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# Changes in the contents of micro- and trace-elements in wine due to winemaking treatments

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## Summary

**Forty-four mineral elements quantified by ICP-OES and ICP-MS were measured in wines, (a) after wine fining, at three pH levels with 10 different bentonites (1 g·l$^{-1}$), (b) after addition of yeast hulls from 2 suppliers to wine (180 and 360 mg·l$^{-1}$). Bentonite fining resulted in statistically significant increases of the large majority of elements, but in significant lower levels of Cu, K, Rb and Zn. The addition of yeast hulls caused a statistically significant depletion of the contents of Ce, Cu, Fe, La, Sb, U, V and Y.**

Key words: mineral elements, wine, winemaking treatments, bentonite, yeast hulls, ICP-OES, ICP-MS.

## Introduction

In the European Community the list of allowed additives, adjuvants and fining agents in winemaking (EC, Regulation of the Council n. 1493/99; EC, Commission Regulation n. 1622/00) comprises clarifying products of which bentonite is the most important. In comparison with other "earths" like kaolin and Spanish earth, the natural clay is more widely used in winemaking. Technologically, the most interesting characteristics of this montmorillonite-type phyllosilicate are its capability to act as settling aid to clarify juice and wine and to remove proteins, thus limiting the risk of protein haze in wine. The composition and structure of bentonites were studied in detail for their physical, chemical and enological peculiarities (JAKOB 1989; RAPP 1989; TRIBERTI and CASTINO 1992; MAUJEAN 1993; BAYONOVE *et al.* 1995; BOULTON *et al.* 1995; LUBBERS *et al.* 1995; MARCHAL *et al.* 1995; POINSAUT and HARDY 1995 a, b, c). For instance, it is ascertained that the exchangeable cations in these sheet-silicates, mainly Mg, Ca and Na, affect both swelling (Na-form bentonites swelling more than Ca-forms) and protein adsorption on the external surface or within the silica layers. The effects of bentonite fining in wine were investigated frequently for the depletion of proteins, amino acids, bioamines, polyphenols, aroma compounds and the changes of the main mineral elements. Few data are available, however, for micro- and, particularly, trace-elements (POSTEL *et al.* 1986; ENKELMANN 1988; MCKINNON *et al.* 1992; LESKE *et al.* 1995; BAUER *et al.* 2001; MOLINA *et al.* 2001).

Few data are reported also concerning the effects of winemaking treatments more recently approved, namely yeast hulls, on the mineral composition of wines (RIBÉREAU-GAYON *et al.* 2003). Biosorption by living and non-living biomass of *Saccharomyces cerevisiae* proved to lower significantly the final amount of heavy metals (VOLESKY *et al.* 1993; VOLESKY and MAY-PHILLIPS 1995). However, it is still unclear if metal cation depletion increases when carried out by living or non-living yeast biomass (BLAKWELL *et al.* 1995).

This paper quantifies changes of the contents of several mineral elements due to the use of bentonites and yeast hulls. Analyses were performed using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). These techniques are of particular interest as they permit - with relatively short time of sample preparation and analysis - multi-element determination and good automation. Moreover, in the range of trace-elements, sufficiently low quantitation limits are reached.

## Material and Methods

Experiments with bentonite: Forty-four mineral elements were analysed by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in white wine (alcohol: 12.1 % vol.; pH: 3.35; total acidity: 5.4 g·l$^{-1}$, as tartaric acid; reducing sugars: < 1 g·l$^{-1}$) after fining with 10 different bentonites obtained from 4 companies in Italy (Tab. 1). The dose of bentonite was 1 g·l$^{-1}$, similar to

Table 1

Characteristics of the bentonites used

| Code | Colour | Form | Characteristics |
|---|---|---|---|
| A | pale beige | powder | - |
| B | pale beige | powder | Na-type, activated |
| C | beige-greyish | powder | - |
| D | grey-greenish | granule | - |
| E | beige-greyish | granule | - |
| F | grey | granule | Na-type, natural |
| G | pale beige | granule | Na-type, activated |
| H | grey | pellet | Na-type, activated |
| I | pale grey-beige | powder | Na-Ca-type, activated |
| L | pale grey-beige | powder | Na-type, activated |

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the highest doses normally used in winemaking. The natural pH of the wine was raised to pH 4.00 by NaOH 0.1 M, then two wine aliquots were separated and acidified with $HNO_3$ 1 % ("Suprapure", Carlo Erba Reagenti, Milan, Italy) to pH 3.50 and pH 3.00, respectively, in order to have 3 levels of pH covering the natural range occurring in wine.

Sample preparation: Each bentonite (45 mg) was hydrated with 0.45 ml Milli-Q water in polypropylene vials previously rinsed with nitric acid. Forty-five ml of a cold stabilized and membrane filtered (0.45 µm) dry white wine were added into each vial. Vials were submitted to gentle shaking (3 h, 70 r.p.m.) and centrifuged (5 min, 4000 r.p.m.). Clear fractions were analysed.

Analysis: Twenty elements (Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Rb, Sn, Sr, V, and Zn) were analysed by ICP-OES, while 24 elements (Be, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Nd, Pb, Pr, Sb, Sm, Th, Tl, Tm, U, Y, and Yb) were analysed by ICP-MS. Each sample treated with bentonite was analysed in parallel with a blank of the same wine at the same pH, similarly stirred and centrifuged.

ICP-OES analysis was run with an Optima 3300 Dual View, equipped with cyclonic spray chamber and auto-sampler AS90 controlled by the software ICP WinLab 1.42 (Perkin Elmer, Norwalk, CT, USA). Operating conditions are reported in Larcher and Nicolini (2001). Standards for Ca, K, Mg and Na were obtained from Merck (Darmstadt, Germany), while Sn was from Baker (Deventer, Holland). Multi-element standards (Merck) were used for the other elements. Ittrium (100 $\mu g \cdot l^{-1}$; Merck) was added automatically as internal standard to correct matrix effects and drift.

ICP-MS analysis was carried out with a HP 4500 series (Hewlett-Packard, Corvallis, USA), equipped with Fassel torch, Babington nebulizer, Scott-type spray chamber, autosampler ASX 500 (CETAC Technologies, Omaha, USA) and HP-4500 Chemstation software. Five ml of wine were added to 0.1 ml of Suprapure nitric acid (68 %, Carlo Erba Reagenti, Milan, Italy) and Milli-Q water to a final volume of 10 ml. Drift and matrix effects were corrected using, as internal standards, an on-line-added solution of Sc, Rh and Tb (Plasma Emission Standard ICP; Aristar, BDH Laboratory Supplies, Lutterworth, England). Four different multi-element calibration standards were used in various concentrations for the external quantification, three from Agilent Technologies, and one from Aristar (ICP-MS Calibration Standard 4). Three spectrum lines, spaced of 0.05 *m/z* units, were used for each isotope. Setting conditions are reported in Tab. 2.

Experiments with yeast hulls: Yeast hulls from 2 suppliers in Italy (coded SO and IT) were added, at 2 levels (180 $mg \cdot l^{-1}$, D1, and 360 $mg \cdot l^{-1}$, D2) and with 3 replicates, to a white and a red wine, both dry, cold-stabilised and sterile filtered (0.45 µm). After gentle shaking (3 h, 70 r.p.m.) and centrifugation (5 min, 4000 r.p.m.), the clear fraction of each sample was analysed by ICP-OES and ICP-MS as in the experiment with bentonites. Each couple of samples (D1, D2) was analysed in parallel with the corresponding untreated controls, adjusted, shaken and centrifuged like the treated samples. The experiment was run at room temperature. The elements of the above-mentioned experiment with bentonite were analysed.

Table 2

Instrumental parameters and setting conditions for the ICP-MS analysis

| Instrumental parameter | Operating conditions |
|---|---|
| RF power (W) | 1380 |
| sampling depth (mm) | 6.00 |
| plasma gas ($l \cdot min^{-1}$) | 1.5 |
| auxiliary gas ($l \cdot min^{-1}$) | 0.60 |
| peri pump (rps) | 0.10 |
| before acquisition: | |
| uptake speed (rps) | 0.30 |
| uptake time (s) | 70 |
| stabilization time (s) | 40 |
| acquisition time (s per element) | 4.5 |
| carrier gas ($l \cdot min^{-1}$) | 1.02 |
| ion lens setting | before each series of samples, with tuning solution to optimize the signal |

Data were statistically analysed using the software package STATISTICA™ for Windows v. 5.1, 1997 (StatSoft Italia S.r.l., Padova, Italy).

## Results and Discussion

Experiments with bentonite: The composition of the control and treated wines is reported in Tab. 3 together with the quantitation limit (QL) of each element assessed according to Hubaux and Vos (1970) and Vanatta and Coleman (1997). The table presents only elements with concentrations >QL for each of the 60 samples and with RSD% <15 for the 30 analyses of the control wine. Compared to the controls (Tukey's test), bentonite-fined wines had significantly different contents of most of the mineral elements, differences being not significant only for Pb ($p$ <0.0542), B, Cr and Sn (Tab. 3). Statistically, bentonite fining resulted in significantly lower levels of Cu, K, Rb and, as expected according to Enkelmann (1988), Zn. Technologically, changes of K, Rb and Zn are negligible, while the Cu depletion (-43 %) is remarkable and interesting, *e.g.* to limit protein-metal haze. The average percentage of depletion of Cu due to bentonite fining was similar to that achieved in wine with a 1-vinyl-imidazole/1-vinyl-pyrrolidone (9:1) copolymer alternative to ferrocyanide treatment in wine (Nicolini *et al.* 2001). Statistically significant increases were observed for the other elements (Tab. 3), confirming that "technological" pollution and secondary contaminations can overlap significantly the natural levels of many elements in wines (Seppi and Sperandio 1978; Medina and Sudraud 1980; Eschnauer 1982; Eschnauer and Neeb 1988; McKinnon *et al.* 1992; Ough 1993; Eschnauer and Scollary 1995; Bauer *et al.* 2001). The changes in the average amounts of Al, Ba, Be, Ca, Cu, Fe, K, Mg, Mn, Na, Ni and Pb observed after

Table 3

Effects of the bentonite fining (1 g · l$^{-1}$) on the mineral content of wine. (QL = quantitation limit; SD = standard deviation; n.s., *, **, *** = not significant difference, $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively)

| | | | ICP technique | QL | Control | | treated with bentonite | | | bentonites (n=3) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | mean (n=30) | SD | mean (n=30) | SD | sign. | A mean | B mean | C mean | D mean | E mean | F mean | G mean | H mean | I mean | L mean | sign. |
| Aluminium | Al | (mg · l$^{-1}$) | OES | 0,004 | 1,14 | 0,04 | 2,50 | 0,68 | *** | 3,04 | 3,14 | 2,33 | 1,72 | 2,55 | 2,18 | 2,57 | 3,56 | 2,03 | 1,92 | *** |
| Boron | B | (mg · l$^{-1}$) | OES | 0,05 | 3,30 | 0,06 | 3,29 | 0,06 | n.s. | 3,27 | 3,24 | 3,32 | 3,29 | 3,34 | 3,28 | 3,28 | 3,27 | 3,29 | 3,30 | n.s. |
| Barium | Ba | (mg · l$^{-1}$) | OES | 0,017 | 0,078 | 0,004 | 0,150 | 0,070 | *** | 0,280 | 0,277 | 0,143 | 0,113 | 0,160 | 0,100 | 0,143 | 0,087 | 0,110 | 0,083 | *** |
| Beryllium | Be | (µg · l$^{-1}$) | MS | 0,06 | 1,25 | 0,08 | 7,11 | 3,38 | *** | 10,3 | 9,99 | 6,31 | 13,1 | 7,31 | 5,25 | 8,42 | 4,56 | 2,51 | 3,34 | *** |
| Calcium | Ca | (mg · l$^{-1}$) | OES | 0,065 | 73,6 | 2,20 | 91,8 | 8,79 | *** | 95,9 | 90,9 | 95,2 | 87,9 | 99,9 | 79,6 | 99,7 | 76,1 | 99,0 | 94,2 | *** |
| Cerium | Ce | (µg · l$^{-1}$) | MS | 0,06 | 0,64 | 0,03 | 6,41 | 4,11 | *** | 7,59 | 7,05 | 7,10 | 9,86 | 5,82 | 9,46 | 5,62 | 2,70 | 4,56 | 4,34 | n.s. |
| Cobalt | Co | (µg · l$^{-1}$) | OES | 1,8 | 3,2 | 0,43 | 5,1 | 0,94 | *** | 4,3 | 4,0 | 6,0 | 4,0 | 5,0 | 4,0 | 6,0 | 6,3 | 5,7 | 5,3 | *** |
| Chromium | Cr | (µg · l$^{-1}$) | OES | 0,6 | 15,0 | 0,66 | 15,2 | 0,77 | n.s. | 14,7 | 14,7 | 15,3 | 14,8 | 15,1 | 14,7 | 15,0 | 17,0 | 15,6 | 15,5 | *** |
| Cesium | Cs | (µg · l$^{-1}$) | MS | 0,01 | 1,78 | 0,12 | 2,07 | 0,62 | * | 1,43 | 1,47 | 2,25 | 1,35 | 1,86 | 1,60 | 2,19 | 3,15 | 2,67 | 2,78 | *** |
| Copper | Cu | (mg · l$^{-1}$) | OES | 0,002 | 0,24 | 0,01 | 0,13 | 0,03 | *** | 0,14 | 0,15 | 0,13 | 0,07 | 0,13 | 0,07 | 0,13 | 0,16 | 0,15 | 0,15 | *** |
| Iron | Fe | (mg · l$^{-1}$) | OES | 0,006 | 1,48 | 0,03 | 1,92 | 0,21 | *** | 1,66 | 1,68 | 2,15 | 1,65 | 2,01 | 2,01 | 2,10 | 2,11 | 1,98 | 1,87 | *** |
| Gallium | Ga | (µg · l$^{-1}$) | MS | 0,12 | 6,23 | 0,55 | 12,10 | 5,95 | *** | 23,50 | 22,87 | 11,53 | 9,60 | 12,93 | 8,53 | 9,83 | 6,57 | 8,80 | 6,87 | *** |
| Gadolinium | Gd | (µg · l$^{-1}$) | MS | 0,04 | 0,08 | 0,01 | 1,07 | 0,82 | *** | 1,84 | 1,66 | 1,13 | 1,69 | 0,92 | 1,21 | 0,78 | 0,34 | 0,55 | 0,58 | n.s. |
| Potassium | K | (mg · l$^{-1}$) | OES | 6 | 585 | 17,52 | 576 | 13,64 | * | 569 | 564 | 579 | 572 | 587 | 581 | 570 | 586 | 580 | 574 | n.s. |
| Lanthanium | La | (µg · l$^{-1}$) | MS | 0,02 | 0,30 | 0,01 | 3,66 | 2,26 | *** | 6,33 | 5,78 | 3,42 | 4,51 | 3,05 | 4,55 | 2,97 | 1,25 | 2,47 | 2,23 | n.s. |
| Lithium | Li | (µg · l$^{-1}$) | OES | 0,2 | 7,0 | 0,2 | 9,4 | 2,7 | *** | 10,7 | 10,7 | 8,0 | 8,0 | 9,0 | 16,3 | 8,0 | 8,7 | 7,3 | 7,3 | *** |
| Magnesium | Mg | (mg · l$^{-1}$) | OES | 0,04 | 66,7 | 1,63 | 68,6 | 1,95 | *** | 67,2 | 68,0 | 69,0 | 65,8 | 69,6 | 66,9 | 69,9 | 71,3 | 68,9 | 69,0 | ** |
| Manganese | Mn | (mg · l$^{-1}$) | OES | 0,001 | 0,83 | 0,02 | 1,12 | 0,16 | *** | 1,28 | 1,26 | 1,06 | 1,09 | 1,05 | 0,85 | 1,08 | 0,93 | 1,34 | 1,25 | *** |
| Sodium | Na | (mg · l$^{-1}$) | OES | 0,09 | 641 | 20 | 654 | 18 | * | 660 | 629 | 661 | 665 | 662 | 651 | 652 | 670 | 643 | 643 | n.s. |
| Neodymium | Nd | (µg · l$^{-1}$) | MS | 0,14 | 0,37 | 0,05 | 3,69 | 2,74 | *** | 5,87 | 5,27 | 3,87 | 5,83 | 3,23 | 4,67 | 3,03 | 1,20 | 1,97 | 1,97 | n.s. |
| Nickel | Ni | (µg · l$^{-1}$) | OES | 4,8 | 20,0 | 1,02 | 21,6 | 2,84 | ** | 20,0 | 20,3 | 20,0 | 20,7 | 26,0 | 20,0 | 20,7 | 22,7 | 23,0 | 22,3 | n.s. |
| Lead | Pb | (µg · l$^{-1}$) | MS | 0,18 | 31,8 | 3,89 | 35,6 | 9,99 | n.s. | 37,3 | 39,9 | 30,1 | 41,5 | 32,2 | 54,8 | 22,4 | 29,5 | 33,9 | 34,5 | *** |
| Praseodymium | Pr | (µg · l$^{-1}$) | MS | 0,04 | 0,07 | 0,01 | 0,86 | 0,61 | *** | 1,36 | 1,24 | 0,85 | 1,29 | 0,73 | 1,14 | 0,71 | 0,28 | 0,50 | 0,48 | n.s. |
| Rubidium | Rb | (mg · l$^{-1}$) | OES | 0,003 | 2,16 | 0,08 | 2,06 | 0,08 | *** | 2,03 | 1,91 | 2,11 | 2,03 | 2,10 | 2,12 | 2,00 | 2,12 | 2,11 | 2,10 | ** |
| Antimony | Sb | (µg · l$^{-1}$) | MS | 0,24 | 0,75 | 0,07 | 0,93 | 0,38 | * | 0,80 | 0,80 | 0,93 | 0,80 | 0,90 | 1,67 | 1,17 | 0,80 | 0,80 | 0,67 | * |
| Tin | Sn | (µg · l$^{-1}$) | OES | 27,4 | 83,8 | 4,88 | 85,4 | 6,16 | n.s. | 87,0 | 85,0 | 86,7 | 78,7 | 89,7 | 79,3 | 87,0 | 89,7 | 87,0 | 84,0 | n.s. |
| Strontium | Sr | (mg · l$^{-1}$) | OES | 0,001 | 0,166 | 0,004 | 0,263 | 0,060 | *** | 0,267 | 0,251 | 0,235 | 0,361 | 0,242 | 0,386 | 0,250 | 0,213 | 0,214 | 0,215 | *** |
| Thallium | Tl | (µg · l$^{-1}$) | MS | 0,10 | 0,10 | 0,00 | 0,36 | 0,09 | *** | 0,40 | 0,40 | 0,43 | 0,23 | 0,40 | 0,27 | 0,37 | 0,47 | 0,30 | 0,33 | ** |
| Uranium | U | (µg · l$^{-1}$) | MS | 0,02 | 0,52 | 0,08 | 2,25 | 1,51 | *** | 0,78 | 0,84 | 2,80 | 2,22 | 4,74 | 3,87 | 3,97 | 1,34 | 0,91 | 1,06 | *** |
| Vanadium | Va | (µg · l$^{-1}$) | OES | 0,8 | 27,7 | 0,64 | 30,5 | 2,47 | *** | 29,7 | 29,0 | 33,0 | 30,0 | 34,7 | 27,7 | 34,3 | 29,7 | 28,7 | 28,7 | *** |
| Yttrium | Y | (µg · l$^{-1}$) | MS | 0,02 | 0,45 | 0,01 | 4,18 | 2,72 | *** | 6,89 | 6,48 | 3,80 | 6,18 | 3,24 | 2,78 | 3,12 | 1,79 | 3,76 | 3,71 | n.s. |
| Zinc | Zn | (mg · l$^{-1}$) | OES | 0,001 | 0,493 | 0,01 | 0,484 | 0,01 | * | 0,459 | 0,470 | 0,485 | 0,472 | 0,488 | 0,494 | 0,491 | 0,502 | 0,492 | 0,489 | *** |

fining agree with those already observed in wines (Postel *et al.* 1986; McKinnon *et al.* 1992; Leske *et al.* 1995; Molina *et al.* 2001; Bauer *et al.* 2001) or expected using synthetic solutions (Enkelmann 1988), but they do not agree with those observed by the quoted authors for Sn and Cr. The increases due to bentonite fining (roughly one order of magnitude) were particularly remarkable for Ce, Gd, La, Nd, Pr and Y. Increases by roughly 4-6 times were observed also for Be, Tl and U. Significant differences among the 10 bentonites were found for Al, Ba, Be, Ca, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Pb, Rb, Sb, Sr, Tl, U, V and Zn (Tab. 3). However, the limited number of observations for each bentonite does not urge to deeper discussions.

In the control wine, Sm (QL = 0.06 µg·l$^{-1}$), Eu (QL = 0.04 µg·l$^{-1}$), Dy (QL = 0.08 µg·l$^{-1}$), Ho (QL = 0.08 µg·l$^{-1}$), Er (QL = 0.08 µg·l$^{-1}$), Tm (QL = 0.06 µg·l$^{-1}$), Lu (QL = 0.10 µg·l$^{-1}$), Th (QL = 1 µg·l$^{-1}$), Yb (QL = 0.1 µg·l$^{-1}$) and Hf (QL = 0.3 µg·l$^{-1}$), all measured by ICP-MS, were close to or under their relevant QL. After bentonite fining the quoted elements were in quantifiable amounts in all the wine samples, reaching the following mean concentrations (n=30): Sm, 0.85 µg·l$^{-1}$; Eu, 0.24 µg·l$^{-1}$; Dy, 1.3 µg·l$^{-1}$; Ho, 0.27 µg·l$^{-1}$; Er, 0.92 µg·l$^{-1}$; Tm, 0.16 µg·l$^{-1}$; Lu, 0.23 µg·l$^{-1}$; Th, 9.7 µg·l$^{-1}$; Yb, 1.3 µg·l$^{-1}$; Hf, 1.1 µg·l$^{-1}$. For Cd (by ICP-MS) and As (by ICP-OES), the mean concentrations in the control wines were 0.8 and 11 µg·l$^{-1}$, with RSDs % rather high, 20 and 30 % respectively. After bentonite fining (n=30), a slight but statistically not significant increase of 10-12 % was observed in the mean concentrations of these two elements. The release of each mineral element from bentonites or the depletion due to the bentonite fining were not significantly affected by the pH of the wine, thus these data are not shown.

Experiments with yeast hulls: Biosorption is the sole mechanism for quick fixing of cations by non-living yeast cell walls (Blakwell *et al.* 1995), a mechanism in which protein-polysaccharide complexes are involved. Metal biosorption by *Saccharomyces cerevisiae* is not modified between 4 °C and 25 °C (Norris and Kelly 1977; White and Gadd 1987), and these temperatures coincide with those used in winemaking. Also exocellular polysaccharides produced by yeasts (Pellerin *et al.* 1997), as well as by bacteria (Scot and Palmer 1990), show biosorption.

In the experiment, 27 mineral elements (Al, B, Ba, Ca, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, Y, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sn, Sr, U, V, Zn) could be quantified; in all the samples, their amounts were above the relevant QL. Since very large differences were observed for the contents of several elements between the white and red control wines, data were expressed as percentage of the control wines.

Statistically assessed by Anova and Tukey's test, treatment induced significant decreases of the contents of Ce, Cu, Fe, La, Sb, U, V and Y (Figure), with a tendency to higher depletion with higher doses. Differences between D1 and D2, however, are not statistically significant in any case. The highest average depletion is that of U (24 % and 36 % for D1 and D2, respectively, without differences between the commercial products used, SO and IT), confirming the capability to reduce the U content of aqueous solutions by non-living biomass of *Saccharomyces cerevisiae* observed by Volesky and May-Phillips (1995). U biosorption from aqueous solutions was already shown to occur for some fungi and their residual biomasses (Nakajima and Sakaguchi 1986, 1993; Bengtsson *et al.* 1995). Also the depletion of Fe is quantitatively important and technologically remarkable (D1: 17 %; D2: 25 %), without differences between SO and IT. Cu depletion (ca. 5-6 %), statistically significant but technologically negligible, was significantly higher using the yeast hulls coded IT (ca. 10 %) compared to SO (ca. 2 %).

## Conclusions

This work evidences the role that some winemaking treatments, namely bentonite and yeast hulls, can play in the final micro- and trace element composition of wine. It was possible to prove that these treatments, as a rule not applied specifically to affect the mineral composition, contribute to increase or deplete the final content of some mineral elements. Such side-activities can be taken into account to reduce the need of specific treatments of metal depletion in wine. Besides, these activities must be considered - and by-passed using large sampling and data-bases - when the mineral composition is used for ascertaining the geographic origin of a wine.

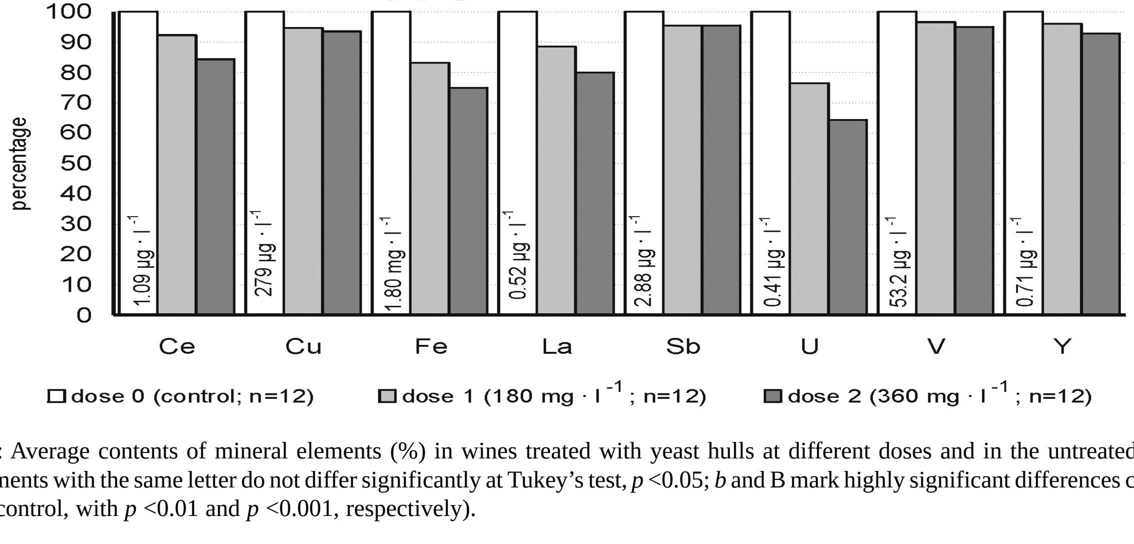

Figure: Average contents of mineral elements (%) in wines treated with yeast hulls at different doses and in the untreated control. (Treatments with the same letter do not differ significantly at Tukey's test, $p$ <0.05; *b* and B mark highly significant differences compared to the control, with $p$ <0.01 and $p$ <0.001, respectively).

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