Metal Concentrations of Red Wines in Southeast Romania

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ABSTRACT

Daily consumption, wine contributes to the requirements of essential elements, such as Ca, Fe, Mn, Mo, Co, Cr, K, Ni, Se and Zn for humans. However, the presence of significant amount of heavy metal in wine may harm the health of consumers. The present work is aimed at establishing the heavy metal content in red wines from Dealu Bujorului vineyard using ICP-MS method for the determination of metals content. In this study 3 red wines obtained from 'Băbească neagră', 'Negru Aromat' and 'Burgund Mare' cultivars were investigated. The wine samples were obtained from micro-wine production under conditions of 2014, 2015, 2016 from Dealu Bujorului vineyard. The determination of 13 elements was performed with ICP-MS. The high level of Ca (64.81-62.49 mg/L), Mg (132.61-101.44 mg/L) and Fe were observed in the wine samples analysed. Heavy metals like As, Cd, U, Hg and Pb was found below acceptable limits. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine. Calcium and magnesium were the most abundant elements in all investigated wine samples. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine.

Keywords: *mineral content, ICP-MS, Vitis vinifera*

INTRODUCTION

Many metals are among the hundreds of different substances commonly found in wines. Only one sample of wine (Australian Shiraz) detected 30 metals with a total concentration of more than 5600 mg/L (Hague *et al.*, 2008). Metals enter a wine as a final product in different ways, while their structure and concentration in wine depend on at least four sources. The first, and frequently mentioned source, involves soil on which a vineyard area is established, and capacity of wine to absorb various mineral sustances (Blesić *et al.,* 2017). The second source is linked to the ways and conditions of grape production, among which applications of pesticides and environmental air pollution are frequently stressed (Angelova *et al.,* 1999). The third source of factors are those related to the alcoholic fermentation and possibly added different substances (oenological substances) during the production of wine (Catarino *et al.,* 2008). The fourth source includes subsequent contaminations of wine with metals by the

Tab. 1. Ecoclimatic conditions in Dealu Bujorului Vineyard

Period	Annual period		Conventional vegetation period			Oenological index
	Average temperature (˚C)	Average precipitation (mm)	Average temperature (˚C)	Insolation (hours)	Average precipitation (mm)	
2003-2013	11.7	470.6	3536.6	1392.7	295.6	4883.6
2014	10.8	450.2	3220.3	1337.0	258.0	4549.3
2015	11.4	525.4	3358.6	1480.5	218.2	4870.9
2016	11.2	690.4	3369.8	1449.5	319.4	4749.9

equipment used during the wine making process, the characteristics of vessels for wine storage, and also the characteristics of a glass used for wine bottles (Kristl *et al.,* 2003).

Metals in wines may have a number of roles, organoleptic characteristics can be influenced positively or negatively, through causes of theier different instabilities, to the fact that wines can be considered sources of metals needed in human diet (Blesić *et al.,* 2017). Besides the metals which are typically abundant in grapes (Ca, Mg and K), metals such as Cu, Fe, Cr, Zn and Mn are necessary or useful in a series of physiological processes in wine yeasts and humas (Marais and Blakhurst, 2009). The high concentration of metals in wines, as well as in other food may jeopardize the consumers health. The fact is that so far there have not been precise characterization of the impact of a number of metals found in food on human health. Only Pb, Hg and Cd are undoubtedly considered toxic, with a certain possibility of toxicity for Ni, Cu, V, Cr, Al and Ag in high concentrations (Marais and Blakhurst, 2009). Consequently, the Organisation International de la Vigne et du Vin (OIV) established maximum acceptable limits for only a few elements in wine (Pb, Cd, Cu, Zn, Na, Ag, As, Br, F and B; OIV International Code of Oenological Practices, 2015).

The aim of this study was to find concentration of the challenged thirteen metals (Ca, Mg, Na, Cu, Fe, As, Cd, Cr, Ni, U, Zn, Hg and Pb) in red wine from the vintage 2014, 2015 and 2016 originating from the Dealu Bujorului vineyard.

MATERIALS AND METHODS

Study area

A total of 21 wine samples were analysed (9 red wines). Samples originated from Dealu Bujorului vineyard (45°52′10″ N, 27°55′8″E) (n = 21). The Dealu Bujorului vineyard is characterized by an alternate landscape, from flat to hilly areas, with altitude between 100 and 225 m and the predominant soil is levigated chernozem having a clayey sand texture with pH between values 7.4 and 8.1. Although they have moisture deficit, natural conditions (ecoclimatic and ecopedological) offer viable ecosystem for the development of vineyard. Centers of vineyard are: Bujoru, Smulti, Oancea, Beresti.

The 2014-2016 period showed a therMPL deficit compared with the average 2003-2013, the maximum deficit of 0.9 ºC was recorded in 2014. Precipitation varied from 450.2 mm/2014 to 690.4 mm/2016. During the vegetation period the optiMPL precipitation (250mm) was recorded in 2014 and 2016, in 2015 the precipitation decreases (31.8 mm) compared with the optiMPL precipitation. The isolation from vegetation period ranges from 1337.0 hours/2014 to 1480.5 hours/2015. The values of the oenological index in 2014 shows that in this vineyard had presented more favorable conditions for red wine and in 2015-2016 values of the oenological index shows there are more favorable conditions for white wines.

Sample collection and microvinification process

The samples used in this experiment were obtained from the wines produced from 'Băbească Neagră', 'Negru Aromat', and 'Burgund Mare' under the conditions of 2014, 2015 and 2016 year, from Dealu Bujorului vineyard. The wine samples resulted from micro-wine production. Micro-vine production it was done according to the methodology described by Bora *et al*. (2016). All wines were providing by the wineries as finished wines in 750 mL glass bottles with cork

Tab. 2. Instrumental conditions for the determination of each element (ICP-MS technique)

Element	Correlation coefficient	LoD* (μg/L)	LoQ*** (μg/L)	BEC** (μg/L)	Element	Correlation coefficient	LoD* (μg/L)	LoQ*** (μg/L)	BEC** (μg/L)
Ca	0.9999	5.66	18.86	20.82	Mg	0.9999	2.73	9.09	9.09
Na	0.9999	3.98	13.25	32.12	Cu	0.9999	0.04	0.13	0.23
Fe	0.9999	5.21	17.35	71.39	As	0.9999	0.23	0.77	0.53
Cd	0.9999	0.02	0.06	0.02	Cr	0.9999	1.66	5.53	0.63
Ni	0.9999	0.05	0.19	0.09	U	0.9999	0.02	0.08	0.00
Zn	0.9999	0.37	1.25	5.40	Hg	0.9999	0.04	0.13	0.12
Pb	0.9999	0.003	0.001	0.002					

*Detection limit; **Background equivalent concentration; ***Quantification limit.

stoppers and were stored at 3-4 °C before analysis. One bottle was used for each sample, and three replicates were taken. All vines were planted since 1979, and the vine plantation was organized with 2.2 x 1 m distance between rows and plants. Vines were pruned according to the Guyot system and were grown on speliers.

Reagents and solutions

Thirteen elements (Ca, Mg, Na, Cu, Fe, As, Cd, Cr, Ni, U, Zn, Hg and Pb) were determined in order to assess their concentration in wines samples. The analysis was made using multielement analysis and ICP-MS technique, after an appropriate dilution, using external standard calibration method. Each sample was analyzed in duplicate and each analysis was prepared from consisted of three replicates. The calibration was performed using XXI CertiPUR multielement standard solution and from individual standard solution of Hg. The intermediate solutions stored in polyethylene bottles and glassware were cleaned by soaking in 10% v/v HNO_3 for 24 hours and rinsing at least ten times with ultrapure water (Milli-Q Integral ultrapure water-Type 1). The accuracy of the methods was evaluated by replicate analyses of fortified samples (10 μL-10 mL concentrations) and the obtained values ranged between 0.8-13.1%, depending on the element. The global recovery for each element was estimated and the obtained values were between 84.6-100.9%.

For quality control purpose, blanks and triplicates samples (n = 3) were analyzed during the procedure. The variation coefficient was under 5% and detection limits (ppb) were determined by the calibration curve method. Limit of detection (LoD) and Limit of quantification (LoQ) limits were calculated according to the next mathematical formulas: LoD = 3SD/s and LoQ = 10 SD/s (SD = estimation of the standard deviation of the regression line; s = slope of the calibration curve).

Sample preparation for determination of metals from wine using ICP-MS.

For the determination of metals from wine samples were used an amount of 0.2 mL wine and adjust 8 mL (7 mL HNO_3 69%+1 mL H_2O_2), after 15-30 minutes the mineralization was performed using a microwave system Milestone START D Microwave Digestion System set in three steps: step I (time 10 min., temperature 200ºC), step II (time 15 min., temperature 200ºC) and step III (time 60 min., ventilation - temperature 35ºC). After mineralization, samples were filtered through a 0.45 mm filter and brought to a volume of 50 mL.

Instrumentation

The determination of metals was performed on mass spectrometer with inductively coupled plasma, iCAP Q Thermo scientific model (ICP-MS), based polyatomic species before they reach the quadrupole mass spectrometer. The instrument was daily optimized to give maximum sensitivity for M^+ ions and the double ionization and oxides monitored by the means of the ratio between Ba^{2+}/Ba^+ and Ce^{2+}/CeO^+, respectively, these always being less than 2%. The experimental conditions were: argon flow on nebulizer (0.84 L/min.), auxiliary gas flow 0.80 L/min., argon flow in plasma 15 L/min., lens voltage 7.31 V; RF power in plasma 1100 W, spray chamber temperature (2.51±1.00 °C). Accuracy was calculated for the elements taken into consideration (0.5-5.0%).

Statistical analysis

The statistical interpretation of the results was performed using the Duncan test, SPSS Version 24 (SPSS Inc., Chicago, IL., USA). The statistical processing of the results was primarily performed in order to calculate the following statistical parameters: average and standard deviation. This data was interpreted with the analysis of variance (ANOVA) and the average separation was performed with the DUNCAN test at $p \leq 0.05$. In order to determine if the concentration of metals can influence each other, the correlation coefficient was calculated using SPSS version 23 Pearson (SPSS Inc., Chicago, IL., USA).

RESULTS AND DISCUSSION

Tables 2-3 give the elemental concentration of the wines for Center Târgu Bujoru, Dealu Bujorului vineyard. For some samples the elemental concentration were not significantly above limit of detection (LOD) and therefore the LOD appers as a lower limit of the range for that particular region. In such cases these samples were not included in the calculations of the mean and standard deviation (sd).

In Table 3 we present the content of major elements in wine samples. Mg and Ca show high concentrations in wine. Mg is an essential micronutrient in plants bening an essential elements in the chlorophyll molecule and, together with calcium contributes to the structure of the cell walls (dos Santos *et al.*, 2010). Mg concentration is quite stable in the analysed wines. In most samples, the concentration varied in the range of 101.44±1.92-132.61±2.43 mg/L with an average of 113.04±4.55 mg/L. Ca is a natural constituent of grapes, although this, may be influenced by the addition of fungicides used for spraying of vines may also contribute to the Ca content of wine (Álvarez *et al.*, 2007). The concentration of Ca varied in the range of 51.36±2.26-64.81±3.36 mg/L with an average of 58.38±2.67 mg/L. Variety 'Burgund Mare' (2014) and 'Băbească Neagră' (2014) has recorded the highest concentration of Mg and Ca while the lowest values were recorded to 'Băbească Neagră' (2014) and 'Burgund Mare' (2016) variety. Just in the case of Mg, Na is stable in the analysed wines. 'Negru Aromat' variety was recorded the higest values [53.49±5.04 mg/L (2015)] and also de loweste values [40.20±1.96 mg/L (2014)] of Na (Tab. 3).

Regarding Fe concentration in wines, this varied in the range of 1.66±0.18-2.35±0.17 mg/L with an average of 1.96±0.11 mg/L. Varietis 'Negru Aromat'[2.35±0.17 mg/L (2015); 2.35±0.14 mg/L (2014)] and 'Băbească Neagră' [2.19±0.15 mg/L (2015)] recorded the higest values.

It is well-known that Cu is one of the most studied element in wine-growing areas. It is effective against a high number of crop pests and it is utilised as a fungicide, a bactericide and also as a herbicide (Provenzano *et al.*, 2010). Different Cu formulations are used against grapevine (*Vitis vinifera L.*) downy mildew and they have a secondary effect on grapevine powdery mildew and on a wide range of other grapevine insect pests and diseases (Boubals *et al.*, 2001). The average value of Cu in wines samples were 0.64 mg/L, with a minimum of 0.50 mg/L and a maximum of 0.75 mg/L. Varietis 'Negru Aromat' [0.75±0.11 mg/L (2014); 0.71±0.03 mg/L (2015)] recorded the higest values while 'Burgund Mare' variety recorded de lowest values [0.50±0.02 mg/L (2014)].

Concentration of Na (60 mg/L) and Cu (1 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine (OIV 2016).

Regarding the content of As, Cd and Cr (Tab. 4), the Cr was recorded the higest values, followed by Cd and As. Concentration of Cr from wines varied in the range of 331.19±2.20 to 672.42±2.93 µg/L with an average of 489.15±5.15 µg/L compared with As concentration (10.09±0.51 µg/L to 14.79±3.28 with an average of 11.66±1.07 µg/L) and Cd (0.11±0.03 µg/L to 0.17±0.02 with an average of 0.13±0.02 µg/L). 'Băbească Neagră' variety recorded the lowest concentration of Cd [0.11±0.03 µg/L (2016)] and Cr [331.19±2.20 µg/L (2015)], in case of As 'Burgund Mare' variety recorded the lowest concentration As [10.09±0.51 µg/L (2014)]. The highest concentration of As and Cr was recorded in wine obtained from 'Burgund Mare' variety [14.79±3.28 µg/L As (2016)] and [672.42±2.93 µg/L Cr (2014)] while 'Băbească Neagră' variety recorded the highest concentration of Cd [0.17±0.02 µg/L (2014)].

Concentration of Ni from wines varied in the range of 528.87±6.51 to 722.07±6.21 µg/L with an average of 616.00±4.98 µg/L. It can be seen as the 'Băbească Neagră' variety were recorded the lowest concentration [528.87±6.51 µg/L Ni (2015)] and at the opposite pole with the highest concentration was recorden in the 'Cabernet Sauvignon' variety [722.07±6.21 µg/L Ni (2014)].

Tab. 3. The content of major element in wine samples (mg/L) (Mean ± standard deviation) (n = 3)

Area	Variety	Years	Total metal concentration				
			Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cu (mg/L)	Fe (mg/L)
			M.P.L.	M.P.L.	M.P.L.	M.P.L.	M.P.L.
			-	-	60 mg/L	1 mg/L	-
Dealu Bujorului Vineyard	'Băbească Neagră'	2014	51.36±2.26 b *β*	132.61±2.43 a *α*	44.55±1.19 bc *αβ*	0.73±0.09 ab *α*	1.66±0.18 e *β*
		2015	53.55±2.00 b *αβ*	122.58±1.10 b *β*	49.84±4.28 a *α*	0.62±0.04 bc *αβ*	2.19±0.15 ab *α*
		2016	56.67±1.07 b *α*	108.12±8.22 c γ	42.62±2.66 c *β*	0.53±0.10 c *β*	1.95±0.07 cd *α*
	'Negru Aromat'	2014	62.49±0.86 a *α*	117.49±5.63 b *αβ*	40.20±1.96 c *β*	0.75±0.11 a *α*	2.35±0.11 a *α*
		2015	55.31±2.32 b *β*	119.75±2.52 b *α*	53.49±5.04 a *α*	0.71±0.03 ab *α*	2.35±0.17 a *α*
		2016	54.28±4.58 b *β*	108.42±6.35 c *β*	41.42±0.87 c *β*	0.61±0.06 bc *α*	1.78±0.07 de *β*
	'Burgund Mare'	2014	64.81±3.36 a *α*	102.85±4.85 c *β*	52.29±3.00 a *α*	0.50±0.02 c *β*	1.74±0.07 de *β*
		2015	52.55±2.32 b *β*	118.49±3.33 b *α*	48.90±2.01 ab *α*	0.63±0.07 abc *α*	2.08±0.16 bc *α*
		2016	56.66±4.16 b *β*	101.44±1.92 c *β*	40.76±1.42 c *β*	0.60±0.06 bc *αβ*	1.85±0.02 de *β*
Average			58.38±2.67	113.04±4.55	45.33±2.21	0.64±0.05	1.96±0.11
Minimum Values			51.36±2.26	101.44±1.92	40.20±1.96	0.50±0.02	1.66±0.18
Maximum Values			64.81±3.36	132.61±2.43	53.49±5.04	0.75±0.11	2.35±0.17
F.			7.009	14.625	10.065	4.602	13.754
Sig.			***	***	***	**	***
Variety		F.	5.169	19.421	1.560	6.207	12.659
		Sig.	**	***	*ns*	***	***
Years		F.	8.808	24.450	23.634	3.561	20.823
		Sig.	**	***	***	*ns*	***
Variety x Years		F.	7.029	7.315	7.533	4.320	10.768
		Sig.	**	**	**	*	***
Avram *et al.*, 2014		2008	63.72	113.24	31.30		
Galgano *et al.*, 2008			83.17±13.91	102.35±15.59	20.97±10.16	0.15±0.06	3.91±1.16
Đurđić *et al.*, 2017			83.10	94.90	8.48	0.13	1.32

Average value ± standard deviation (n = 3). Roman letters represent the significance of the variety difference (*p ≤ 0.05*). Greek letters represent the significance of the same variety cultivated in other year's difference (*p ≤ 0.05*). The difference between any two values, followed by at least one common letter, is insignificant. M.P.L. = Maximum Permissible Limit.

The results obtained are compared with those obtained by Paneque *et al.,* 2017 (400.00 µg/L Ni average value), Karataş *et al.,* 2015 [460.00±0.30 µg/L Ni (2011) Cabernet Sauvignon] and in the case of the results obtained by Thiel *et al.,* 2004 (24.9 µg/L Ni average value), Geana *et al.,* 2014 (18.39 µg/L Ni Dragasani vineyard) these results are significantly lower than those obtained in this research (Tab. 4).

Concentration of Zn from wines varied in the range of 2134.29±6.32 µg/L to 3254.83±4.89 µg/L with an average of 2612.22±8.41 µg/L Zn, compared with U concentration 0.13±0.01 µg/L to 0.31±0.04 µg/L with an average of 0.19±0.02 µg/L. As the accumulation of these two metals is similar, lowest concentration was recorded in the 'Băbească Neagră' variety [0.13±0.01 µg/L U (2016)], [2134.29±6.32 µg/L Zn (2015)], while 'Burgund Mare' variety recorded the highest concentration [0.31±0.04 µg/L U (2014)], [3254.83±4.89 µg/L Zn (2014)]. The results obtained are compared with those obtained by Geana *et al.,* 2014 [0.86 µg/L U and 563.08 µg/L Zn (average value) Dragasani vineyard], Paneque *et al.,* 2017 (2800 µg/L Ni average value). Concernig the results presented by Karataş *et al.,* 2015 [5070.00±850.00 µg/L Zn Syrah (2011), 4490.00±13.00 µg/L Zn Tannat (2011)] and also by Thiel *et al.,* 2004 (0.55 µg/L U average value), these results are significantly higher than those obtained in this research (Tab. 4).

Regarding Hg and Pb concentration from wines, this varied in the range of 0.19±0.02 µg/L to 0.43±0.04 µg/L Hg, 21.28±1.52 µg/L to 55.10±3.49

Tab. 4. The content of toxic elements in wine samples (µg/L) (Mean ± standard deviation) (n = 3)

Area	Variety	Years	Total metal concentration							
			As (µg/L)	Cd (µg/L)	Cr (µg/L)	Ni (µg/L)	U (µg/L)	Zn (µg/L)	Hg (µg/L)	Pb (µg/L)
			M.P.L.	M.P.L.	M.P.L.	M.P.L.	M.P.L.	M.P.L.	M.P.L.	M.P.L.
			0.2 mg/L	**0.01 mg/L**	-	**1 mg/L**	-	**5 mg/L**	-	**0.15 mg/L**
Dealu Bujorului Vineyard	'Băbească Neagră'	2014	13.58±0.95 ab α	0.17±0.02 a α	578.55±9.91 b α	530.89±8.78 f β	0.30±0.02 a α	2341.52±18.00 c β	0.24±0.05 b α	55.10±3.49 a α
		2015	14.48±1.09 a α	0.11±0.04 b β	331.19±2.20 g γ	528.87±6.51 f β	0.13±0.02 c β	2134.29±6.32 d γ	LOQ e β	52.59±1.52 a α
		2016	12.49±2.52 abc α	0.11±0.03 ab β	399.27±8.49 d β	582.73±5.46 b α	0.13±0.01 c β	2563.60±8.62 b α	0.23±0.02 bc α	22.52±1.37 d β
	'Negru Aromat'	2014	11.38±1.01 bc β	0.15±0.06 ab α	376.27±1.65 e β	722.07±6.21 a α	0.18±0.03 b α	2572.22±4.21 b α	0.43±0.04 a α	28.08±6.70 c β
		2015	14.17±0.48 ab α	0.14±0.03 ab α	434.62±5.22 c α	543.87±6.36 e γ	0.15±0.02 c β	2146.62±11.52 d β	LOQ e γ	52.87±1.91 a α
		2016	12.32±1.74 abc $\alpha\beta$	0.13±0.02 ab α	337.59±8.59 fg γ	579.32±0.58 b β	0.14±0.02 c $\alpha\beta$	2563.09±1.62 b α	0.20±0.01 d β	21.28±1.52 d β
	'Burgund Mare'	2014	10.09±0.51 c β	0.13±0.08 ab α	672.42±2.93 a α	633.37±1.32 b α	0.31±0.04 a α	3254.83±4.89 a α	LOQ e β	35.46±2.76 b β
		2015	13.96±1.14 ab $\alpha\beta$	0.11±0.03 b α	425.95±8.49 c β	544.26±0.53 e γ	0.13±0.02 c β	2146.75±7.85 d γ	LOQ e β	53.24±2.00 a α
		2016	14.79±3.28 a α	0.14±0.04 ab α	343.92±3.36 f γ	565.48±1.24 d β	0.14±0.01 c β	2573.14±4.15 b β	0.19±0.02 cd α	22.32±0.94 d γ
Average			11.66±1.07	0.13±0.02	489.15±5.15	616.00±4.98	0.19±0.02	2612.22±8.41	0.17±0.02	35.69±2.21
Minimum Values			10.09±0.51	0.11±0.03	331.19±2.20	528.87±6.51	0.13±0.01	2134.29±6.32	< 0.14	21.28±1.52
Maximum Values			14.79±3.28	0.17±0.02	672.42±2.93	722.07±6.21	0.31±0.04	3254.83±4.89	0.43±0.04	55.10±3.49
F.			3.184	1.764	1069.134	448.420	44.455	4825.922	123.940	77.502
Sig.			*	*ns*	***	***	***	***	***	***
Variety		F.	1.304	1.079	559.329	398.493	10.510	3055.576	88.617	23.161
		Sig.	*ns*	*ns*	***	***	**	***	***	***
Years		F.	6.589	3.393	2156.113	710.507	135.790	10524.531	244.890	243.673
		Sig.	**	*ns*	***	***	***	***	***	***
Variety x Years		F.	2.421	1.293	780.548	342.340	15.760	2861.790	81.127	21.587
		Sig.	*ns*	*ns*	***	***	***	***	***	***
Avram *et al.*, 2014		2008	21.12	0.22						35.90
Đurđić *et al.*, 2017			16.10	1.99	5.49			635.00		47.80

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \le 0.05$). Greeks letters represent the significance of the same variety cultivated in other year's difference ($p \le 0.05$). The difference between any two values, followed by at least one common letter, is insignificant. M.P.L. = Maximum Permissible Limit.

Tab. 5. Pearson correlation matrix between the main analysed wine parameters

	Ca	Mg	Na	As	Cr	Ni	U	Zn	Hg	Pb
Ca	1.000									
Mg	-0.438**	1.000								
Na	0.075	0.129	1.000							
As	-0.497**	0.190	0.128	1.000						
Cr	0.288	0.077	0.418*	-0.418*	1.000					
Ni	0.728**	-0.306	-0.312	-0.568**	0.071	1.000				
U	0.325	0.133	0.202	-0.401*	0.899**	0.196	1.000			
Zn	0.708**	-0.630**	-0.088	-0.629**	0.538**	0.579**	0.553*	1.000		
Hg	0.170	0.023	-0.785**	-0.223	-0.224	0.592**	0.035	0.144	1.000	
Pb	-0.401*	0.708**	0.616**	0.333	0.304	-0.528**	0.233	-0.565**	-0.534**	1.000

*the correlation is significant at $p < 0.05$ in 95%; ** the correlation is highly significant at $p < 0.01$, in 99%; N = 27. In the case of Cu, Cd and Fe concentration from wine, these metals heave not registered any correlation coefficient.

μg/L Pb with an average of 0.17±0.02 μg/L Hg and 35.69±2.21 μg/L Pb. In the case of Hg, the higest concentration were recorded at 'Cabernet Sauvignon' variety [0.43±0.04 μg/L Hg (2014)] and the lowest concentration were recorded at Burgund Mare' variety [0.19±0.02 μg/L Hg (2016)]. Pb recorded the lowest concentration at 'Cabernet Sauvignon' variety [21.28±1.52 μg/L Pb (2016)], and the higest concentration were recorded at Băbească Neagră' variety [55.10±3.49 μg/L Pb (2014)]. The results obtained are lower then obtained by Voica *et al.,* 2009 [0.64±0.00 μg/L Hg, 21.74±0.00 μg/L Pb], Paneque *et al.,* 2017 [50.00±10.00 μg/L Pb], Geana *et al.,* 2014 (0.86±0.55 μg/L U).

Concentration of As (0.2 mg/L), Cd (0.01 mg/L), Ni (1 mg/L), Zn (5 mg/L), and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine (OIV 2016).

The results indicated that Romanian wines are rich in Ca, Mg, Cr there are moderately rich in Na, Fe, Ni, Cu and shows a low concentration of As, Cd, U, Zn, Hg and Pb.

The Pearson correlation between the elements analysed in wine

In order to determine if the concentration of metals can influence each other, the Pearson correlation coefficient was calculated for each studied parameter as it shown in (Tab. 5). A Pearson correlation coefficient value higher than 0.5 shows a strong correlation between the analysed varieties, a positive correlation between the two parameters shows that both parameters increased, a negative correlation indicates that a parameter increased while the second one decreased and vice-versa.

These provide a large number of both positive and negative correlations between the concentration of elements from wines. There are some relevant examples: Mg & Ca, As & Ca, Cr & Na, Cr & As, Ni & Ca, Ni & As, U & As, U & Cr, Zn & Ca, Zn & Mg, Zn & As, Zn & Cr, Zn & Ni, Hg & Na, Hg & Ni, Pb & Ca, Pb & Mg, Pb & Na, Pb & Ni, Pb & Zn, Pb & Hg. In the case of Cu, Cd and Fe the values of the Pearson correlation coefficient for these parameters displayed no correlations.

Based on the previous Pearson correlation index, through this present research have been shown that the concentration of some metals from wine can influence each other.

CONCLUSION

In this study the characterisation of Romanian wines according to their elemental composition was performed. Calcium and magnesium were the most abundant elements in all investigated red and white wines samples. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine (OIV 2005). Based on the previous Pearson correlation index, through this present research have been shown that the concentration of some metals from wine can influence each other.

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