Influence of Vintage on Cu, Fe, Zn and Pb Content in Some Croatian Red Wines

M. BANOVIĆ, J. KIRIN, N. ĆURKO and K. KOVAČEVIĆ GANIĆ*

Faculty of Food Technology and Biotechnology, University of Zagreb, 10000 Zagreb, Croatia
**E-mail: mbanovic@pbf.hr*

Abstract: Knowledge of the content of heavy metals is important because of their impact on the wine stability or on the health of the consumers. The presence of heavy metals in wines is a consequence of an action of various factors such as conditions of the cultivation and processing of grapes and production, stabilisation or storage of wine. In this work determination of heavy metals (Cu, Fe, Zn and Pb) content in red wines was carried out. Selected wine was Plavac mali, Croatian autochthonous sort, produced by various producers during the three consecutive vintages. The aim of this work was to examine whether the wines produced in different vintage, and by various producers, vary according to the content of heavy metals. For the determination of heavy metals content, the atomic absorption spectrometry (AAS) was used. Content of heavy metals ranged between 0.235–1.122 mg Cu/l, 0.809–6.202 mg Fe/l, 0.266–2.434 mg Zn/l and 0.107–0.3355 mg Pb/l. Data analysis showed statistically significant differences only between producers for iron and copper content.

Keywords: wine; vintage; heavy metals

INTRODUCTION

The mineral content of wines may be influenced by many factors such as mineral composition of soil, viticultural practices, environmental conditions, processing, clarification procedure or storage conditions. Heavy metals, decreased during fermentation, resulting in 0–50% of original amount. Increased concentrations in wine resulted from contamination during post-fermentation processing (Zoecklin *et al.* 1995; Ibanez *et al.* 2008). The quantity of metal content in wine is of great interest, because of their influence on wine quality, hygienic and dietetic characteristics as well as their toxicological implications (Fernandez 1988). Some of them participate in fermentative processes, some are indispensable for plant and animal growth in small concentrations, but become toxic in higher doses (Ribéreau-Gayon *et al.* 2006). One of the main interests is to use the mineral content to characterise the wines by their authenticity and geographical origin (Álvarez *et al.* 2007). Regarding the technological aspects, an important role of metalic ions is in oxido-reductive reactions resulting with wine browning, turbidity, case and astringency. The most reactive in these reactions are copper, iron and manganese (Cacho *et al.* 1995).

MATERIAL AND METHODS

The red wines from Croatian subregion Midle and South Dalmatia were collected during three vintage years (A, B, C) from then wine producers (1–10). The wines were produced from autochthonous vine sort Plavac mali. Before measuring, 20 ml of wines were mineralised at 540°C (Schnell-Verascher). Prepared ashes were dissolved by 10 ml 10% HNO_3 and diluted up to 25 ml with bidistilled water. Atomic Apsorption Spectrophotometer was used (Varian SpectrAA-300) for content determination of heavy metals (Anonymous 1989). Working standard solutions were prepared from standards produced by Merck. ANOVA and multiple range Duncan's test were used for the calculation of differences between heavy metal concentrations (Montgomery 1984).

RESULTS AND DISCUSSION

The results of measuring of heavy metals in red wines are summarised in Tables 1 and 2. Presented results are averages of three measurements of each sample. According the Croatian wine regulation the maximal content allowed of the determined metals in red wines is: 1 mg Cu/l, 20 mg Fe/l, 5 mg Zn/l and 0.3 mg Pb/l) (Anonymous 2005). The role of copper in wine is multiple: it is indispensable trace element for normal functions of plant issues, at low doses it is involved in oxidative transformations that take place in red wine ageing, promotes oxidation of iron and white casse. At the concentrations around 1 mg/l cause turbidity. At high doses it is toxic, which is justifies the legal limit of 1 mg/l (Ribéreau-Gayon *et al.* 2006). The copper concentration ranged from 0.281 to 1.230 mg/l (Table 1). In the most of the wines copper content was below toxical and technological limits of 1 mg/l. However, in some of this wines copper concentrations could promote both of the aspects (Ibanez *et al.* 2008). Wines always contain a few mg/l of iron coming from the grapes

Table 1. Copper and iron concentrations (mg/l) in red wines

Producer	Copper (mg/l)			Iron (mg/l)		
	Vintage A	Vintage B	Vintage C	Vintage A	Vintage B	Vintage C
1	0.613[bcd]	0.815[b]	1.23[a]	3.700[cde]	4.560[c]	5.524[ab]
2	0.706[b]	0.741[bc]	0.335[fg]	4.800[abc]	2.470[efg]	2.165[e]
3	0.523[cde]	0.490[defg]	0.505[cdef]	4.100[bcd]	5.850[ab]	4.340[bcd]
4	0.654[bc]	0.625[bcd]	*0.587[bcd]*	2.577[gh]	2.809[def]	6.202[a]
5	0.506[cdef]	0.548[cdef]	0.620[bc]	3.009[def]	0.809[h]	2.931[e]
6	0.421[defgh]	0.250[h]	0.212[h]	1.221[h]	1.210[h]	2.506[e]
7	0.495 [cdefg]	1.122[a]	0.541[bcde]	5.382[ab]	2.903[de]	2.659[e]
8	0.281[h]	0.392[fgh]	0.321[fgh]	2.631[efg]	3.917[bcd]	1.922[e]
9	1.113[a]	0.603[cde]	0.727[b]	1.721[gh]	1.241[gh]	2.374[e]
10	0.403[efgh]	0.375[gh]	0.287[gh]	5.450[a]	5.876[a]	5.230[abc]

Differences between samples with the same characters are not significant

Table 2. Zinc and lead concentrations (mg/l) in red wines

Producer	Zinc (mg/l)			Lead (mg/l)		
	Vintage A	Vintage B	Vintage C	Vintage A	Vintage B	Vintage C
1	0.624	1.532	0.896	0.189	0.163	0.107
2	0.399	1.584	0.445	0.207	0.154	0.067
3	0.480	0.504	0.661	0.169	0.133	0.125
4	0.464	0.451	0.572	0.147	0.210	0.206
5	0.555	0.266	0.309	0.187	0.233	0.140
6	0.472	0.326	0.647	0.243	0.230	0.229
7	0.627	0.882	2.434	0.351	0.176	0.310
8	0.607	0.792	0.785	0.229	0.110	0.191
9	0.832	0.551	1.151	0.201	0.355	0.214
10	0.568	0.897	1.430	0.187	0.295	0.176

(2–5 mg/l). The higher contents come from soil, equipment, and stabilisation treatments (Ribéreau-Gayon *et al*. 2006). At low concentrations iron acts in metabolism as an enzyme activator, stabiliser and functional component of proteins. At higher than trace level iron has other roles: altering redox systems of the wine, affecting sensory characteristics, participating in the formation of "white" and "blue" casses (Zoecklin *et al*. 1995). In analysed wines (Table 1) the content of iron ranged between 0.809 mg/l and 6.202 mg/l. In some wines the content of iron did not exceed the allowed maximum of 20 mg/l but in concentrations over 5 mg/l it could promote negative effects on the wine quality. Zinc as trace element plays a major role in plant growth, and its traces are naturally present in wine. Higher concentration may come from vineyard, equipment or prolonged maceration. In that case it can have negative effect on sensory characteristics of the wine (Ibanez *et al*. 2008). In all wines the zinc content was lower then allowed 5 mg/l (Table 2). Lead is the heaviest common metal. It accumulates in living organisms mainly in bones and teeth. The possible sources of lead are all stages in the winemaking processes. In some wines the content of lead was a little over the allowed limit of 0.3 mg/l, possibly reached from the equipment (Ribéreau-Gayon *et al*. 2006). We can conclude that the differences between copper and iron content are result of different winemaking processes. The content of heavy metals over allowed limits indicates that the wine producers must be more careful corcerning the heavy metal sources in their wines.

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