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Determination, Estimation of Dietary Intake and Target Hazard Quotients of Heavy Metals in Wines from the Bosnia and Herzegovina Market

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Abstract
Metals in red and white wines may stem from both natural and anthropogenic sources, with their concentration serving as an important parameter influencing wine consumption. The objective of this study was to determine the metal content in available wine samples from the Bosnia and Herzegovina market. Eight samples of red wine and seven white wine samples were analysed. Cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) were determined in these samples given their potential impact on wine quality and thus human health. Metal determination was conducted using flame atomic absorption spectrometry (FAAS). Limit of detection values were calculated using two methods for standard solution preparation, utilising distilled water and 10 % ethanol as blanks. Moreover, a human health risk assessment of trace elements present in wine samples was conducted. The concentrations of Cr, Cu, Fe, Mn, and Zn in the samples were found to be below the maximum allowed limits according to the regulations set by the International Organization of Vine and Wine, as well as the national regulations of Bosnia and Herzegovina, the European Union and Croatia. The content of Cd, Co, Ni, and Pb in all wine samples was below the detection limit of FAAS. The data obtained indicated that consuming 250 ml of wine samples appeared to be safe regarding the health risk associated with the potentially toxic metal intake. However, consumers should remain aware of other potential risks associated with excessive wine consumption. Regarding winemakers and the wine industry, to reduce the metal content in wine, monitoring of metal content should extend beyond just the grapes to include soil, air quality at the vineyard locations, and at different stages of the winemaking process since metal content in wine has an impact on the sensory attributes and overall quality of the wine.

Keywords
Red wine, white wine, metals, risk assessment, FAAS

1 Introduction

Wine, a globally consumed beverage, offers health benefits when consumed in small to moderate amounts. Clinical research in animal models suggests that wine may protect against cardiovascular disease, atherosclerosis, hypertension, type 2 diabetes, neurological diseases, and metabolic syndrome. The mechanism of action has been linked to its antioxidant, lipid-regulating, and anti-inflammatory properties, derived from both its alcoholic and polyphenolic components.[1] However, excessive consumption of alcohol, including wine, can have detrimental effects such as brain cell death and liver cirrhosis, as well as an increased risk of stroke and various cancers (breast, oral cavity, esophagus, liver). Excessive alcohol consumption is particularly risky in terms of cancer development.[2] Alcoholic beverages, including wine, have been integral to the human diet since ancient times.[3] Analytically, wine samples present a fairly complex matrix due to their composition of water, ethanol (typically between 9 % and 15 %), various organic acids, carbohydrates, and inorganic compounds. While some metals are essential to the human body in low concentrations, higher doses can pose health risks, such as poisoning, circulatory system diseases, nervous system diseases, and cancer. The metal content in wine can result from many factors: soil mineral composition, migration of metals from soil through plant roots, agricultural practices using fertilisers and pesticides, environmental conditions and pollution, methods of grape preparation and processing, as well as storage methods. Stainless steel tanks, wooden barrels, or bottles can also influence the metal content in wine, as grapes and wine can remain in prolonged contact with these materials.[4] In 2016, Bosnia and Herzegovina (BiH) imported nearly six times more wine than it exported,[5] with major imports coming from Croatia, Serbia, Montenegro, and North Macedonia, and exports mainly to Croatia, Germany, Serbia, and China. In BiH, the average annual wine production is about 5 million L, which ranks it 54th globally. This amount constitues only 0.02 % of the world's total wine production.[5] Wine consumption per capita in BiH was 2 l in 2002, 3.6 l in 2016, and has now reached around 7 l, according to a report by the *United States Department of Agriculture (USDA) Foreign Agricultural Service*.[6] The report indicates that wine consumption has been steadily increasing in Bosnia and Herzegovina since 2002, and that a significant amount of wine is imported from other markets since domestic production does not meet the population's demand. Given these circumstances, there is limited research on certain

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trace elements in wine from the BiH market, and the associated health risks.[7–9] Since metals are both natural components and potential contaminants in wine, monitoring their content is crucial for assessing human uptake and exposure to their harmful effects. Seventy percent of lead intake by the human body occurs through the consumption of food and beverages, and the highest content of lead is in wine.[9] The aims of this study were: a) to determine the metal content in red and white wine from the BiH market; b) to investigate whether the preparation method of calibration curve standards influences the metal content in wine samples; namely, in this study, standards were prepared using two methods: some in distilled water, and others in 10 % ethanol by volume; c) to estimate the dietary intake and target hazard quotients for metals taken through wine consumption from BiH market; and d) to compare the obtained results with the regulation of International Organization of Vine and Wine (OIV), and national regulations of BiH, EU, and Croatia, and determine if wines from the BiH market are contaminated with metals.

2 Experimental

2.1 Sample preparation and measurement

All substances used were of analytical grade and supplied from Merck (Darmstadt, Germany). Double-distilled water was used for analysis. Wine samples (*n* = 15) were obtained from the BiH market for analysis, comprising 7 white wine and 8 red wine samples. In the laboratory, the samples were preserved by transferring 80 ml of each sample into 100-ml polyethylene bottles and adding 1 ml of concentrated HNO_3. This preservation step aimed to inhibit microbial activity, which could otherwise affect the analysis results, and to maintain the analysed metals in solution. Metal content (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) was determined using a Varian Fast Sequential Atomic Absorption Spectrometer, AA240FS (Australia). All wine samples were analysed in triplicate. Two types of blanks were prepared to determine variations in metal content: one using distilled water and the other a 10 % ethanol solution. Basic data for the wine samples are presented in Table 1.

2.2 Quality control

Glassware and sample vessels were immersed in 1 mol l^{-1} HNO_3 for 24 h and subsequently washed with double-distilled water. The precision and accuracy of the analytical technique were further evaluated through recovery tests by spiking analysed samples with aliquots of metal standards. To cover the analytical measurement range, the wine samples were spiked with standard solutions of each metal at three different concentration levels. Recovery values ranged from 95 % to 105 % for all analysed metals, as shown in Table 2. The limit of detection (LOD) for the applied method was determined using three times the standard deviation of the signal from the blank solutions. The LOD values with distilled water and ethanol as blanks were as follows: Cd (0.002 mg l^{-1}; 0.004 mg l^{-1}), Co (0.005 mg l^{-1}; 0.006 mg l^{-1}), Cr (0.006 mg l^{-1}; 0.007 mg l^{-1}), Cu (0.004 mg l^{-1}; 0.008 mg l^{-1}), Fe (0.007 mg l^{-1}; 0.010 mg l^{-1}), Mn (0.2 mg l^{-1}; 0.3 mg l^{-1}), Ni (0.02 mg l^{-1}; 0.02 mg l^{-1}), Pb (0.01 mg l^{-1}; 0.02 mg l^{-1}) and Zn (0.002 mg l^{-1}; 0.005 mg l^{-1}).

Table 1 – Wine samples descriptive data
Tablica 1 – Osnovni podatci o uzorcima vina

	Wine sample code	Grape variety	Country of origin	Year of production
White wine	W1	Italian Riesling	Serbia	2010
	W2	Žilavka	BiH	2007
	W3	Žilavka and following sorts Bena, Krkošija	BiH	2008
	W4	Italian Riesling	Serbia	2010
	W5	Žilavka	BiH	2007
	W6	Žilavka	BiH	2007
	W7	Graševina	Serbia	2008
Red wine	R1	Vranac	BiH	2009
	R2	Vranac and following sorts Merlo, Cabernet Sauvignon	Serbia	2009
	R3	Blatina	BiH	2009
	R4	Prokupac and following sorts Vranac, Pinot Noir	Serbia	2010
	R5	Vranac	BiH	2008
	R6	Prokupac and Vranac	Serbia	2010
	R7	Pinot Noir	Croatia	2009
	R8	Vranac	BiH	2011

Table 2 – Recovery values for wine samples with known analyte addition
Tablica 2 – Vrijednosti analitičkog povrata za uzorke vina s poznatim dodatkom analita

Metal	Recovery / %
Cd	95
Co	97
Cr	96
Cu	99
Fe	105
Mn	100
Ni	102
Pb	97
Zn	96

2.3 Daily intake, target hazard quotients, and hazard index

The calculation of daily intake of the heavy metals from wine consumption is crucial and depends on factors such as the consumer's body weight, metal concentration in the wine, and the volume of wine consumed. To determine the estimated daily intake (EDI; mg/kg bw/day) of heavy metals through human wine consumption, the Eq. (1) was used.[10,11]

$$\mathrm{EDI} = \frac{C_\mathrm{M} \cdot V_\mathrm{R} \cdot Ef \cdot Ed}{bw \cdot At} \tag{1}$$

C_M is the mass concentration of individual metal in the wine (mg l^{-1}), V_R is the average daily consumption ration for adult wine drinkers (250 ml per person per day), *Ef* is the exposure frequency (365 days/year) and *Ed* is the exposure duration (70 years), *bw* represents the average body weight (kg): 65 kg for woman and 70 kg for men, and *At* is the time period over which the dose is averaged (365 days/year multiplied by the number of exposure years, assumed to be 65 years in this study).[10,11]

The target hazard quotients (THQ) were calculated as the ratio of EDI to the reference oral dose (RfD), using Eq. (2). THQ values represent the health risk associated with wine consumption, and RfD is the reference oral dose for each heavy metal (mg kg^{-1} bw/day). The RfD values used were: 1.5 mg kg^{-1} bw/day (Cr); $4 \cdot 10^{-4}$ mg kg^{-1} bw/day (Cu); $7 \cdot 10^{-7}$ mg kg^{-1} bw/day (Fe); 0.14 mg kg^{-1} bw/day (Mn); 0.3 mg kg^{-1} bw/day (Zn), obtained from the United States Environmental Protection Agency (US EPA).[12]

$$\mathrm{THQ} = \frac{\mathrm{EDI}}{\mathrm{RfD}} \tag{2}$$

The US EPA suggests that a THQ value less than 1 indicates a trace element exposure level that is not harmful, while a THQ greater than 1 indicates potential harm to the human body.[12] The total of the THQs found for each individual element *i* was used to estimate the cumulative chronic risk (hazard index, or HI) related to a wine sample (Eq. (3)). HI values equal to or less than 1 indicate little risk, while higher values suggest increased danger.

$$\mathrm{HI} = \Sigma \mathrm{THQ}i \tag{3}$$

3 Results and discussion

3.1. Metal content in red and white wine

One of the aims of this study was to determine the content of nine metals: Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in seven samples of white wine and eight samples of red wine from the BiH market. Table 3 presents the results of determined metals in red and white wine with standards prepared in distilled water, while Table 4 presents the metal content in red and white wine with standards prepared in 10 % ethanol.

Table 3 – Metal content in wine samples with standards prepared in distilled water
Tablica 3 – Sadržaj metala u uzorcima vina sa standardima pripremljenim u destiliranoj vodi

		Metal content / mg l^{-1}				
Wine sample		Cr	Cu	Mn	Fe	Zn
White wine	W1	0.059	0.326	0.566	3.184	0.299
	W2	0.055	0.207	0.699	0.848	0.235
	W3	0.074	0.201	0.665	2.491	0.234
	W4	0.074	0.330	1.011	2.367	0.497
	W5	0.097	0.188	0.974	4.004	0.314
	W6	0.072	0.008	0.523	0.567	0.003
	W7	0.112	0.279	0.337	3.229	0.082
Average		0.078	0.220	0.682	2.384	0.238
Red wine	R1	0.094	0.413	0.625	2.586	0.476
	R2	0.093	0.116	1.156	2.776	0.283
	R3	0.106	0.168	0.725	3.699	0.549
	R4	0.106	0.103	1.237	2.768	0.329
	R5	0.192	0.258	1.163	3.046	0.376
	R6	0.113	0.057	1.150	2.075	0.313
	R7	0.114	0.054	1.687	1.871	0.196
	R8	0.152	0.217	1.071	2.934	0.254
Average		0.121	0.173	1.102	2.719	0.347

Table 4 – Metal content in wine samples with standards prepared in 10 % ethanol
Tablica 4 – Sadržaj metala u uzorcima vina sa standardima pripremljenim u 10 %-tnom etanolu

		Metal content / mg l^{-1}				
Wine sample		Cr	Cu	Mn	Fe	Zn
White wine	W1	0.028	0.394	0.652	3.889	0.392
	W2	0.019	0.253	0.818	1.028	0.322
	W3	0.025	0.242	0.750	2.919	0.314
	W4	0.023	0.387	1.133	2.760	0.623
	W5	0.037	0.233	1.116	4.838	0.407
	W6	0.008	0.011	0.547	0.581	0.049
	W7	0.043	0.319	0.356	3.648	0.135
Average content		0.026	0.263	0.767	2.809	0.320
Red wine	R1	0.023	0.483	0.694	2.991	0.603
	R2	0.017	0.139	1.287	3.175	0.369
	R3	0.021	0.195	0.774	4.102	0.676
	R4	0.016	0.103	1.313	3.023	0.408
	R5	0.094	0.289	1.223	3.318	0.457
	R6	0.020	0.069	1.238	2.277	0.397
	R7	0.024	0.061	1.840	2.071	0.251
	R8	0.059	0.239	1.149	3.186	0.316
Average content		0.034	0.197	1.190	3.018	0.435

The content of Cd, Co, Ni, and Pb in all analysed red and white wine samples was below the LOD of the applied method.

The average metal content in the red and white wine samples followed the order: Fe > Mn > Zn > Cu > Cr, and this order remained consistent regardless of whether the standards were prepared in distilled water or in 10 % ethanol.

The results presented in Tables 3 and 4 indicate that the average content of all determined metals, except for Cu, was higher in red wine compared to white wine. This higher metal content in red wine may be attributed to the production process of red wines, where the fermentation process involves the grape skins, which contain metals and other components. In contrast, white wines undergo pressing first, during which the skins are removed, followed by the fermentation process.

Fig. 1 shows that the content of all determined metals, except chromium, in both the red and white wine samples was higher when using the standard with 10 % ethanol. This result may be due to the fact that the analysed metals are less soluble in alcohol than in water. Additionally, unlike other determined metals, chromium compounds with alcohol are known, which may have contributed to the different results for chromium. Alcohol evaporated faster in the flame, potentially leading to atomisation at a different part of the flame profile, thus resulting in different absorbance values, and it is known that only the atomisation of chromium took place in the reduction flame among all the analysed metals, owing to its distinct behaviour. The highest content of Cr among all the red and white wine samples was observed in red wine sample R5 (distilled water) at 0.192 mg l^{-1}, while the lowest content was found in white wine sample W6 (10 % ethanol). Chromium in wine can originate from vessels in which the wine is stored during the production process, or from substances applied to protect the grapes from various pests, which may contain toxic chromium compounds. Additionally, impurities occurring during fermentation and the use of chromium oxide after bottling could contribute to its presence.[13] *Dumitriu et al.*[11] suggest that the chromium content in wine may decrease during the aging process due to interactions of Cr with proteins, polyphenols, and sugars. The Cu content in

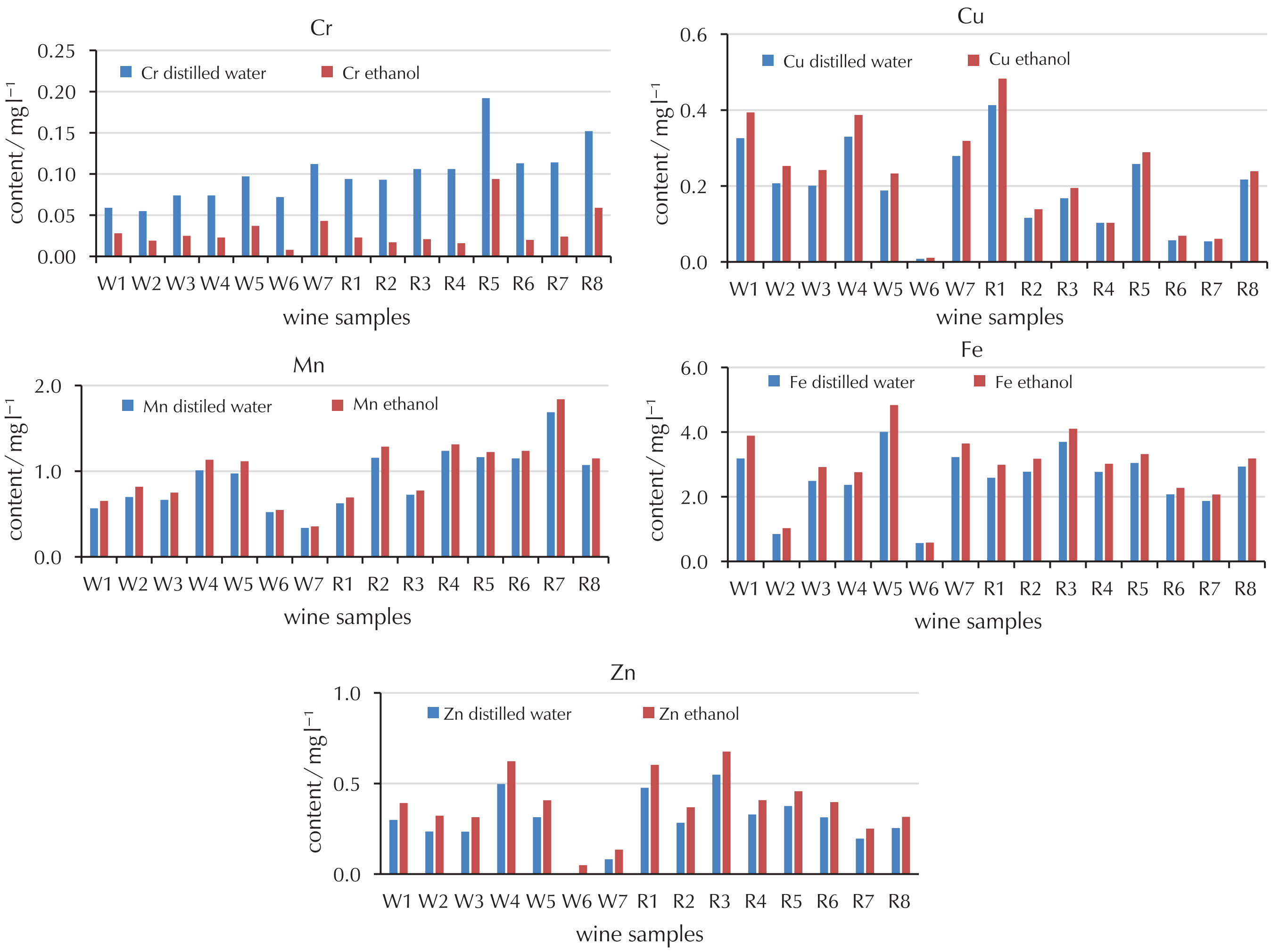

Fig. 1 – Comparison of metal content in wine using standards prepared in distilled water and 10 % ethanol
Slika 1 – Usporedba sadržaja metala u vinu primjenjujući standarde pripremljene u destiliranoj vodi i 10 %-tnom etanolu

all wine samples ranged from 0.008 mg l^{-1} (W6, distilled water) to 0.483 mg l^{-1} (R1, 10 % ethanol). Wines with Cu content exceeding 1 mg l^{-1} exhibit a metallic bitter taste; however, in this study, all analysed samples had Cu content lower than 0.5 mg l^{-1}. The presence of Cu in wine can be attributed to the use of herbicides and fungicides containing copper sulphate, as well as to the addition of copper post-fermentation to precipitate the formed sulphide.[13,14] Mn content in all wine samples ranged from 0.337 mg l^{-1} (W7, distilled water) to 1.840 mg l^{-1} (R7, 10 % ethanol). Mn, Cu, Fe, and Zn are utilised in winemaking for their ability to bind to yeast and activate metalloenzymes during alcoholic fermentation. The main Mn content in wine may originate from the soil where the grapes are grown, with higher Mn content typically found in soils with low pH.[11,15] The lowest Fe content among all the wine samples was found to be 0.567 mg l^{-1} (W6, distilled water), while the highest Fe content was 4.102 mg l^{-1} (R3, 10 % ethanol). No Fe content in the wine samples exceeded 4 mg l^{-1}; among all the determined metals, iron content was the highest. Iron is absorbed by the vine from the soil, with the grape stalks having the highest iron content, contributing to the higher iron levels in red wine compared to white wine. *Torović et al.*[14] stated that the Fe content in wine reflects its presence in the grapes and seeds, as prolonged contact of grape skin and seeds with the must during winemaking leads to higher Fe levels.

The lowest zinc content in all analysed wine samples was 0.003 (W6, distilled water), while the highest was 0.676 (R3, 10 % ethanol). None of the samples exceeded a zinc content of 0.6 mg l^{-1}. The zinc content was higher in red wine than in white, possibly due to the equipment used in the wine production and storage processes. In addition, Zn is known as an element with very high mobility in soil, making it easily absorbed by grapes.The results of this study were compared with the maximum allowed values according to OIV regulations,[16] national regulations of Bosnia and Herzegovina,[17] regulations of the European Union (EU)[18], and national regulations of Croatia.[19] The maximum permissible values of metals in wine are presented in Table 5. The results of other studies conducted worldwide were not included in the table as the metal content in wine varies based on factors such as the grape variety, climate, environmental conditions, pollution, wine production and storage processes, and the age of the wine.

According to the values presented in Table 5, we can state that the content of all determined metals in the wine samples from the BiH market does not exceed the maximum permissible values according to the mentioned regulations.

Table 5 – Maximum allowed metal content according to OIV, and national regulations of BiH, EU, and Croatia
Tablica 5 – Maksimalno dopušteni sadržaji metala prema OIV i nacionalnim propisima BiH, EU-a i Hrvatske

Element/ Regulation	Cr	Cu	Mn	Fe	Zn
BiH	ND*	1 mg kg^{-1}	ND	white wine 10 mg kg^{-1} red wine 20 mg kg^{-1}	ND
OIV	ND	1 mg l^{-1}	ND	ND	5 mg l^{-1}
EU	ND	1 mg l^{-1}	ND	white wine 10 mg kg^{-1} red wine 20 mg kg^{-1}	5 mg l^{-1}
Croatia	0.1 g l^{-1}	1 g l^{-1}	ND	white wine 10 mg kg^{-1} red wine 20 mg kg^{-1}	5 mg l^{-1}

ND* – not defined

3.2 Health risk assessment for red and white wine consumption

The metals determined in the red and white wine samples from the BiH market were used to calculate the EDI, THQ, and HI. The EDI of metals (standards prepared with distilled water) for both men (EDIm) and women (EDIf) are presented in Table 6, while the EDI of the metals (standards prepared with 10 % ethanol) are shown in Table 7.

Recommended daily allowances for the analysed metals are: Cr 2.2 µg/kg/bw/day, Cu 15–500 µg/kg/bw/day, Fe 10–18 mg/kg/bw/day, Mn 2–5 mg/kg/bw/day, and Zn 1000 µg/kg/bw/day.[20–22]

The results of the THQ for determined metals using standards with distilled water and standards with 10 % ethanol are presented in Tables 8 and 9.

Although THQ is not a measure of risk, the results presented in Tables 8 and 9 indicate that THQ values for all analysed metals were below 1, which suggests no health concerns, and confirms that consuming 250 ml *per* day is safe for consumers. The average THQ values for males and females for individual metals determined in the red and white wine samples using standards prepared

Table 6 – EDI for determined metals (calibration standards prepared with distilled water) via consumption of red and white wine from the BiH market

Tablica 6 – EDI za određivane metale (kalibracijski standardi pripremljeni s destiliranom vodom) kroz konzumiranje bijelog i crvenog vina s tržišta BiH

Sample	Cr		Cu		Fe		Mn		Zn	
	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf
	$\cdot 10^{-3}$ mg/kg/day									
W1	0.211	0.244	1.16	1.35	11.4	13.2	2.02	2.34	1.07	1.24
W2	0.196	0.228	0.739	0.857	3.03	3.51	2.50	2.90	0.839	0.973
W3	0.264	0.307	0.718	0.833	8.90	10.3	2.38	2.75	0.836	0.969
W4	0.264	0.307	1.18	1.37	8.45	9.80	3.61	4.19	1.78	2.06
W5	0.346	0.402	0.671	0.779	14.3	16.6	3.48	4.03	1.12	1.30
W6	0.257	0.298	0.029	0.033	2.03	2.35	1.87	2.17	0.011	0.012
W7	0.400	4.64	0.996	1.16	11.5	13.4	1.20	1.40	0.293	0.340
R1	0.336	0.389	1.48	1.71	9.24	10.7	2.23	2.59	1.70	1.97
R2	0.332	0.385	0.414	0.480	9.91	11.5	4.13	4.79	1.01	1.17
R3	0.379	0.439	0.60	0.696	13.2	15.3	2.59	3.00	1.96	2.27
R4	0.379	0.439	0.368	0.427	9.89	11.5	4.42	5.12	1.18	1.36
R5	0.686	0.795	0.921	1.07	10.9	12.6	4.15	4.82	1.34	1.56
R6	0.404	0.468	0.204	0.236	7.41	8.59	4.11	4.76	1.12	1.30
R7	0.407	0.472	0.193	0.224	6.68	7.75	6.03	6.99	0.70	0.812
R8	0.543	0.630	0.775	0.899	10.5	12.2	3.83	4.44	0.907	1.05

Table 7 – EDI in mg/kg/day for determined metals (calibration standards prepared with 10 % ethanol) *via* consumption of red and white wine from the BiH market

Tablica 7 – EDI u mg/kg/day za određivane metale (kalibracijski standardi pripremljeni u 10 % etanolu) kroz konzumiranje bijelog i crvenog vina s BiH tržišta

Sample	Cr		Cu		Fe		Mn		Zn	
	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf	EDIm	EDIf
	$\cdot 10^{-3}$ mg/kg/day									
W1	0.10	0.116	1.41	1.63	13.9	16.1	2.33	2.70	1.40	1.62
W2	0.068	0.079	0.904	1.05	3.67	4.26	2.92	3.39	1.15	1.33
W3	0.089	0.104	0.864	1.002	10.4	12.1	2.68	3.11	1.12	1.30
W4	0.082	0.095	1.38	1.60	9.86	11.4	4.05	4.69	2.23	2.58
W5	0.132	0.153	0.832	0.965	17.3	20.0	3.99	4.62	1.45	1.69
W6	0.029	0.033	0.039	0.046	2.07	2.41	1.95	2.27	0.18	0.20
W7	0.154	0.178	1.14	1.32	13.0	15.1	1.27	1.47	0.48	0.56
R1	0.082	0.095	1.72	2.00	10.7	12.4	2.48	2.87	2.15	2.50
R2	0.061	0.070	0.496	0.576	11.3	13.1	4.60	5.33	1.32	1.53
R3	0.075	0.087	0.696	0.808	14.6	17.0	2.76	3.21	2.41	2.80
R4	0.057	0.066	0.368	0.427	10.8	12.5	4.69	5.44	1.46	1.69
R5	0.336	0.389	1.03	1.20	11.8	13.7	4.37	5.07	1.63	1.89
R6	0.071	0.083	0.246	0.286	8.13	9.43	4.42	5.13	1.42	1.64
R7	0.086	0.099	0.218	0.253	7.40	8.58	6.57	7.62	0.90	1.04
R8	0.211	0.244	0.853	0.990	11.4	13.2	4.10	4.76	1.13	1.31

Table 8 – THQ of the analysed metals (standards prepared with distilled water) calculated separately for male (m) and female (f)
Tablica 8 – THQ vrijednosti analiziranih metala (standardi s destiliranom vodom) izračunate odvojeno za muškarce (m) i žene (f)

Sample	Cr		Cu		Fe		Mn		Zn	
	THQm	THQf	THQm	THQf	THQm	THQf	THQm	THQf	THQm	THQf
	$\cdot 10^{-3}$									
W1	0.140	0.163	29.1	33.8	16.2	18.8	14.4	16.7	3.56	4.13
W2	0.131	0.152	18.5	21.4	4.33	5.02	17.8	20.7	2.80	3.24
W3	0.176	0.204	17.9	20.8	12.7	14.7	17.0	19.7	2.79	3.23
W4	0.176	0.204	29.5	34.2	12.1	14.0	25.8	29.9	5.92	6.86
W5	0.231	0.268	16.8	19.5	20.4	23.7	24.8	28.8	3.74	4.34
W6	0.171	0.199	0.714	0.828	2.89	3.36	13.3	15.5	0.036	0.041
W7	0.267	0.309	24.9	28.9	16.5	19.1	8.60	9.97	0.976	1.13
R1	0.224	0.260	36.9	42.8	13.2	15.3	15.9	18.5	5.67	6.57
R2	0.221	0.257	10.4	12.0	14.2	16.4	29.5	34.2	3.37	3.91
R3	0.252	0.293	15.0	17.4	18.9	21.9	18.5	21.4	6.54	7.58
R4	0.252	0.293	9.20	10.7	14.1	16.4	31.6	36.6	3.92	4.54
R5	0.457	0.530	23.0	26.7	15.5	18.0	29.7	34.4	4.48	5.19
R6	0.269	0.312	5.09	5.90	10.6	12.3	29.3	34.0	3.73	4.32
R7	0.271	0.315	4.82	5.59	9.55	11.1	43.0	49.9	2.33	2.71
R8	0.362	0.420	19.4	22.5	15.0	17.4	27.3	31.7	3.02	3.51

Table 9 – THQ of analysed metals (standards prepared with 10 % ethanol) calculated separately for male (m) and female (f)
Tablica 9 – THQ vrijednosti analiziranih metala (standardi s 10 % etanolom) proračunate odvojeno za muškarce (m) i žene (f)

Sample	Cr		Cu		Fe		Mn		Zn	
	THQm	THQf	THQm	THQf	THQm	THQf	THQm	THQf	THQm	THQf
	$\cdot 10^{-3}$									
W1	0.067	0.077	35.2	40,8	19.8	23.0	16.6	19.3	4.67	5.41
W2	0.045	0.052	22.6	26.2	5.24	6.08	20.9	24.2	3.83	4.45
W3	0.059	0.069	21.6	25.0	14.9	17.3	19.1	22.2	3.74	4.34
W4	0.055	0.063	34.5	40.0	14.1	16.3	28.9	33.5	7.42	8.60
W5	0.088	0.102	20.8	24.1	24.7	28.6	28.5	33.0	4.85	5.62
W6	0.019	0.022	0.982	1.14	2.96	3.44	14.0	162	0.583	0.677
W7	0.102	0.119	28.5	3.30	18.6	21.6	9.08	10.5	1.61	1.86
R1	0.055	0.063	43.1	50.0	15.3	17.7	17.7	20.5	7.18	8.33
R2	0.041	0.047	12.4	14.4	16.2	18.8	32.8	38.1	4.39	5.09
R3	0.05	0.058	17.4	20.2	20.9	24.3	19.7	22.9	8.05	9.33
R4	0.038	0.044	9.20	10.7	15.4	17.9	33.5	38.8	4.86	5.63
R5	0.224	0.259	25.8	29.9	16.9	19.6	31.2	362	5.44	6.31
R6	0.048	0.055	6.16	7.14	11.6	13.5	31.6	36.6	4.73	5.48
R7	0.057	0.066	5.45	6.32	10.6	12.3	46.9	54.4	2.99	3.47
R8	0.14	0.161	21.3	24.7	16.3	18.9	29.3	34.0	3.76	4.36

with distilled water or 10 % ethanol were in the following order: Cu > Mn > Fe > Zn > Cr, and in red wine: Mn > Cu > Fe > Zn > Cr.

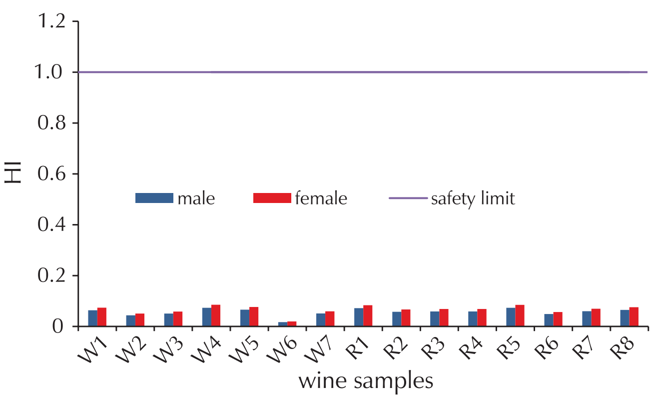

Fig. 2 – Hazard index (HI) for metals (standards prepared with distilled water) detected in wines
Slika 2 – Indeks opasnosti (HI) za metale (standard s destiliranom vodom) određene u vinu

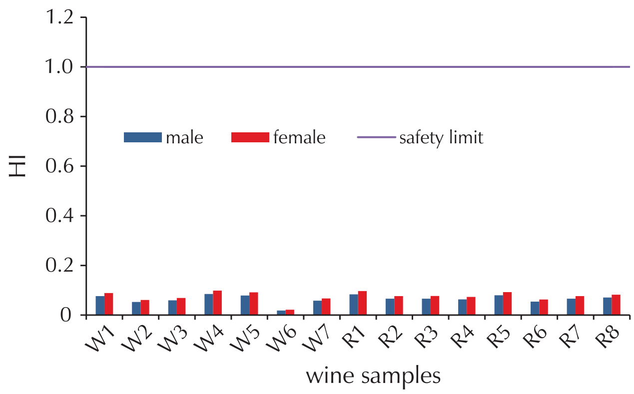

Fig. 3 – Hazard index (HI) for metals (standards prepared with 10 % ethanol) detected in wines
Slika 3 – Indeks opasnosti (HI) za metale (standard s 10 % etanolom) određene u vinu

The HI values presented in Figs. 2 and 3 for individual elements were significantly lower than 1, indicating no potential risk for individuals upon consuming red or white wine. The HI values were slightly higher for females compared to males, and they were also higher when the metals were determined using standards with 10 % ethanol. The difference in HI levels between males and females could be attributed to differences in average weight and age. People are constantly exposed to various amounts of metals through the air, water, and food they consume, highlighting the importance of being mindful of their metal intake, and the potential effects of accumulation in the body.

4 Conclusion

This study presents the results of metal content (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in seven white and eight red wine samples commercially available on the BiH market, along with a health risk assessment, and potential impact of calibration standard preparation methods (standards in distilled water *vs* standards in 10 % ethanol) on the metal content. Cr, Cu, Fe, Mn, and Zn were found to be present in both red and white wine samples at concentrations below the maximum allowed limits according to OIV regulations, and the national regulations of BiH, EU, and Croatia. The content of Cd, Co, Ni, and Pb in all samples was below the limit of detection of the applied method.

Using calibration standards prepared with 10 % ethanol resulted in higher content of all determined metals, except Cr. The EDI values for Cr, Cu, Fe, Mn, and Zn in the red and white wine samples (standards prepared in distilled water or 10 % ethanol) were below the recommended daily allowance values. The THQ and HI values did not exceed 1 for all determined metals in all analysed wine samples, regardless of whether the standards for the calibration curve were prepared in distilled water or 10 % ethanol. In terms of metal content, THQ and HI values indicate that individuals consuming 250 ml of wine per day should not experience negative health effects. However, it is essential for individuals to be mindful of other sources of heavy metal exposure, as wine is not the only route of exposure. Future research should focus on analysing metal content at various stages of grape preparation for wine production, as well as during the wine preparation and fermentation processes. Additionally, we should not ignore the influence of the soil and methods for protecting the vines from insects and diseases on the wine metal content. Insights from these analyses could provide recommendations to winemakers on how to ensure lower metal content in their wines.

List of abbreviations
Popis kratica

FAAS – flame atomic absorption spectrometry
– plamena atomska apsorpcijska spektrometrija

LOD – limit of detection
– granica detekcije

BiH – Bosnia and Herzegovina
– Bosna i Hercegovina

EU – European Union
– Europska unija

OIV – International Organization of Vine and Wine
– Međunarodna organizacija za vinarstvo i vinogradarstvo

EDI – estimated daily intake
– procijenjeni dnevni unos

RfD – reference dose
– referentna doza

THQ – target hazard quotient
– ciljani koeficijent opasnosti

HI – hazard index
– indeks opasnosti

US EPA – United States Environmental Protection Agency
– Agencija za zaštitu okoliša Sjedinjenih Američkih Država

ND – not detected
– nije detektirano

EDIm – estimated daily intake for men
– procijenjeni dnevni unos za muškarce

EDf – estimated daily intake for women
– procijenjeni dnevni unos za žene

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SAŽETAK

Određivanje, procjena unosa konzumiranjem i koeficijent ciljane opasnosti za teške metale u vinu s tržišta u Bosni i Hercegovini

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Metali u crvenom i bijelom vinu mogu nastati iz prirodnih i antropogenih izvora, a koncentracija metala može biti važan parametar koji utječe na konzumaciju vina. Cilj ovog rada bio je utvrditi sadržaj metala u dostupnim uzorcima vina s tržišta u Bosni i Hercegovini (BiH). Analizirano je osam uzoraka crvenog vina i sedam uzoraka bijelog vina. U uzorcima vina određeni su kadmij (Cd), krom (Cr), kobalt (Co), bakar (Cu), željezo (Fe), mangan (Mn), nikl (Ni), olovo (Pb) i cink (Zn), jer ti elementi mogu utjecati na kvalitetu vina, a time i na zdravlje ljudi. Metoda primijenjena za određivanje metala bila je plamena atomska apsorpcijska spektrometrija (FAAS). Vrijednosti granice detekcije izračunate su za dvije metode pripreme standardnih otopina, koristeći se destiliranom vodom i etanolom kao kontrolnim uzorcima. Nadalje, provedena je procjena rizika za zdravlje ljudi s obzirom na elemente u tragovima prisutne u uzorcima vina. Koncentracije Cr, Cu, Fe, Mn i Zn u uzorcima vina bile su ispod maksimalno dopuštenih granica prema propisima Međunarodne organizacije za vinovu lozu i vino i nacionalnim propisima BiH, Europske Unije i Hrvatske. Sadržaj Cd, Co, Ni i Pb u svim uzorcima vina bio je ispod granice detekcije FAAS-om. Dobiveni podatci pokazali su da se konzumacija 250 ml uzoraka vina čini sigurnom s obzirom na zdravstveni rizik povezan s unosom potencijalno toksičnih metala, ali potrošači bi trebali biti svjesni drugih potencijalnih rizika povezanih s prekomjernom konzumacijom vina. Što se tiče vinara i vinske industrije, da bi smanjili sadržaj metala u vinu, trebali bi pratiti sadržaj metala ne samo u grožđu već i u zemljištu, u zraku na lokaciji vinograda i nakon različitih faza procesa proizvodnje vina, jer sadržaj metala u vinu utječe na senzorne karakteristike i kvalitetu vina.

Ključne riječi
Crveno vino, bijelo vino, metali, procjena rizika, FAAS

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