DETERMINATION OF THE GEOGRAPHICAL ORIGIN OF WINES BY MEANS OF THE MINERAL CONTENT AND THE STABLE ISOTOPE RATIOS: A REVIEW

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Abstract

Numerous works have shown that the mineral composition of plants is influenced by the element levels in the ground, by fertilization methods, by the physiological aspects typical of the species from which they are produced, as well as by the technological conditions of production when it deals of transformation alimentary products.
Therefore the multielement content method represents a valid tool for the determination of the origin of vegetable products.

The current review contains the information present in literature concerning the influence of trace element concentration, or of minerals in general, and the stable isotope analysis in the geographical determination of wine origin.

The most frequently used analytical techniques for mineral and isotope determination in wines are spettrophotometry by atomic absorption and the techniques evolved from it and the isotope ratio mass spectroscopy. The statistical techniques used are multivariate analysis, as PCA (principal component analysis), DA (discriminant analysis), CA (canonical analysis) and CLA (cluster analysis). These techniques have proven useful in the differentiation of wines and in their classification according to the place of origin.

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Riassunto

Numerosi lavori hanno dimostrato che la composizione minerale delle piante è influenzata dal livello degli elementi nel suolo, dalle modalità di fertilizzazione dei terreni, dagli aspetti fisiologici tipici delle specie da cui sono prodotti, oltreché dalle condizioni della tecnologia di produzione allorché si tratti di prodotti alimentari di trasformazione.

Pertanto risulta che il contenuto degli elementi minerali rappresenta un valido strumento per la determinazione dell'origine dei prodotti vegetali.

La presente review contiene le informazioni presenti in letteratura riguardanti l'influenza della concentrazione degli elementi in tracce, o dei minerali in genere, e l'analisi degli isotopi stabili nella determinazione geografica dell'origine dei vini.

Le tecniche analitiche più utilizzate per la rilevazione dei minerali e degli isotopi nei vini sono la spettrofotometria per assorbimento atomico e le tecniche evolute da essa derivate e la spettroscopia di massa a rapporto isotopico. Le tecniche statistiche più utilizzate sono le analisi multivariate, come la PCA (principal component analysis), la DA (discriminant analysis), la CA (canonical analysis) e la CLA (cluster analysis). Queste tecniche si sono rivelate utili nella differenziazione dei vini e nella loro classificazione in base al luogo d'origine.

Keywords: Wines, geographical origin, mineral elements, stable isotope ratios, multivariate analysis.

Introduction

The mineral elements contained in vegetable organisms are present in different quantities: conventionally speaking elements such as Ca, P, Mg, S, K and Cl, when present in quantities of from 1 to 3% in dry samples, are defined as macroelements, whereas elements whose presence is less than 1,000 mg/g of dry sample are defined as trace elements.

Many of these elements are essential for plant growth and development (es: Zn, Cu, Mo, Fe, Mn, Co and Se), some of them and others are present as elements implicated in the environmental contamination, others are present following contamination due to the production process trial (1-2).

The trace element diffusion in the food chain is one of the most important indicators of environmental conditions. In fact, ground composition influences the presence of oligoelements in vegetable and in animal organisms that nourish on them. The relationships between environment

and food chain are tightly correlated both to geologic factors such as petrography, rock mineralogy, landscape and climate, as well as to factors specifically correlated to soil chemistry and which concern element transfer methods from the rocks to the ground, to the plants and to human organisms. All these factors have been widely studied and carefully described in hundreds of works published by Prof. Anke and his research group at the University of Jena in prestigious international journals and the collected papers of the conferences dedicated specifically to the study of metal (3).

For this reason in recent years different works have been carried out to study trace element content and stable isotope ratios as indicators of food industry product origin, for instance the reviews of Arvanitoyannis et al., 1999 and Suhaj et al., 2005 (4-5).

In the present review the study of the determination of wine origin as a function of the mineral element content and the stable isotope ratios will be considered. This argument is also interesting for its relevance to nutritional quality evaluation of the foodstuff, for the possible verification of adulteration and for an analysis of its place in the agricultural and food industry chain of production.

The theme of food product authenticity is currently of great interest, above all as concerns foodstuff that have an additional value, for instance origin certified products, for which elevated cost in comparison to the generic alimentary products, is justified by the very strict relationship existing between the product quality and the zone of origin. Particularly for wines some countries have passed specific legislation regarding wine origin, for example in Italy: Denomination of Controlled Origin (DOC); in France: Appellation d'Origine Controlée (AOC); in England: Appellation of Controlled Origin (AOC), etc.

The geographical origin of wines as a function of the mineral content and of the stable isotope ratios.

We have opted here to report on the research done country by country.

● **Italy**: In a study carried out in Abruzzo the lithium, potassium and rubidium content has been analyzed: 28 types of vines (14 red and 14 white) were planted in double in two different territories of said region with different soil and climate characteristics. The 56 samples of wine, produced from said vines, were submitted to analysis for atomic absorption and to multivariate statistical analysis.

The data obtained, elaborated through the LDA, have shown how this statistical approach is able to differentiate both the territory of origin and the colour of the wines (red or white) with an overall classification success of 100%. The data distribution expressed as discriminant scores along the first two eigenvectors as a function of colour and soil and as a function of nationality are reported respectively in Figure 1 and in Figure 2. From this study it can be seen that the territory variable, as a function of the geographically determined soil and climate conditions, is more important than the other parameters in establishing wine origin (6).

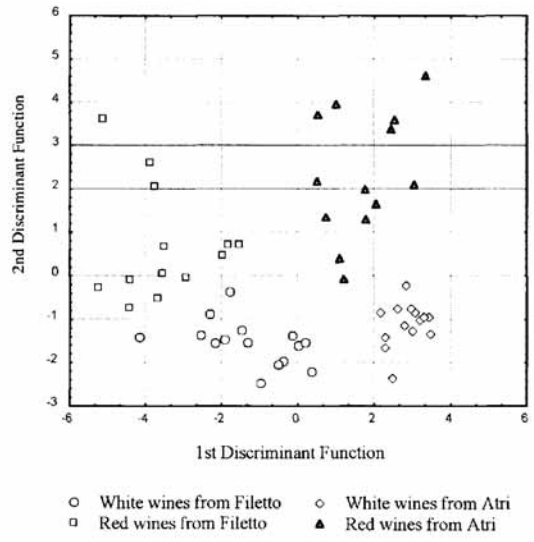

Fig. 1 - Distribution of data exspressed as discriminant scores along the first two eigenvectors as a function of colour and soil (from Del Signore, 2003).

● In sparkling wines produced by the classical method, coming from well-known Italian zones such as Trentino, Franciacorta and Oltrepò Pavese, 60 mineral elements have been analyzed. Analyses have detected the presence of an extreme datum among the trace elements, specifically an elevated content of Cs. The other elements were found to be at normal levels according to the relevant literature (7).

The data interpretation was done with discriminant analysis, after having substituted the extreme datum with the average of the affiliation group (Franciacorta) and eliminating Fe, as it is mostly of a technogenic

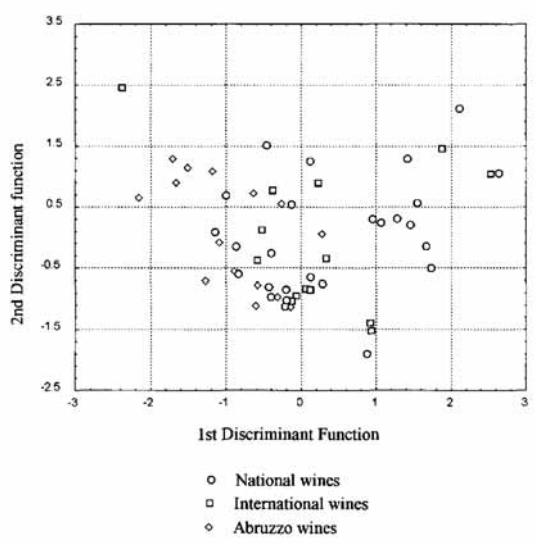

Fig. 2 - Distribution of data exspressed as discriminant scores along the first two eigenvectors as a function of nationality (from Del Signore, 2003).

origin, and Cu, whose presence is influenced by the treatments to which vineyards are submitted. The analysis stepwise forward has reduced the elements to 21, or rather Sr, Li, B, W, Rb, As, Ba, Ga, Nb, Zn, Cd, Zr, Sb, Te, K, Al, Pb, Ce, Cr, Sn and Ca; on the basis of these elements the canonical functions have explained the totality of the variance.

The functions, of which the first was loaded positively with Li, B and W and the second with negative sign from Sr, Li, B, Rb and from Zr with positive sign, have shown that 100% of the samples were correctly attributed to the zone of origin, proving that it is possible to discriminate among the sparkling wines produced in various zones on the basis of mineral composition. The sample distribution according to the two canonical functions is reported in Figure 3 (8).

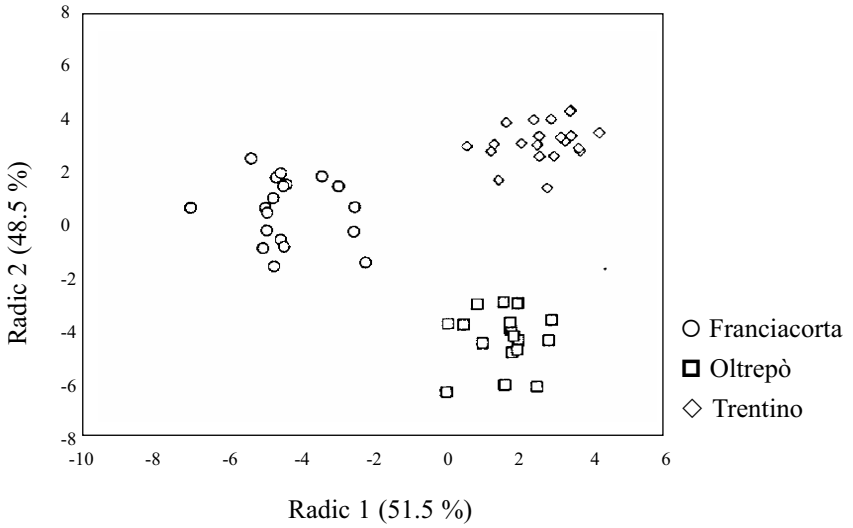

Fig. 3 - Samples distribution according to the two canonical functions (from Nicolini et al., 2003).

● The macro-, micro-elements and lanthanides content, has been determined in 120 samples of DOC (Denomination of Controlled Origin) red wines produced in the years 2000, 2001 and 2002, coming from Basilicata, Calabria and Campania. Elemental composition has been used in multivariate statistical analysis to discriminate the wines according to the geographical origin. The elements have been determined by atomic absorption spectrometry and ICP-MS, while the data obtained have been elaborated with the least significant difference LSD test ($p<0.05$) and one-way analysis of variance (ANOVA), to determine for every element the principal effect of the region and the year of production on multielemental composition of wines. The results obtained indicate that elemental analysis provides a good prospect for wine discrimination according to the regions, even if the element composition did not depend on the year of wine production.

The Canonical Variate Analysis show that wines discrimination in function of the geographical origin is based on Ag, B, Ca, Cd, Eu, Fe, Ga, La, Lu, Mn, Nd, Pr, Sm, Th, Tm, V, Yb and Zr for Basilicata, Al, B, Fe, Mg, Mn, Ti, Tl, Sc and Zn for Calabria, Ba, Eu, K, I, Rb and Tl for Campania. Therefore these elements can be used as a fingerprint wines of from these

important wine-producing regions and they represent reliable bases for wine authenticity evaluation (9).

● **France**: For the geographical characterization of wines and musts the data concerning the trace element concentration was combined with the stable isotope analysis. This procedure is prefered by French researchers because it is often able to furnish detailed information on the geographical origin of wines. Ninety six samples of grape and musts coming from the five greatest vine-growing regions, or rather Alsace, Beaujolais, Bordeaux, Burgundy and Champagne, collected during the year of 1989, have been analyzed. The results obtained, after integrating the stable isotope analysis with the trace elements concentration, have shown that when some elements such as Zn, Ca, Sr and Mg are used in combination with stable isotope ratios the correct classification of samples increases from 78 to 89%. The three dimensional representation of discriminant analysis using a combination of the most discriminating isotopic ratios and trace element data is reported in Figure 4 (10).

● The following year the same group of research published another work on the stable isotope analysis in combination with the element content in grape juices and in wines involving 2H-NMR spectroscopy and isotopic ratio mass spectroscopy, that was carried out in combination with elemental determinations performed by atomic absorption spectroscopy using flame and thermal ionisation.

One hundred and sixty five samples coming from some vine-growing areas in French located in Alsace, Burgundy, Beaujolais and the Loire Valley were analyzed. Moreover the samples coming from Burgundy were selected with regard to four typical denominations, or rather Côtes de Nuits, Côtes de Baune, Côtes Chalonnaises and Mâconnais, with the aim of finding an effective system for distinguishing wines from small production areas. A complete statistical evaluation of data was carried out from the analysis of the variance of the principal components; the sample classification according to the typical denominations furnished by discriminant analysis was equal to around 100% (11).

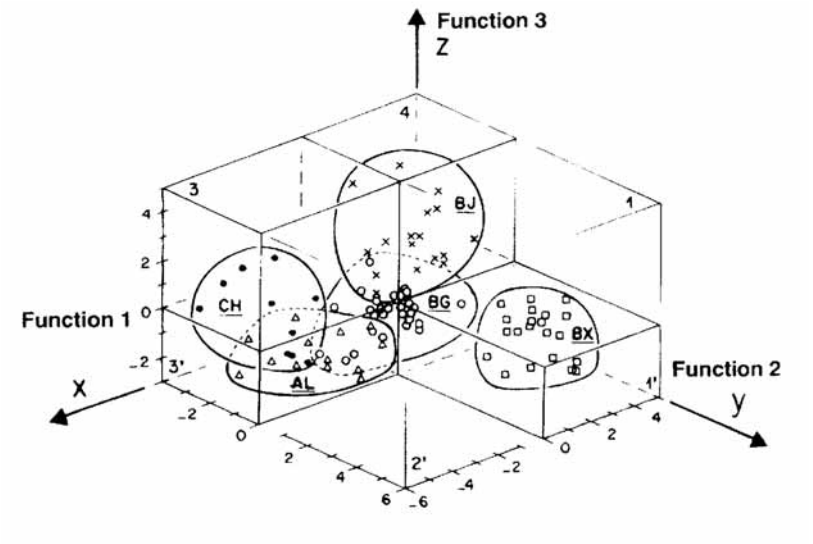

Fig. 4 - Three dimensional representation of the discriminant analysis using a combination of the most discriminating isotopic ratios and trace element data. Symbols: Beaujolais (BJ, X); Burgundy (BG, ○); Bordeaux (BX, □); Champagne (CH, ●); and Alsace (Al, Δ) (from Day et al., 1994).

● The potential authentication of wines through the use of the combination of isotope analyses and trace elements has also been effectuated for the purpose of differentiating the smaller production areas: the Bordeaux region has been considered from which wine samples obtained by grapes coming from different AOC (Appellation of Controlled Origin) areas collected during various years have been analyzed with the purpose of obtaining a consistent database on the values of isotopes and trace elements. The determination of the relationship of stable isotope ratios has allowed for a strong differentiation of the wines of 10 under study with denominations in the Bordeaux zone, showing moreover that significant variations are correlated to the year of production. When the data obtained by the isotope analyses are combined with the trace element content the geographical characterization of samples strongly improves. Focusing attention exclusively on the Médoc area, the analyses of the variance show that some elements such as Li, Ba, Ga and Sr are strongly correlated to the nature of the vineyard and they can represent a good system for product discrimination. Through the use of data obtained from the analyses of iso-

tope and from trace elements concentration of Ba, Ga, V and Sr, it is possible to correctly classify the greater part of wines coming from the Médoc (95%), Côte de Bourg (85%) and Graves (85%) areas, whereas with use of single isotopes a classification of 50% is obtained (12).

● **Spain**: As early as 1987 some Spanish researchers had tried to establish the geographical origin of wines based on the mineral element content. In fact, considering 64 wine samples including most of the Certified Brand of Origin, Spanish table wines and many others coming from different Spanish regions, the concentration of 18 elements has been determined through Flame Emission and Conventional Atomic Absorption Spectrophotometry. The purpose of the study was to evaluate the importance of the principal metals, or in trace, in the differentiation of Spanish wines according to their area of origin. In this work it was noted that among these wines there were some differences in the element concentration present due to the region of origin and wine-making technology (13).

● Other research carried out in Spain were used atomic spectroscopy to identify the presence of some trace elements in 42 white wines of Galicia. The data were elaborated using the chemometric multivariate techniques, that involving cluster analysis and also discriminant analysis. The content of macro and microelements of wines coming from Galicia was used to differentiate the samples coming from Rías Baixas (Certified Brands of Origin) from the other two Certified Brands of Origin from Galicia, Ribeiro and Valdeorras, which are produced in different areas and are possible substrates for falsification.

The PCA and the cluster analysis have shown the connection of the sample groups analyzed to their territory of origin. While the Ca, Na, K and Fe levels in wines can be influenced by regional variations in the land fertilization practices and in the wine-making process, Li and Rb content in wines can be used for obtaining with extreme precision the region of origin of wines.

The samples coming from different territories than Rías Baixas can be correctly classified; this points out how to detect the frauds against the consumers, since the probability of classification of a non-Rías Baixas wine being accepted as genuine is practically nil (14).

● **Canary Islands**: To differentiate the wines coming from the Canary Islands 161 wine samples of different types, white, rosé, red and sweet wines, produced in the years 1995, 1996 and 1997, belonging to eight Denominations of Origin located in four islands: Tenerife, El Hierro, La Palma and Lanzarote, were analyzed.

The metals were classified in three groups: rare earths (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U), lead isotope ratios (208/206Pb, 208/204Pb, 207/204Pb, 206/207Pb, 206/204Pb and 208/207Pb) and other metals (Te, Re, Pt, Au, Tl, Be, Pd, Cd, Sn, Sb, Cs, Co, Ga, As, Zr, W, Li, V, Ni, Pb, Ti, Cu, Zn, Rb, Sr, Ba). Analyses have been realized with ICP-MS.

Some samples were eliminated because they introduced anomalous values of some elements, perhaps due to contamination, or because all the elements and the isotopes have not been analyzed. The final matrix was constituted by 158 samples and 45 variables.

The data have been elaborated with the Soft Indipendent Modelling Class Analogy (SIMCA) technique, showing how this technique is able to discriminate among the different Denominations of Origin. Moreover it was found that the exclusive use of rare earths or lead isotope ratios makes it impossible to build a valid model because the system is endowed with a low specificity.

However the model realized with other elements as object of investigation, either alone or in combination with lead isotope ratios, is able to give results similar to the ones obtained using all the variables.

Particularly in the modelling with all the variables, Sr, Te, Ho, Er and Yb metals, are able to discriminate La Palma island from the others and Rb, Be, Zr and W discriminate Lanzarote from the rest. The stable isotope ratios seem to behave similarly to each other as isotopic ratio 206/207Pb discriminates the greater number of pairs of DO.

The modelling with “lead isotope ratios” and “other metals” has shown a sensibility between 81 and 92% and a specificity similar to the model built with all the variables. In the model with “rare earths” 16 variables have been considered: Tb, Ho, Tm, Lu, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, Th and U.

The percentage of the variance explained by category is surprisingly elevated, between 88 and 98%, probably due to the fact that the space is constituted by 16 variables with three components. The sensibility of the model of every Denomination of Origin (DO) is always equal to around 80%.

In the model with the “other metals” 23 variables have been considered: Te, Re, Pt, Au, Tl, Be, Cd, Sn, Sb, Cs, Co, As, Zr, W, V, Ni, Pb, Ti, Cu, Zn, Rb, Sr and Ba. The sensibility of the model of every DO was between the 85 and 100%. The specificity of Abona, El Hierro and Lanzarote DO is maintained and it is similar to the one obtained using all

the variables. The innovative aspect introduced in this work is the use of cluster analysis to show the analogies between SIMCA boxes of a model and the definition of the distance among the models based on the sensibility and the specificity for the eight DO with the five groups of considered variables (15).

● In 83 red wines coming from the Canary Islands eleven metals (K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Sr, Li and Rb) have been determined, with the purpose of differentiating wines according to their geographical origin. Using the principal component analysis the dimension space has been reduced to five principal components that explain the 76.4% of total variance and wines have tendency to separate themselves according to the island of origin.

Moreover, applying the stepwise LDA, Li, Sr, Mg, Mn, Ca, K, Fe and Zn were selected and three significant statistically discriminating functions have been obtained. As a result a recognition ability of 94.0% and a prediction ability of 90.4% have been found.

Introducing all the variables in LDA, the results obtained have been very similar: 95.2% of recognition ability and 89.1% of prediction ability. Moreover, applying the artificial neural networks by back propagation dividing the samples in two sets, the training set, consistent in 80% of the samples and the test set, constituted by the remaining 20%, the best results were obtained with a net of architecture 4 x 5 x 4 being the input layer formed by Li, Sr, Mg and Mn and the output layer by categories as neurons. The results obtained were excellent, because for Lanzarote and La Palma the recognitions and prediction abilities were equal to 100% (16).

● **Spain and England**: In a work realized on 112 Spanish and English wines 48 elements have been dosed through the inductively coupled plasma mass spectrometry (ICP-MS) with the purpose of verifing if the mineral composition was able to establish their region of origin.

The data obtained have been elaborated with the statistical technique of discriminant analysis and have shown that with this procedure it is possible to differentiate the wines coming from three different Spanish areas, as well as to differentiate the Spanish white wines from the English wines. When red and rosé wines are included in the discriminant analysis, the English and Spanish wines can be separated with 95% accuracy.

The classification of 55 Spanish wines samples according to the three regions of origin (Somontano, Cariñena and Rioja) using 48 elements with Genstat program, had a degree of accuracy of 100% and is reported in Figure 5 (17).

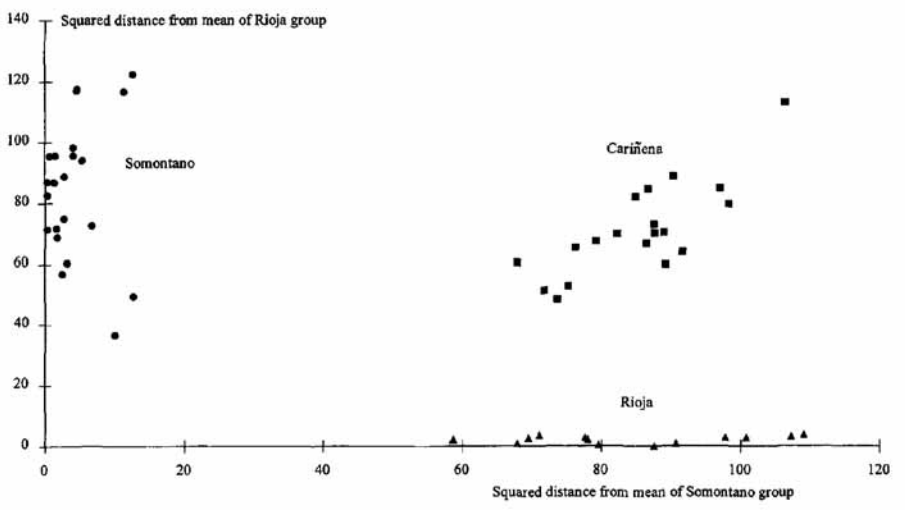

Fig. 5 - Classification of Spanish wines according to the region of origin using 48 elements with Genstat (from Baxter et al., 1997).

In conclusion it has been shown that mineral element content represents a valid tool in the determination of the region of origin of wines.

● **Germany**: The concentration of some trace elements has been determined in 70 German wines coming from four regions: Pfalz, Rheinhessen, Nahe and Franken. The investigation was carried out by activation analysis and investigated as a function of the zone of origin, grape variety and year of production. From the data obtained it was possible, using the numerical taxonomy, to cluster all the wines of one region because of their similarity in trace element patterns (18).

● In 88 wine samples coming from four well-known wine-producing regions of Germany inductively coupled plasma mass spectometry (ICP-MS) was used to determine the concentration of As, Be, Co, Cs, Ga, Li, Nb, Ni, Rb, Te, Ti, W, Y, Zr, Mo, Cd, Sb, Tl, U and the rare earth elements. The results obtained were subsequently been elaborated by data analytical methods realizing a prediction rate applying cross validation of 88.6%. An improvement of this rate could be expected where effects of the geographical origin and regional wine production could be differentiated. The representation of wine groupings by principal component analysis and discriminant analysis are reported respectively in Figure 6 and Figure 7 (19).

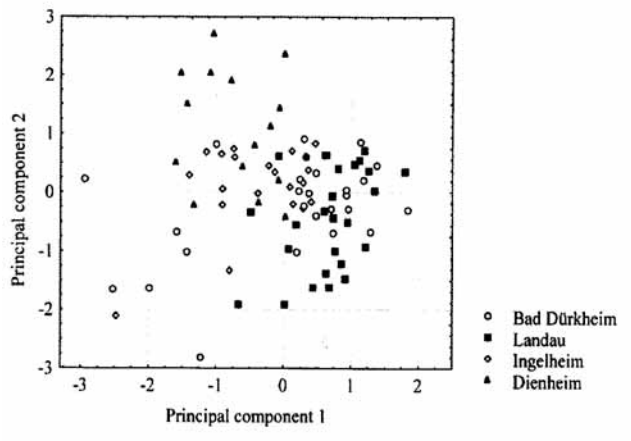

Fig. 6 - Representation of wine groupings by principal component analysis (1st versus 2nd pc) (from Thiel et al., 2004).

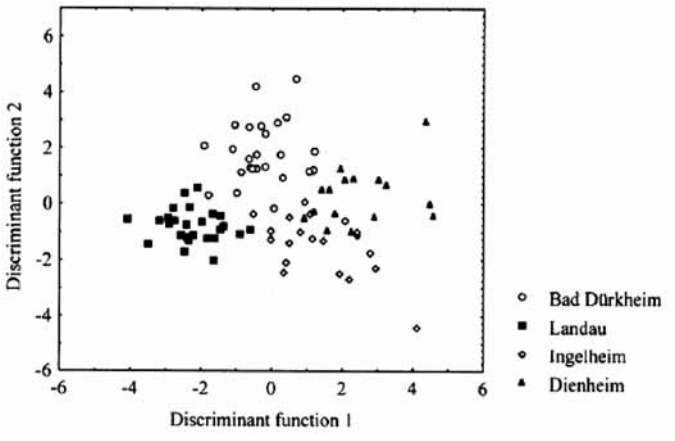

Fig. 7 - Representation of wine groupings by discriminant analysis (1st versus 2nd discriminant function) (from Thiel et al., 2004).

● **Portugal**: In a study carried out by Portuguese researchers the production of two different wine typologies has been examined, from the vineyard to the end product, with the purpose of investigating the relative influence of soil pattern and of wine-making process on the multielemental composition.

From the study it has emerged that the two wine-making processes studied, one modern to produce table wine and the traditional, to produce fortified wine, influence multielemental composition of wines.

Some elements such as Cd, Cr, Cu, Fe, Ni, Pb, V and Zn, have been found in wines as contaminants during the wine-making process in fortified wine, while Al, Cr, Fe, Ni, Pb and V in table wine. Moreover significant correlations among the multielemental composition of wine and of respective grape juice ($R=0.997$ and 0.979 for table and fortified wines, respectively $n=31$, $P<0.01$) have been found as well as between that in wine (median of the two studied wines) and the soil of provenance ($R=0.994$, $n=19$, $P<0.01$), for the element set determined in common in the different types of samples. These results demonstrate the utility of the elemental patterns of both soil and wine as fingerprints of the origin of studied wines (20).

● **South Africa**: Trace element content as a means for determinating geographical origin of wines has been considered in three important regions of South Africa: Stellenbosch, Robertson and Swartland. In this study 40 elements in 40 wines have been determined; of these elements only 20, that is: Li, B, Mg, Al, Si, Cl, Sc, Mn, Ni, Ga, Se, Rb, Sr, Nb, Cs, Ba, La, W, Ti and U, showed differences in the averages of the three areas. Through discriminant analysis, the function based on Al, Mn, Rb, Ba, W, and Ti concentration was able to correctly discriminate wines of every region. Particularly the data have shown that a correct wine classification in one group equal to 100% existed when the discriminant functions were based on Al, Mn, Rb, Ba and W for Stellenbosch, Se, Rb, Cs and Ti for Robertson and Al, Mn, Rb, Sr, Ba and Ti for Swartland (21).

● **Europe**: In line with the directives of the Wine Database European Project 63 chemical parameters such as the macros and trace elements, isotopic ratios, classical parameter and biogenic amines have been analyzed, in 400 samples of wine coming from some European nations, or more precisely, Hungary, Romania, the Czech Republic and from South Africa. Analyses showed that it was possible to obtain some excellent rates of classification based on chemical parameters such as the isotopic ratios or trace element concentration and that wines coming from South Africa clearly differentiate themselves in comparison to the samples coming from the European continent. Moreover, for the commercial wines it has been shown that the isotopic ratios change greatly in respect to the year of production. The same discrimination has been obtained for authentic wines which were harvested in the same years and isotopic ratios is shown useful

in the discrimination of commercial wine coming from South Africa.

The discrimination among native Hungarian samples in comparison to the samples coming from the Czech republic and from Romania has been more difficult to realize, while the discrimination between the Czech republic and Romania has been relatively simple. However with PLS discriminating models using the whole set of 63 parameters, it was possible to obtain a perfect discrimination of the different wine samples (22).

Conclusion

The classification of wines by their geographical origins is an argument of significant interest both for the producer and for the consumer: various analytical and statistical systems have been proposed for identifying their zones of production, also because the factor "origin" has a considerable importance correlated to the quality of these products.

The mineral element content and the stable isotope ratios have been shown to be useful in the determination of the geographical origin of wines; in the majority of cases through statistical multivariate elaboration of data a discrimination of 100% has been obtained. The number and the types of elements sufficient to discriminate the production areas varies in function of the origin zone and the vines. From this point of view the greater the number of dosed elements, the more elevated the probability of obtaining discriminations close to 100%. An optimal discrimination has often been obtained introducing the analysis of Lithium and Rubidium, probably because such elements don't suffer the influence of technological processing.

Moreover from the studies realized it can be deduced that while the metal content is able to differentiate with great accuracy wines according to the geographical origin, the stable isotope ratios is a useful indicator to differentiate, above all, the year of production.

In general the introduction of analytical and statistically evolved techniques also satifies the demand from consumers, who and more are asking for alimentary products of certified quality and that are safe from the point of view of hygene and health.

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REFERENCES

(1) H. MASCHNER, "Introduction, definition, and classification of mineral nutrients", in *Mineral nutrition of higher plants*, Accademic Press, London, 1995, 3-5.

(2) Z.L. HE, X.E. YANG, P.J. STOFFELLA, "Trace elements in agroecosystems and impacts on the environment", *J. Trace Elem. Med Biol. 2005*, 19, 125-140.

(3) Macro and Trace Elements Workshop, Vol. 1-23, years 1981-2006, Friedrich Schiller University, Jena, Schubert-Verlag Leipzig.

(4) I.S. ARVANITOYANIS, M.N. KATSOTA, E.P. PSARRA, E.H. SOUFLEROS, S. KALLITHRAKA, "Application of quality control methods for assessing wine authenticity: use of multivariate analysis (chemometrics)", *Trends Food Sci. Technol. 1999*, 10, 321-336.

(5) M. SUHAJ, M. KOREŇOVSKÁ, "Application of elemental analysis for identification of wine origin", *Acta Alimentaria 2005*, 34 (4), 393-401.

(6) A. DEL SIGNORE, "Environmental discrimination of wines using the content of lithium, potassium and rubidium", *J. Trace Elem. Med. Biol. 2003*, 17 (1), 57-63.

(7) H. ESCHNAUER, "Spurenelemente und Ultra-Spurenelemente in wein", *Naturwiss. 1986*, 73, 281.

(8) G. NICOLINI, R. LARCHER, L.BONTEMPO, "Caratterizzazione della composizione di base e del contenuto di elementi in micro-quantità ed in tracce in spumanti italiani elaborati con il metodo classico", *Riv. Vitic. Enol. 2003*, 4, 29-44.

(9) F. GALGANO, F. FAVATI, M. CARUSO, T. SCARPA, A. PALMA, "Analysis of trace elements in southern Italian wines and their classification according to provenance", *Food Sci. Technol. 2008*, 41, 1808-1815.

(10) M.P. DAY, B. ZHANG, G.J. MARTIN, "The use of trace element data to complement stable isotope methods in the characterization of grape musts", *Am. J. Enol. Vitic. 1994*, 45 (1), 79-85.

(11) M.P. DAY, B. ZHANG, G.J. MARTIN, "Determination of the geographical origin of wine using joint analysis of elemental and isotopic composition. II. Differentiation of the principle production zones in France for the 1990 vintage", *J. Sci. Food Agric. 1995*, 67 (1), 113-123.

(12) G.J. MARTIN, M. MAZURE, C. JOUITTEAU, Y.-L. MARTIN, L. AGUILE, P. ALLAIN, "Characterization of the geographic origin of Bordeaux wines by a combined use of isotopic and trace element measurements", *Am. J. Enol. Vitic. 1999*, 50 (4), 409-417.

(13) C. FERNANDEZ-PEREIRA, J. ORTEGA, A. MARTIN, "Contribution of the major and trace metallic elements to the characterization of Spanish wines", *Alimentaria 1987*, 24 (179), 39-44.

(14) M. LATORRE, C. GARCÍA-JARES, B. MEDINA, C. HERRERO, "Pattern recognition analysis applied to classification of wines from Galicia (Northwestern Spain) with Certified brand of origin", *J. Agric. Food Chem. 1994*, 42, 1451-1455.

(15) M. BARBASTE, B.MEDINA, L. SARABIA, M.C. ORTIZ, J.P PÉREZ-TRUJILLO, "Analysis and comparison of SIMCA models for denominations of origin of wines from the Canary Islands (Spain) builds by means of their trace and ultratrace metals content", *Anal. Chim. Acta 2002*, 472, 161-174.

(16) C. DÍAZ, J.E. CONDE, D. ESTÉVEZ, S.J. PÉREZ OLIVERO, J.P. PÉREZ TRUJILLO, "Application of Multivariate Analysis and Artificial Neural Networks for the differentiation of red wines from the Canary islands according to the island of origin", *J. Agric. Food Chem. 2003*, 51, 4303-4307.

(17) M.J. BAXTER, H.M. CREWS, M.J. DENNIS, I. GOODALL, D. ANDERSON, "The determination of the authenticity of wine from its trace element composition", *Food Chem. 1997*, 60 (3), 443-450.

(18) H. SIEGMUND, K. BACHMANN, "Die Lagezuordnung von Weinen durch Bestimmung des Spurenelementmusters", *Z. Lebensm. Uners.-Forsch. 1977*, 164, 1-7.

(19) G. THIEL, G. GEISLER, I. BLECHSCHMIDT, K. DANZER, "Determination of trace elements in wines and classification according to their provenance", *Anal. Bioanal. Chem. 2004*, 378, 1630-1636.

(20) C.M.R. ALMEIDA, M.T.S.D. VASCONCELOS, "Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin", *J. Agric. Food Chem. 2003*, 51, 4788-4798.

(21) P.P. COETZEE, F.E. STEFFENS, R.J. EISELEN, O.P. AUGUSTYN, L. BALCAEN, F. VANHAECKE, "Multi-element analysis of South African wines by ICP-MS and their classification according to geographical origin", *J. Agric. Food Chem. 2005*, 53, 5060-5066.

(22) X. CAPRON, J. SMEYERS-VERBEKE, D.L. MASSART, "Multivariate determination of the geographical origin of wines from four different countries", *Food Chem. 2007*, 101, 1585-1597.