DETERMINATION OF METALS CONTENT IN HOMEMADE TRANSYLVANIAN WHITE WINES

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Abstract: The mineral (K, Na, Ca, Mg, Al, Fe, Cr, Mn, Cu, Ni, Zn, As and Pb) content of homemade white wines from Transylvania were analysed using inductively coupled plasma mass spectrometry. The results showed that all studied metals were below the maximum acceptable limits set both by the Romanian legislation and the International Organisation of Vine and Wine, except Cu and Zn in one sample. The high Cu, Mn and Zn contents found in one sample is probably as a consequence of the intensive use of metal based pesticides.

Keywords: metals, homemade wine, metal sources

INTRODUCTION

Wine is a worldwide known alcoholic beverage, generally made by fermentation of grape juice. Its compositions and properties are related to the origin and age of the wine (Du et al., 2012). Along its main constituents (water and ethanol), it contains a great variety of organic (saccharides, amino acids, phenols) and inorganic substances (metals) of both endogenous and exogenous origin (Grindlay et al., 2011). The endogenous sources are related to the soil on which the grapes were grown, the grape variety and the climatic conditions. The exogenous sources originate in production practices during grape growth and wine making, as fertilization, environmental contamination and oenological practices (Grindlayet al., 2011; Tariba, 2011).

Metals have an important role in wine quality, as it may determine the wine colour (Al, Cu, Fe, Ni, Zn), taste (Cu, Fe, Mn), cloudiness (Cu, Fe, Al). Moreover, these elements in trace amounts may offer beneficial health effects, while in higher amounts along other metals (Pb, Cr, As, Cd) may also have potentially toxic effects on wine consumers (Tariba, 2011). There are several papers that study the metal contents in wine all over the world (Lara et al., 2005; Kment et al., 2005; Jos et al., 2004; Galani-Nikolakaki et al., 2002; Moreno et al., 2008; Frias et al., 2003, Bora et al., 2015). Among them the most determination techniques used are inductively coupled plasma mass spectrometry (ICPMS), followed by inductively coupled plasma optical emission spectrometry, electrothermal atomic absorption spectrometry and flame atomic absorption spectrometry (Grindley et al., 2011).

In the homemade winemaking the grapes are crushed with or without the separation of stem, the must is transferred in oak barrels for fermentation under anaerobic conditions with or without addition of sugar and sulphur dioxide. Pomace and wine are separated by decantation. Homemade wines are not commercially available but consumed in the household without any quality control or determination of toxic elements.

The objective of this paper was to determine the metal content in homemade Transylvanian white wines in order to verify the use of pesticides, fungicides and fertilizers during grape growing and the winemaking process.

MATERIALS AND METHODS

Homemade white wines were collected in 2015 from seven local producers in Transylvania (Sebes-W1, Lechinta-W2, Teaca-W3, Aiud-W4, Turda-W5, Blaj-W6, Beclean -W7) who cultivate their grape and produce wine by traditional procedures. The grapes are cultivars of *Vitis vinifera* and are grown in mixed cultures. Wine is produced from a blend of various grape types. Samples were stored in polyethylene bottles at 4 °C before analysis. All reagents were of analytical grade.

Before analysis the alcohol was removed from the wine by heating 50 ml of sample on hotplate at 80 ^{o}C. The samples were cooled and 10 ml of 65% HNO_3 and 30 ml 30% H_2O_2 were added stepwise to destroy the organic matrix and heated to reflux. After cooling the remaining solution was transferred to a 50 ml volumetric flask and diluted to volume with ultrapure water. The solutions were then filtered through filter paper. The metal contents were determined by inductively coupled plasma mass spectrometry using the ELAN DRC II Spectrometer (Perkin Elmer, Canada).

RESULTS AND DISCUSSION

The metals concentrations in homemade white wines are presented in Table 1, while the maximum acceptable limits (MAL) set by the Romanian legislation (GD 1134/2002) and the International Organisation of Vine and Wine (OIV, 2015) are presented in table 2.

Table 1

Metals concentration in homemade white wines

Element	Unit	W1	W2	W3	W4	W5	W6	W7
K	mg/l	690	980	710	910	820	190	430
Na		7.65	6.88	10.1	6.89	8.87	22.5	12.6
Ca		70.5	83.5	66.5	56.0	69.0	48.2	46.5
Mg		84.5	95.0	104	80.5	87.0	48.1	58.8
Al	µg/l	7.7	30.9	15.1	68.7	18.9	230	240
Fe		1.83	2.08	2.39	3.58	1.93	4.04	3.58
Cr		54.7	74.1	60.0	104	52.8	21.2	31.7
Mn		69.8	81.3	75.3	123	63.9	737	1520
Cu		57.0	26.0	44.0	41.0	56.0	470	1540
Ni		4.1	2.5	3.9	5.7	4.3	14.4	32
Zn		293	248	228	200	284	370	600
As		0.6	0.9	0.8	1.3	0.6	1.3	8.3
Pb		0.4	0.4	0.5	0.5	0.4	8.0	15

Concentrations of major elements in wines decreased in the order K>Mg>Ca>Na ranging between 190- 980 mg/l (K), 6.88-22.5 mg/l (Na), 46.5-83.5 mg/l (Ca) and 48.1-104 mg/l (Mg), while the concentration of trace elements decreased in the order Zn>Mn>Cr=Cu>Al>Ni>Fe>As>Pb, except for W6 and W7 where high contents of Cu, Zn

and Mn were found. The low contents of Na and Ca suggest that in the winemaking process clarifying agents (bentonites) was not added (Woldemariam et al., 2011).

The concentration of metals were below the MALs set both by the Romanian legislation and the International Organisation of Vine and Wine in case of samples W1-W6, while in case of sample W7 the Cu and Zn concentrations exceeded the corresponding MALs. A possible explanation for the high Cu and Zn values in wine W6 is the use of metal based pesticides.

Table 2

Maximum acceptable limits of metals according to Romanian legislation and OIV guidelines

Element	Maximum acceptable limits (mg/l)	
	GD 1134/2002	*OIV*
Cu	1	1
Pb	0.2	0.15
Zn	5	5
Na	60	80
As	0.2	0.2
Al	8	-

High concentrations of Cu that exceeds the MAL were found also in various wines from Croatia, Serbia and Spain (Banovic et al., 2009; Razic et al., 2007; Conde et al., 2002). This high concentration of Cu is of exogenous sources and was attributed to the use of copper based pesticides. Although Zn is naturally present in wine in low concentrations, the high contents found in sample W7 affects the taste of wine and is also attributed to the excessive use of pesticides. The Mn content was low in samples W1-W5 and much higher in samples W6 and W7. Although there is no MAL for Mn, its concentration is monitored during the manufacturing process as it can determine the oxidation of wine and formation of acetaldehyde (Cacho et al., 1995).

The Fe, Ni and Cr concentrations in all wines were low probably as a consequence that no metallic equipments were used during the manufacturing process of our samples. The low Fe concentration indicates that all wines are stable. The instability of wine usually appears at Fe concentrations higher than 10 mg/l (Galani-Nikolaiki et al., 2002). The low As concentration in all wines suggests that pesticides bases on arsenate was not used in the vineyards.

CONCLUSIONS

The results indicated that although the homemade wines quality and their metallic content were not strictly monitored the majority of the studied samples comply with the existing regulation and are safe for consumption. The cultivation of grapes without excessive use of fertilizers and pesticides and the traditional winemaking process without addition of chemicals and storage in wood barrels assure the low content of metals in the wine.

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