{86}Sr$ (media e desvio padrão, n =3) obtida em dez amostras de diferentes vinhos de mesa (T_1-T_6) e de vinhos licorosos (F_1-F_4), de cinco regiões Portuguesas, Douro (R_1), Dão (R_2), Bairrada (R_3), Borba (R_4) e Madeira (R_5), e de uma região Francesa, Bordéus (R_6) (Almeida e Vasconcelos, 2001).

composition, pointing out to the usefulness of the ratio $^{87}Sr/^{86}Sr$ for wine provenance determination. Nevertheless, it was not possible to differentiate all the wines regions only through this strontium ratio, indicating that it should be used together with other discriminating parameters.

Very recently, Barbaste *et al.* (2002) studied eleven wines of different origins and found clear difference among wines produced on basaltic, mixed and granitic soil areas, which corroborates the suitability of $^{87}Sr/^{86}Sr$ as fingerprint of wine origin.

CONCLUSIONS

Regarding multi-element composition it was found, for both studied wines, that the elemental concentration variations observed throughout the vinification processes should not be a preventive of the usefulness of wine multi-element composition for its provenance determination. The multi-element composition of the provenance soil (Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Ni, Pb, Rb, Sr, V, Zn and La, Ce, and Nd) was significantly correlated with that of the wines. Therefore, multi-elemental patterns of wines and their precursors, including provenance soil, seem to have potentialities as tools for establishing the origin of the wines.

As concerns the strontium isotope ratio, for the two studied wines from the Douro wine-district, the winemaking processes did not change this parameter, as it was statistically identical in the wine and provenance soil. On the other hand, statistically significant differences were observed among $^{87}Sr/^{86}Sr$ of wines of different regions. Therefore, $^{87}Sr/^{86}Sr$ is very promissory as fingerprint of the wine origin.

A representative number of wines from different Portuguese regions, as well as from other countries, deserves to be studied in terms of multi-elemental composition and strontium isotope ratio in order to establish regional patterns and enable the discrimination of wines by regions for detecting/preventing wine frauds.

ACKNOWLEDGMENTS

To "Fundação para a Ciência & Tecnologia", Lisbon, Portugal, for C. M. R. A. Ph. D. scholarship (PRAXIS XXI/BD/16028/98) and equipment (Proj. 27/ M/90).

RESUMO

Composição multi-elementar e razão isotópica de estrôncio como marcadores da região de proveniência de vinhos

Com o objectivo de investigar as potencialidades da composição multi-elementar e da razão $^{87}Sr/^{86}Sr$ como marcadores da região de proveniência de um vinho, seleccionaram-se duas vinhas da região vinícola do Douro e determinou-se ambos os parâmetros no solo, no mosto e nos vinhos produzidos. Seguidamente avaliou-se a influência relativa do solo de proveniência e do processo de vinificação na composição multi-elementar e na razão $^{87}Sr/^{86}Sr$ dos vinhos (um vinho de mesa e um vinho licoroso, ambos tintos). Determinou-se também a razão $^{87}Sr/^{86}Sr$ em dez vinhos provenientes de diferentes regiões.

Constatou-se que apesar dos processos de vinificação alterarem (aumentando ou diminuindo) as concentrações de diversos elementos nos vinhos, existiam correlações significativas e lineares entre as composições multi-elementares do vinho e do respectivo mosto preparado no laboratório (sem contacto com o sistema de vinificação), bem como entre a composição das matrizes do vinho e do solo de proveniência. Os valores de $^{87}Sr/^{86}Sr$ foram estatisticamente idênticos nos vinhos, nos respectivos mostos e no solo de proveniência. Por outro lado, encontraram-se diferenças significativas entre os valores da razão $^{87}Sr/^{86}Sr$ em vinhos de diferentes regiões de origens.

Estes resultados indicam que a composição multi-elementar conjuntamente com o valor da razão $^{87}Sr/^{86}Sr$ poderão funcionar como impressões digitais da região de proveniência de um vinho. É, portanto, de esperar, que uma base de dados com estes parâmetros para diferentes vinhos seja muito útil para discriminar vinhos por regiões de origem no sentido de detectar/prevenir fraudes vinícolas.

RESUME

Potentialités de la composition multi-élémentaire et du rapport $^{87}Sr/^{86}Sr$ des vins comme empreintes digitales de sa provenance

Dans ce travail on a évalué les potentialités de la composition multi-éléments et du rapport $^{87}Sr/^{86}Sr$ comme outils pour la détermination de la provenance du vin. Dan ce but, en avons recherché

l'influence relative du sol et du procédé de vinification pour deux vins de la région du Douro, Portugal. Le rapport $^{87}Sr/^{86}Sr$ a également été déterminé dans dix vins provenant de régions d'origine différents.

Les procédés de vinification influencent la composition en minéraux des vins, toutefois on a obtenu des corrélations significatives et linéaires entre la composition en multi-éléments du vin et celle du moût correspondant (préparés dans le laboratoire donc sans aucun contact avec le système de vinification), il en est de même entre celles du vin et du sol de provenance. Le rapport $^{87}Sr/^{86}Sr$ est statistiquement identique dans les vins, les moûts correspondants et le sol de provenance. En plus, des différences significatives dans le rapport $^{87}Sr/^{86}Sr$ existent entre des vins de différentes régions d'origine. Donc, la composition en multi-éléments et le rapport $^{87}Sr/^{86}Sr$ semblent être utilisable comme une empreinte de l'origine d'un vin.

On suppose qu'une base de données de ces paramètres serait très utile pour caractériser les vins selon leur région d'origine ceci il va permettre la détection/prévention des fraudes vinicoles.

REFERENCES

Almeida C.M., 2003. *Isotopic and multi-element characterisation of wine for identification of lead contamination sources and of the provenance region.* PhD thesis, Faculty of Sciences, University of Porto, Portugal.

Almeida C.M., Vasconcelos M.T., 2001. ICP-MS determination of strontium isotope ratio in wine in order to be use as a fingerprint of its regional origin. *J. Anal. At. Spectrom.,* **16**, 607-611.

Almeida C.M., Vasconcelos M.T., 2002. Advantages and limitations of the semi-quantitative operation mode of an inductively coupled plasma-mass spectrometer for multi-element analysis of wines. *Anal. Chim. Acta* **463**, 165-175.

Almeida C.M., Vasconcelos M.T., 2003a. Lead contamination in wines: from the vineyard to the final product. *J. Agric. Food Chem.* **51**, 3012-3023.

Almeida C.M., Vasconcelos M.T., 2003b. Multi-element composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin. *J. Agric. Food Chem.* **51**, 4788-4798.

Angelova V., Ivanov A., Braikov D., Ivanov K., 1999. Taux de métaux lourds (Pb, Cu, Zn and Cd) dans les vins du cépage mavrud provenant d'une région polluée par les industries. *J. Int. Sci. Vigne Vin* **33**, 119-131.

Barbaste M., Robinson K., Guilfoyle S., Medina B., Lobinski R., 2002. Precise determination of the strontium isotope ratios in wine by inductively coupled plasma sector field multicollector mass spectrometry. *J. Anal. At. Spectrom.* **17**, 135-137.

Baxter M.J., Crews H.M., Dennis M.J., Goodall I., Anderson D., 1997. The determination of the authenticity of wine from its trace element composition. *Food Chem.* **60**, 443-450.

Eschnauer H., Jakob L., Meierer H., Neeb R., 1989. Use and limitations of ICP-OES in wine analysis. *Mikrochim. Acta* **3**, 291-298.

Forstner U., 1995. Land contamination by metals: global scope and magnitude of problem. *In: Metal speciation and contamination of soil.* 1-24. Allen H., Huang C., Bailey G., Bowers A. (eds.), Lewis Publishers, CRC Press Inc., USA.

Greenough, J.D., Longerich H.P., Jackson S.E., 1997. Element fingerprinting of Okanagan Valley wines using ICP-MS: relationships between wine composition vineyard and wine colour. *Australian J. Grape Wine Res.* **3**, 75-83.

Horn P., Hölzl S., Todt W., Matthies D., 1998. Isotope abundance ratios of Sr in wine provenance determinations, in a tree-root activity study and of Pb in a pollution study on tree-rings. *Isotopes Environ. Health Stud.* **34**, 31-42.

Jakubowski N., Brandt R., Stuewer D., Eschnauer H., Gortges S., 1999. Analysis of wines by ICP-MS: Is the pattern of the rare earth elements a reliable fingerprint for the provenance. *Fresenius J. Anal. Chem.* **364**, 424-428.

Kristl J., Veber M., Slekovec M., 2002. The application of ETAAS to the determination of Cr, Pb and Cd in samples taken during different stages of the winemaking process. *Anal. Bioanal. Chem.* **373**, 200-204.

Taylor V. F., Longerich H. P., Greenough J. D. 2003. Multi-element analysis of Canadian wines by inductively coupled plasma mass spectrometry (ICP-MS) and multivariate statistics. *J. Agric. Food Chem.* **51**, 856-860.

Teissedre P.L., Cabanis M.T., Cabanis J.C., 1993. Comparison of 2 mineralization methods for determination of lead by electrothermal atomic absorption spectrometry – application to soils, vine-leaves, grapes, musts, rapes and lees samples. *Analusis* **21**, 249-254.