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Evaluation of the Contents of Cooper, Iron dhe Zinc in Selected Wines From Western Part – Kosovo

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Abstract: Wine consumption delivers macroelements and microelements necessary for the proper metabolism, to perform different functions in the body. The concentrations of Cu, Fe and Zn were determined in nine brands of Kosovo white and red wines by flame atomic absorption spectrometer (FAAS) after digesting the wine samples with 0.1M HNO_3.

The Cu concentrations varied from 0.01 to 0.45 mg/L in wines, and the Fe concentrations fluctuated from 1.12 to 8.90 mg/L, while the Zn levels were in the range from 0.11 to 0.44 mg/L. The contents of Cu, Fe and Zn showed that Kosovo brends wines could serve as good dietary sources of the essential microelements, and the determined values were within the allowed metals levels in wines for human consumption.

1. Introduction

Wine composition also greatly affects its quality. Mineral composition of wines is useful for many reasons. Firstly, the concentration of elements in wine is useful information to viniculturists and oenologists for controlling the process of obtaining high-quality wine. Secondly, the mineral composition could be used as a wine fingerprint and represents one of the criteria for evaluating the authenticity of wine (1,2,3).

The mineral content of wines may be influenced by many factors such as soil geochemistry, vinicultural practices, clarification procedure and wine processing equipment(4). The concentration of metals in wine is of great significance as it affects their conservation and color, in addition to impacting the organoleptic properties of wine such as aroma, color, flavorǰ freshness, and taste(5,6,7). Previous studies show that, the mineral content in wine decreased during fermentation, whereas increased concentrations in wine resulted from contamination during post-fermentation processing (8,9). Regarding the technological aspects, an important role of metalic ions is in oxido-reductive reactions (Cu, Fe, and Mn) resulting with wine browning, turbidity, case and astringency (10,11).

Many studies have shown that moderate consumption of red wine may improve health and longevity when it is done in combination with a balanced diet (13,14). The wine is a good nutritional source for essential minerals such as iron (Fe) and zinc (Zn) [3,15], and other metals such as copper (Cu) which are considered both an essential and a non-essential element. In toxicological view, minerals in excess may cause serious health consequences or result in the long-term bioaccumulation in the body. [16,17].

The World Health Organization and various regulatory agencies have established recom- mended maximum limits for the concentration of metals in beverages and water utilized in human consumption. In addition, individual countries have rules restricting maximum metal content in wines, which have to be met in order to export wine to these consumer markets. For example, Cu and Zn content must be <5 mg/L by law in wines sold in Australia and Germany [58]. The office International de la Vigne et du Vin (OIV) sets the limits for Cu at 1 mg/L whereas for Zn at 5 mg/L [19,20]. Italy has established the following legal levels in wine: 1 mg/L Cu, and 5 mg/L Zn [20].

Wine quality depends greatly on its metal composition. For example, concentrations of Fe >5 mg/L generally induces haze formation and oxidative spoilage of the wine [2]. Concentration of Cu(II) above 1 µg/mL and Fe(III) ions above 7 µg/mL can give unpleasant, astringent tastes in addition to producing cloudiness in wines that have high pH or high concentration of tannic substances [21,22].

The aim of this study was to assess the concentration of copper (Cu), iron (Fe), and zinc (Zn) in the Kosovo wine. We examined the concentration of metals depending on the type of wine (red, and white), the alcohol content (≥ 12 and < 12%) and the age of wine (≤ 2 and > 2 years). In addition, the concentrations of metals in the Kosovo wines were compared with the metal content in the non-Kosovo wines.

2. Experimental

Reagents and materials

All reagents used were of analytical grade (Sigma-Aldrich). Stock standard solutions were prepared daily by the appropriate dilution of Titrisol standards containing 1000 mg L-1 Fe, Cu or Zn. High purity water was used to prepare the standard solutions.

Sample preparation

Several types of wine samples were investigated: Kosovo wine samples were given from vineries and several other commercially bottled wines (Kosovo wines) were purchased from the market. Labels descriptions of the analyzed wine samples are presented in Table 1.

TABLE 1. Label description of the wine samples

Sample No.	Sample label	Year	Alco. Con.	Vinery
1	Stone Castle (white wine)	2017	11.0 %	Stone Castle - Rahovec
2	Merlot	2012	13.0 %	Sefa Wine
3	Cabernet Sauvignon	2016	12.5.%	Bodrumi i vjetër
4	Stone Castle Riesling	2016	12.0 %	Stone Castle - Rahovec
5	Vranac	2016	11.0 %	Bodrumi i vjetër
6	Stone Castle (red wine)	2015	13.5 %	Stone Castle - Rahovec
7	Stone Castle (Chardonnay)	2018	13.0 %	Stone Castle - Rahovec
8	Illyrian Riezling	2016	12.0 %	Biopak
9	Vranac	2017	13.0%	Local market

An aliquot of 5 mL of wine sample was mixed with 1.0 mL of 2 M HCl solution and further diluted to 5.0 mL with distilled water, and then directly nebulized in an air–acetylene flame under the optimal instrumental parameters (background correction for zinc was required). Fe, Cu and Zn were determined by AAS in the air-acetylene flame using standard calibration curves. All determinations were performed on untreated wine samples; only nitric acid was added to lower the pH (1.0 mL of concentrated acid to 100 mL sample, the resulting pH being 1.5).

Apparatus/analysis

The atomic absorption measurements were realized with a „Shimadzu" 6800 atomic absorption spectrometer equipped with a deuterium background corrector and single element hollow cathode lamp of Cu, Fe and Zn. An air–acetylene flame was utilized for all the elements. The calibration range, wavelengths and slit values are reported in Table 2.

TABLE 2. Calibration range, wavelength and slit value

Characteristics of analysis	Fe	Cu	Zn
Wavelength (nm)	248.3	213.9	324.8
Slit With (nm)	0.2	0.5	0.5
Lamp mode	BGC-D_2	BGC-D_2	BGC-D_2
Calibration range, mgL^{-1}	0.5-10.0	0.1-0.4	0.1-0.5

3. Results And Discusion

Essential metals such as Cu, Zn, and Fe are required for a wide range of physiological processes and have certain nutritional benefits. However, their excessive intake may lead to both acute and chronic toxicity. For example, intake of elevated Cu in wine can induce gastrointestinal symptoms, such as nausea, vomiting, diarrhea, and abdominal and muscle pain. Prolonged intake of elevated Cu can damage the liver and kidneys [23].

The results of measuring of heavy metals in in the examined wine samples are summarised in Tables 3. The measured concentrations of iron (Table 3) show that these varied in range from 1.91 ("Cabernet Sauvignon") to 8.90 mg L–1 ("Vranac"). The concentrations of copper in the different wines also differed a lot, i.e., from 0.01 mg L–1 (Merlot, Sefa Vine) to 0.45 mg L–1 (Cabernet Sauvignon, Bodrumi i Vjetër), while the zinc concentrations covered a somewhat narrower range, from 0.11 (Merlot, Sefa Vine) to 0.44 mg L–1 (Stone Castle Riesling).

TABLE 3. Average content of Fe, Cu and Zn in the examined wine samples

Sample No.	Sample label	Fe (mgL^{-1})	Cu (mgL^{-1})	Zn(mg^{-1})
1	Stone Castle (white wine)	3.56±0.14	0.14±0.001	0.37±0.02
2	Merlot	2.79±0.13	0.01±0.002	0.11±0.01
3	Cabernet Sauvignon	1.91±0.10	0.45±0.014	0.31±0.02
4	Stone Castle Riesling	2.30±0.11	0.13±0.010	0.44±0.03
5	Vranac	8.90±0.31	0.03±0.003	0.21±0.01
6	Stone Castle (red wine)	3.46±0.15	0.09±0.001	0.39±0.02
7	Stone Castle (Chardonnay)	1.12±0.08	0.17±0.009	0.43±0.03
8	Illyrian Riezling	1.99±0.11	0.35±0.013	0.35±0.02
9	Vranac	2.13±0.12	0.02±0.001	0.29±0.02

The allowed levels of metal in wines are defined by standards. The established allowed values of the standards differ from country to country, even though there are common standards prescribed by the International Office for Grapes and Wines (IOW) (Table 4).

TABLE 4. Maximum acceptable limits of certain metals in wine according to OIV and national legislations of several countries

Trade organization or country	Concentration/mg L^{-1}						Reference
	As	Cd	Pb	Fe	Cu	Zn	
OIV	0.2	0.01	0.15		1.0	5.0	[20]
Australia	0.1	0.05	0.2	-	5.0	5.0	[19]
Brazil	-	0.2	0.5	-	-	-	[29, 33]
Croatia	0.2	0.01	0.2	20	1.0	5.0	[5]
Germany	0.1	0.01	0.3	-	5.0	5.0	[19]
Hungary	0.05	0.02	0.25	-	1.0	-	[33]
Italy	-	-	0.3		10.0	5.0	[19]
South Africa	0.2	0.01	0.2	10	1.0	5.0	[34]

Wines always contain a few mg/l of Fe coming from the grapes (2–5 mg/l). Fe in wines, in concentrations over 5 mg/l it could promote negative effects on the wine quality whereas in concentration greater than 10 mg l^{-1} [5], could poses a major problem that appears is instability of wines. According by previous publication [24], the main source of Fe contamination was the soil where the grapes are produced, as well as the utensils and machinery used during the production and processing. Concentrations above 10 mg l^{-1} were found in wine samples from Greece [24], Hungary [25], and Serbia [26].

The role of Cu in wine is multiple: it is indispensable trace element for normal functions of plant tissues, 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 above 1 mg/l cause turbidity.

Increased quantities of Cu (more than 1 mg l^{-1}) were found in wines from Australia [27], Brazil [28], Croatia [39], Jordan [30], and Spain [31]. Especially high values of Cu, up to 6.8 mg l^{-1}, were found in wine samples from the Czech viticulture region, and were attributed to the application of pesticides [21]. Our results showed that Cu concentration in commercially available Kosovo wines was significantly lower than the maximum permissible limit of 1 mg l^{-1}. Zn plays a major role in plant growth, and its traces are naturally present in wine [33]. Higher concentrations can have negative effect on sensory characteristics of wine. Zn content of wines increases if Zn containers are used during the processing and aging stages and also when Zn-containing pesticides are applied [24]. Maximum acceptable limit of Zn in wine is set to 5.0 mg l^{-1} [29], and none of the wines reported in Table 2 exceeded this limit.

4. Conclusion

The analysis of elements composition is important because of the effect they seem to have on organoleptic properties of wine but also of their toxicity in the case of excessive intake. Metal content in wine is regulated in order to prevent negative effect on organoleptic characteristics or excessive intake resulting in toxic effects. The content of metals in wine varies widely depending on the country. On the basis of the results obtained for the heavy metal amounts (Fe, Cu and Zn) in Kosova wine samples, we can conclude that these results are in line according to the OIV.

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