INCIDENCE OF SEVERAL WINEMAKING TREATMENTS AND PROCEDURES ON THE ELEMENTAL COMPOSITION OF GRAPES AND WINE

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Mineral elements in wine have always been studied mainly in relation to their chemical stability in wine and their toxicity (*e.g.* HACCP). For several elements contamination of the product during the whole grape and wine industry production cycle leads to significant increases in natural concentrations, which instead depend largely on the soil. In the last few years the reasons for carrying out analysis of microelements and trace elements have extended, going beyond traditional practice and becoming a useful parameter for discriminating the geographic origin of must and wines.

The article summarises a series of studies realised at the Istituto Agrario di S. Michele all'Adige in the field of ICP-OES and -MS analysis of mineral elements applied to oenology, with the scope of understanding to what extent technological choices in relation to vinification may affect the mineral composition of wines. Details and further information are given in the literature [J. Agric. Food Chem. 2003, 51, (20) , 5956-5961; Italian Journal of Food Science 2001, 13(2), 237-245; Riv. Vitic. Enol., 2003, 56(4): 29-44 and 45-48; Vitis, 2004, 43(1): 41-45; Journal of Commodity Science 2004, 43(1): 21-29; Mitteilungen Klosterneuburg 2004, 54, 25-32; Hyphenated Techniques in Grape and Wine Chemistry, Ch. 8, Wiley & Sons, ISBN: 978-0-470-06187-9].

MINERAL COMPOSITION OF GRAPES

Mineral composition was analysed for dozens of samples of grapes from 10 varieties picked at technological maturity. The presence of some elements appeared to be linked to more or less marked exogenous contributions, due to phytosanitary treatments or dust and earth deposits. This was highlighted by comparing data regarding natural grapes as compared to grapes washed with a diluted nitric acid solution. Indeed, this treatment lowered the maximum content of various elements, including in particular Cu and Al, and to a lesser extent K, Mg, Pb and Sn.

Further research carried out to check the different depletion capability of 44 elements using alternative washing approaches (water under vigorous shaking, 0.2 % acetic acid and 0.2 % citric acid) proved the highest removal capability of the citric solution. However, a grape washing approach in the winemaking protocols has to be carefully considered paying attention to the remarkable consume and pollution of drinking water.

The copper content on grapes has shown a constant tendency to reduce in the last decade and sulphur residues, measured after preparation of a new analytical method in HPLC, were over 2 mg/Kg only in 10% of the around 160 samples analysed, however always remaining well below the Italian legal limit (50 mg/Kg).

MINERAL COMPOSITION OF WINES

An extensive selection of commercial wines was evaluated. The contents measured were essentially in agreement with the typical contents given by Eschnauer [Naturwissenschaften, 1986; 73, 281-290] for each element, often being close to (Ba, Ca, Pb, Sn, Sr, Zn) or below (Ag, Cr, Li, Mn, Ni, V) the lower limits of these intervals. For Ag, Cd, Co and Sn only a few samples exceeded the respective quantification limits, with a maximum of 7.6 µg/L for Ag, 5.9 µg/L for Cd, 8.1 µg/L for Co, and 75 µg/L for Sn. As compared to still white wines, the content in red wines was significantly higher, around 20-30% for Ba, Mg and Ni, c. 40-70 % for B, Fe, K, Li, Pb and Sr, and c. 100 % for Rb. The only element usually present in significantly lower quantities in red wines was Ca (c. -13 %), as a result of easier precipitation of its salts at the higher pH typical of red wines. As compared

to still white wines, the content of Spumante wines was usually significantly lower, around 10-30% for Ba, B, Ca, Cr, K and Sr, and c. 60 % for Cu.
Studies realised at the Institute starting from the 1960s have showed a gradual reduction in the content of Ca, Mg, Fe, Pb and Zn in wines as a result of technological improvements. In contrast with this, wines produced in the last few years have shown significant increases in potassium content.

The ordinary choice of the yeast strain to be inoculated to carry out fermentation, without multiplication phases, can significantly affect the final content of some metals in wines. As observed when fermenting 11 white musts with 4 commercial strains (20 g/hL), it is possible to trace back to the strains statistically significant differences in Co, Cu, Mg, Na, Pb, Sr and Zn, together with technologically relevant differences in Cu, Zn and Pb. These may be linked to the different capacity of the yeasts to produce H_2S able to precipitate metals, but also to bioabsorption mechanisms on the cell wall or the different metabolic needs of the yeasts.

EFFECTS OF OENOLOGICAL TECHNIQUES

The effects of technological intervention not specifically designed to affect mineral content, but which may nevertheless modify this through realises, adsorption, exchange etc. were investigated.

The treatments carried out with different bentonites significantly modified the total content of 40 out of 44 elements studied. B, Cr, Sn and Pb were not modified statistically, albeit with differences between the different bentonites. K, Rb and Zn diminished significantly, but in technologically negligible quantities, whereas the decrease in Cu (-43%) was interesting. Statistically significant increases were noted for all the other elements, particularly marked in the case of Ce, Gd, La, Nd, Pr and Y (c. 10 times the control) and Be, Tl and U (4-6 times). No differences attributable to pH in the interval from 3.00 to 4.00 for technologically correct quantities of bentonite (max. 1 g/L) were observed.

The use of yeast hulls (180 mg/L and 360 mg/L) from two different suppliers led to statistically significant increases in levels of Ce, Cu, Fe, La, Sb, U, V and Y, the effect being in line with the dose used. The largest percentage reduction was for U (c. 24 % and 36 %). The reduction in Fe content was also shown to be quantitatively important and technologically significant (c. 17 % and 25 %). The average reduction in Ce content was at the most around 15%, whereas the reduction in Sb, V and Y did not exceed 10%. The reduction in Cu was significantly different for the two commercial products (2 and 10 %).

The use of tannin and gum arabic may also influence the mineral profile of wines. Analysing the possible contribution made by 21 tannins distributed in Italy by 7 different companies, and assuming the addition of 200 mg/L, it was observed that significant increases could be recorded in relation to Sn (c. 20 times greater), U (c. 10 times), Pd (c. 6 times), Pr and La (double). Of technologically or sensorially significant macroelements, increases of 7 mg/L in Na could result from the addition of some tannins. For all the other elements the variations were altogether negligible, also in terms of health (e.g. for Pb and Cd).

Gum arabic may also give rise to significant increases in La, Pr and Th (c. 4-6 times) in wines, also contributing to increases of up to 3 mg/L in Na.

In the light of the technological effects on the mineral profiles of wines noted above, it would appear to be interesting and in some ways surprising to observe that multi-element analysis – alone or jointly together with other analytical approaches – may be a useful tool for the geographical traceability of oenological products. Some examples are the capacity to distinguish Spumante wines produced in Trentino, Oltrepò and Franciacorta, Mueller-Thurgau wines produced in different areas within a single regional area and wines from national macro-areas.