INFLUENCE OF MICRO-, MACROELEMENTS AND HEAVY METALS ON WINE QUALITY

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Abstract
From the chemical point of view wine is a complex mixture of water, sugar, inorganic and organic materials. There are some factor which influence wine composition: grape varieties, soil type, the climate, type of culture, agrochemical product (fertilizers and pesticides) and the practices used for wine making. These factors are directly involved in wine and wine characterization. Besides the quality issues that these heavy metals create in the wine, they also affect the health of wine consumers. The aim of this paper is to determine the qualitative charateristics of wine, but also to determine the quantitative of five elements: Na, Mg, Cu, Pb, and Cd from wine, using FAAS. The bilogical material used was compoused by the varieties: Fetească albă, Fetească regală, Riesling Italian *and Pinot gris grown in Silvania vineyard. The values obtained for alcoholic strength, total acidity, residual sugar and dry extract is specific for the four analysed varieties. The average concentration of metals in samples of wine was: 39.17±1.11 mg/L (Na); 101.08±0.89 mg/L (Mg); 0.60±0.03 mg/L (Cu) and 0.13±0.01 mg/L (Pb), in case of Cd concentration of this heavy metal are below the detection limit. Concentration of micro-, macroelements and heavy metals in wine samples was recorded below the recommended health limits of the International Organization of Vine and Wine. Correlation analysis revealed a number of strong correlation between the qulitative characteristics of wine and concentration of micro-, macroelements and heavy metals.*

Keywords: elements content, FAAS technique, *Vitis vinifera L.*, Pearson Correlation

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1. INTRODUCTION

Wine is a food product, obtained exclusively by total/partial alcoholic fermentation of fresh grapes, whether or not pressed, or by must fermentation and also is one of the most widely consumed beverages in many country of the world, which has been well-known since the early periods of civilization (Tariba 2011). From the chemical point of view wine is a complex mixture of water, sugar, ethanol, amino acids, polyphenolic compounds, anthocyanins, inorganic and organic materials (Bora et al., 2015b; Dalipi et al., 2015; Monici et al., 2003; Voica et al., 2009).
The composition of wine is influenced by many factors related to the specific production area: grape varietes, culture, soil and climate, winemaking, transport and storage (Dehelean and Voica, 2011). The information about the quantitative concentration of various components of wine al all stages of wine making allows winemaker to control the process of obtaining highquality wine that possesses a certain taste, bouquet, color, flavor, and transparency.
Authenticity of wine is a subject of on going concern and has been extensively investigated, is a guaranteed by strict guidelines laid down by the responsible national authorities (e.g. Institut National des Appellation & Origines in France, or the Australian Wine and Brandy Corporation in Australia) which include sensory evaluation, chemical analyses and examination of the records kept by wine producers (Dion 2008).
A major interest resides in the fact that elements content can be used to characterize the wines by their geographical origin, minerals being the most appropiate composition elements for discrimination according to geographical origin, because they bring a direct

relationship with the composition of the soil on which vines are grown (Avram et al., 2014; Alvarez et al., 2007; Frias et al., 2002; Kruzlicova et al., 2013).

Soil contamination by macro-, micro and toxic elements from waste dumpsite has been a major concen due to their toxicity, threat to human life and environment (Ebong et al., 2014). The analysis for certain elements in wines is of special interest due to their toxicity in case of excessive intake, and also the effect they seem to have on the organoleptic properties of wine (Lara et al., 2005; Galani-Nikolakaki et al., 2002). The presence of these elements can influence the wine making process or can change the taste and quality of the final product but the content of metals in wine can be attributed to natural sources (the atmospheric deposition of airborne particulate matter on grapes and transfer of metals from the soil via the root to the grapes and finally to wine) and to contamination during the wine-making process (Pyrzynska 2004).

Moderate wine consumption contributes of many essential metals, including Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Zn. Wine contains macro-, elements concentration > 10 mg/L (Na, K, Mg, Ca), micro-elements concentration < 10 µg/L (Cr, As, Cd, Ni) (Voica et al., 2009). Soil element composition affects the presence of oligo elements in vegetable and in animal organisms that feed on them (Van der Linde et al., 2010; Dinca et al., 2016). The soil mineral content and the vine ability to uptake and accumulate the elements in the grape berry, several other factors (e.g., environmental contamination, agricultural practices, wine-making treatments) may contribute to the elemental composition of the wines (Geana et al., 2013; Dinca et al., 2016).

The content of some metals in wine has been determinate by several technique, among them, flame atomic absorption spectrometry (FAAS) (Lara et al., 2005; Ortega et al., 1999; Onianwa et al., 1999), electrothermal atomic absorption spectrometry (ETAAS) (Lara et al., 2005; Karadjova et al., 2002), inductively coupled plasma mass spectrometry (ICP-MS) (Lara et al., 2005; Rodushkin et al., 1999; Marengo and Aceto, 2003), inductively coupled plasma optical emission spectrometry (ICP-OES) (Lara et al., 2005; Wuilloud et al., 2001; Aceto et al., 2002). For this purpose, inductively coupled plama mass spectrometry (ICP-MS), one of the more versatile technique, is used to determinated the multi-element composition of samples or the isotopic ration of elements (Coetzee et al. 2005).

The aim of this study was to determine the qualitative characteristics of wine, but also to evaluate five elements: Na, Mg, Cu, Pb and Cd in four grapevine cultivars: Fetească albă, Fetească regală, Riesling Italian and Pinot gris. Determination of metals and heavy metal concentrations has been performed by flame atomic absorption spectrophotometry (FAAS).

2. MATERIAL AND METHOD

Four vine varieties for high quality white wines were used in the research: Fetească albă, Fetească regală, Italian riesling, Pinot gris, grafted on the rootstock Berlandieri x Riparia Kobber 5 BB and cultivated in the area of Șimleul Silvaniei, Zalău and Halmeu in the vineyard of Silvania. Silvania vineyard is situated in the vast region of Silvaniei Hills, in the northwest of the country, Salaj and Satu Mare. Geographical position of this vineyard it is between parallels $47^0 04'$ and $47^0 35'$ similar to the Cotnari vineyard. Vineyard of Silvania it is the most northerly vineyard of Roamania.

The grape samples was collected in 2012 at full matturity, and aproximate 10 kg of grapes / variety were collected from 15 vines / repetion. Three repetitions / variety were used, placed in radomized blocks. The grapes were harvested from the top, middle and lower of each vine, grapes exposed to the sun, but also from shaded, thus obtaining a homogeneous samples. For grape sampling disposable rubber gloves were used. After sampling, the samples was placed in sealable plastic bag, they were numbered and shipped as soon as possible to the laboratory for analysis. The grape samples were pressed (manually) with the laboratory press and the must wast obtained followed by the process of microvinification which resulted in the samples of wine. The wines produced in laboratory had only sulphitation treatments (SO_2), without interering with other stabilization techniques than alter the content of macro-, microelemets.

Determination of Na, Mg, Cu, Pb, Cd was performed using Perkin Elmer Aanalyst 800 (Shelton, USA) and the method of analysis used is flame atomic absorption spectrometry (FAAS). Wine samples were diluted with ultrapure water so that the metallic ions concentration analyzed being in the most commonly limit of the device.

The standard solution developed for the calibration curves of each of metals analyzed were prepared daily by dilution of 1000 mg/L certified chemicals standards solution (Merck, Darmstadt, Germany). Solutions were prepared using ultrapure water obtained from a system Barnstead Easypure RoDi, D13321 model (England), and suprapure quality chemicals (Merck, Darmstadt, Germany). For each element analyzed was prepared in the same conditions a blank sample (control) to check the purity of the reagents used for this determinations. The variation coefficients were under 10% and detection limits (mg/L) was determined by the calibration curve method. Limit of detection (LOD*) and limit of quantification (LOQ**) and other operation conditions are shown in Table 1.

The **alcoholic strenght** (% vol.) were determined using the ebulliometric method, STAS 6182/2-70, which is based on the principle of temperature difference between boiling water and ethyl alcohol (78.4^{0}C), wine being a hydroalcoholic mix.

The **total acidity** (titrable acidity) is defined as the total substances with acid reaction present in wine, and which can be titrated with an alkaline solution in the presence of an indicator. The total acidity of wine were determined by tritrimetric method, STAS 6182-1:2008. The principle of this method lies in the titration/neutralization of the acids from wine with a sodium hydroxide solution with known normality and factor, in the presence of phenolphthalein as an indicator, after the removal of carbon dioxide. Results was calculated using the formula:

Total acidity (in tartaric acid) = 0.75 x n x f (g/L),

n = NaOH 0.1 N; f = factor = 0.9963.

The total **dry extract** was determined accordin to STAS 6182/9-80, using the direct method, consistin in evaporating a volume of wine sample (50 mL) using the water bath. The total extract are all nonvolatile matter which in specific physical conditions do not volatilizate. From chemical point of view, this matter is represented by: glycerol, fixed organic acids (malic, tartaric, succinic and lactic acid), 2,3 butylene glycol, sugars, nitrogen, tannins, gums, etc. The formula (g/L):

Dry extract = $[(m_2 - m_1) / V] \times 100$,

m_1 = weight of the empty capsule; m_2 = weight of the capsule with the extract; V = volume of wine (mL).

Reducing sugars were detemined to STAS 6182-18:2009. The principle of the method consists in treating the sample to be analyzed which is the dealcoholized wine with a solution of basic lead acetate, in order to precipitate the protein substances. Dosing of sugar was conducted using the Bertrand method.

Table 1: Instrumental conditions for the determination of each element

Element	Wavelength	Slit (nm)	Correlation coefficient	Flame (2300^0 C)	Background correction	LOD*	LOQ**
Na	589.0	0.2	1.000000	air-acetylene	-	0.012	0.039
Mg	202.6	0.7	1.000000	air-acetylene	deuterium	0.190	0.632
Cu	324.8	0.7	0.999997	air-acetylene	deuterium	0.019	0.063
Pb	283.3	0.2	0.999993	air-acetylene	deuterium	0.053	0.017
Cd	228.8	0.7	0.999999	air-acetylene	deuterium	0.028	0.093

Statistical analyses was performed using the statistical software package SPSS (version 23.0; SPSS Inc., Chicago, IL., USA). The data were expressed as mean ± standard deviation (SD) of three replications foe each sample analyzed. In order to determination the significance differences among values, analysis of variance (ANOVA) and DUNCAN multiple range test (MRT) was performed. Pearson' s corelation was done using version 23.0 of SPSS (SPSS Inc. Chicago, IL., USA).

3. RESULTS AND DISCUSSION

Qualitative characteristics of tested cultivars in areas studied

By analyzing each variety, it has been noted that wine showed varying alcohol content. Different between variants were statistically assured ($F = 3.339$, $p = 0.007$), between variant is a distinct signification. The highest alcohol amount was recorded in Pinot gris from Șimleul Silvaniei (13.12 % vol.) and Riesling Italian (12.34 % vol.) from the same area. The other varieties taken into study were statistically equal (Feteasca alba (12.11 (% vol.) from Zalău and 12.16 (% vol.) from the same area). A lower alcoholic strength was recorded by the three varieties from Halmeu area (Feteasca alba (10.95 % vol.); Riesling Italian (10.88 % vol.); and Pinot gris (10.77 % vol.)). Halmeu is often not an area suited for cultivation of vines, most often the obtained wine being current table wine. The location had the bigghest influence on the alcohol degree ($F = 12.329$, $p \leq 0.000$), while factor variety ($F = 0.688$, $p = 0.568$) and interaction between the two factors (location x variety) ($F = 1.669$, $p = 0.172$) they had no influence on this character.
In the case of total acidity (g/L $C_4H_6O_6$) it can be observed that the values are statistically very similar, different between variants were statistically assured ($F = 15.213$, $p \leq 0.000$), between variant is a very significant influence.

Table 2: Qualitative characteristics of tested cultivars in areas studied

Variety	Location	Alcohol (% vol.)	Total acidity (g/L $C_4H_6O_6$)	Residual sugar (g/L)	Dry extract (g/L)
Fetească albă	Șimleul Silvaniei	12.22±0.86 abc γ	7.41±0.32 ab γ	2.74±0.24 a γ	27.47±1.09 a β
	Zalău	12.11±0.73 abcd γ	7.14±0.50 ab γ	1.80±0.16 de γβ	19.64±1.74 d β
	Halmeu	10.95±0.51 cde γ	6.94±0.12 ab γ	3.00±0.12 a γ	21.24±2.11 cd γ
	Average*	**11.76±0.18**	**7.16±0.19**	**2.51±0.06**	**22.78±0.52**
Fetească regală	Șimleul Silvaniei	11.51±0.48 bcde γ	7.02±0.04 ab γ	2.71±0.23 a γ	25.80±2.80 ab γ
	Zalău	12.11±0.76 abcd γ	7.00±0.12 ab γ	2.06±0.07 cde γβ	21.09±1.48 cd β
	Halmeu	11.41±1.06 bcde γ	7.01±0.15 ab γ	2.67±0.24 ab γ	20.19±1.44 d β
	Average*	**11.68±0.29**	**7.01±0.06**	**2.48±0.10**	**22.36±0.77**
Riesling Italian	Șimleul Silvaniei	12.34±0.41 ab γ	7.13±0.46 ab γ	2.88±0.12 a γ	26.31±2.30 ab γ
	Zalău	11.56±0.27 bcde γβ	7.17±0.47 ab γ	2.03±0.06 cde β	27.25±0.32 ab γ
	Halmeu	10.88±0.49 de β	6.80±0.19 b γ	2.14±0.18 cd β	19.54±0.81 d β
	Average*	**11.59±0.11**	**7.03±0.16**	**2.35±0.06**	**24.37±1.03**
Pinot gris	Șimleul Silvaniei	13.12±0.14 a γ	7.15±0.40 ab γ	2.36±0.30 bc γ	27.76±1.70 a γ
	Zalău	12.16±0.92 abcd γ	7.55±0.54 a γ	1.74±0.20 e β	24.03±2.17 bc γβ
	Halmeu	10.77±0.73 e β	7.03±0.11 ab γ	2.84±0.26 a γ	21.18±2.19 cd β
	Average*	**12.02±0.41**	**7.24±0.22**	**2.31±0.12**	**24.32±0.28**
	Average*	***11.76±0.13***	***7.11±0.07***	***2.41±0.03***	***23.46±0.32***
Sig.		*p = 0.007*	*p = 0.394*	*p ≤ 0.000*	*p ≤ 0.000*
Location		***	ns	***	***
Sig.		p ≤ 0.000	p = 0.123	p ≤ 0.000	p ≤ 0.000
Variety		ns	ns	ns	ns
Sig.		p = 0.568	p = 0.408	p = 0.119	p = 0.052
Location x Variety		ns	ns	***	**
Sig.		p = 0.172	p = 0.598	p ≤ 0.000	p = 0.004

Average value ± standard deviation (n=3). Greek letters is significance of difference $P \leq 0.05$ for the same variety grown in different areas. The difference between any two values, followed by at least one common letter, is insignificant. Significance of area, variety, and interaction of these factors area x variety was tested for $P \leq 0.05$ (*), $P \leq 0.01$ (**), and $P \leq 0.0001$ (***).

The highest value of this parameter it was recorded in Pinot gris from Zalău area (7.03 g/L $C_4H_6O_6$) the lowest values was recorded in Riesling Italian from Halmeu area (6.80 g/L $C_4H_6O_6$). In this case we can see that the two factor, location (F = 2.292, p = 0.123) and variety (F = 1.003, p = 0.408) also the interaction between the two factors (location x variety) (F = 0.775, p = 0.598) had no influence on this character, the values obtained are well above the significance threshold (p = 0.050).
The residual sugar content (g/L) was very significantly influenced by the location factor (F = 59.048, p ≤ 0.000) and also from the interactions between the location x variety (F = 7.129, p ≤ 0.000), while factor variety has no influence on this charater (F = 2.159, p = 0.000). Different between variants were statistically assured (F = 15.213, p ≤ 0.000), between variant is a very significantly influence. The highest residual sugar content has recorded in varieties grown in area from Șimleul Silvaniei (Fetească albă (2.74 g/L); Fetească regală (2.71 g/L); Riesling Italian (2.88 g/L)), while varieties Pinot gris (2.84 g/L) and Fetească albă (3.00 g/L) has recorded the highest residual sugar in area of Halmeu. The lowest residual sugar content was recorded in varieties grown in the area of Zalău (Fetească albă (1.80 m/L); Pinot gris (1.74 g/L)).
The highest content of total dry extract was recorded in wine from varieties Fetească albă (27.47 g/L) and Pinot gris (27.76 g/L), between this two varieties is not any statistical difference, followed by varieties Fetească regală (25.80 g/L) from Șimleul Silvaniei area; Riesling Italian (26.31 g/L) from Șimleul Silvaniei and the same variety from Zalău (27.25 g/L). The lowest content of total dry extract was recorded in varieties from areas Zalău (Fetească albă 19.64 g/L) and Halmeu (Riesling Italian 19.54 g/L). The location factor had the bigghest influence on dry extract (F = 37.035, p ≤ 0.000), while the interaction of factors (location x variety) had a distinctly significant influence (F = 4.437, p = 0.004). Variety in this case has not any influence on this character (F = 2.966, p = 0.052).

The content of macro-, microelement and heavy metals in wine in areas studied

The content of wine in elements varies depending on the grape variety, the area of production, the raw material processing technology, and applied treatments on must and wine. Red wines, but also flavored ones, contain more minerals than white wines. During the fermentation of must, and also during the storage of wine, the mineral content decreases due to assimilation by yeasts, but also due to precipitation and their deposit (Bora et al., 2015a). It should be noted that certain elements in wine such as Na, Cu, Pb and Ca at different stages of wine are of great interest because of legal requirements (Voica et al., 2009).
Na, as macroelement is widespread in nature, but wine it ca be found in very low concentration (10-40 mg/L). In the case of wine produced from grapes that was harvested from the sea areas or planted wines on halomorphic soils and indigenous vine plantation, this macroelement concentration may increase. The O.I.V codex allow a maximum sodium content of 60 mg/L (2.6 mEq/L). Regarding the Na concentration from wine (Table 3) it can be seen that the highest concentration of Na was recorded in wine made from Fetească regală variety (55.09 mg/L) cultivated in area of Zalău, followed by varieties Fetească albă (48.96 mg/L) from Șimleul Silvaniei area, and Pinot gris (41.89 mg/L in Șimleul Silvaniei and 15.95 mg/L in Halmeu). Lowest concentration of these metals was recorded in wine made from Fetească albă (25.86 mg/L) from Halmeu area. The differences between variants were statistically assured (F = 2.875, p = 0.015). In this case accumulation of Na in wine was influence by the interaction between the two factors (location x variety) (F = 3.363, p = 0.015).
The results are comparable to those obtained by Avram et al., (2014) (33.10 mg/L), Galgano et al. (2008) (28.47±12.7 mg/L), and higher than those presented by Kment et al., (2005) (14.7±12.7 mg/L). The values of Pérez et al., (2011) are significantly higher than those presented by present study (57.7±30.5 mg/L)

and as those presented by Paneque et al., (2010) (42.4 mg/L).

Comparing the results for Na with the maximum set by the OIV codex (60 mg/L), it can be noted that all tested cultivars registered Na concentration well below this limit.

Wine always contains less calcium than the must, responsible for this decrease in calcium concentration is the alcohol which helps the insolubilization of calcium tartrate. White wines have a much higher concentration of calcium than red wines, normally the concentration of Ca in wine is between 80-150 mg/L (Bora et al., 2015).

The highest concentration of Mg in wine was recorded in varieties Fetească albă (116.08 mg/L from Halmeu), Fetească regală (117.17 mg/L from Zalău), Riesling Italian (113.23 mg/L from Zalău and 123.53 mg/L from Halmeu) and Pinot gris variety (129.26 mg/L from Zalău; 121.21 mg/L from Halmeu), these are statistically egual.

Table 3: The content of macro-, microelement and heavy metals in wine in areas studied (mg/L)

Variety / *Vitis vinifera*	Location / Areas	MLA*	MLA*	MLA*	MLA*	MLA*
		Na	Mg	Cu	Pb	Cd
		60 mg/L	-	1 mg/L	0.2 mg/L	0.01 mg/L
Fetească albă	Şimleul Silvaniei	48.96±7.42 ab *γ*	80.60±13.11 bc *β*	0.83±0.13 a *γ*	0.11±0.02 a *γ*	ULD
	Zalău	33.97±13.41 bc *γβ*	60.98±11.32 cd *β*	0.46±0.34 ab *γβ*	0.13±0.10 a *γ*	ULD
	Halmeu	25.86±4.73 c *β*	116.08±20.15 a *γ*	0.17±0.13 b *β*	0.14±0.06 a *γ*	ULD
	Average*	**36.26±4.44**	**85.89±4.67**	**0.49±0.12**	**0.13±0.04**	**-**
Fetească regală	Şimleul Silvaniei	35.12±13.10 bc	51.45±16.38 d *β*	0.62±0.17 a *γ*	0.14±0.09 a *γ*	ULD
	Zalău	55.09±5.59 a *γ*	117.17±17.32 a *γ*	0.48±0.31 ab *γ*	0.08±0.04 a *γ*	ULD
	Halmeu	33.73±4.99 bc *β*	80.79±12.55 bc *β*	0.64±0.17 a *γ*	0.11±0.08 a *γ*	ULD
	Average*	**41.31±4.52**	**83.14±2.53**	**0.58±0.08**	**0.11±0.03**	**-**
Italian riesling	Şimleul Silvaniei	36.04±9.55 bc *γ*	131.20±4.71 a *γ*	0.85±0.10 a *γ*	0.13±0.09 a *γ*	ULD
	Zalău	37.12±5.13 bc *γ*	113.23±11.78 a *β*	0.49±0.23 ab *γβ*	0.14±0.09 a *γ*	ULD
	Halmeu	33.55±6.38 bc *γ*	123.53±5.17 a *γβ*	0.54±0.14 ab *β*	0.17±0.06 a *γ*	ULD
	Average*	**35.57±2.28**	**122.65±3.96**	**0.63±0.07**	**0.15±0.02**	-
Pinot gris	Şimleul Silvaniei	41.89±11.53 ab *γ*	88.10±9.41 b *β*	0.59±0.27 a *γ*	0.17±0.13 a *γ*	ULD
	Zalău	42.77±2.72 ab *γ*	129.26±15.09 a *γ*	0.73±0.15 a *γ*	0.12±0.11 a *γ*	ULD
	Halmeu	45.95±5.11 ab *γ*	121.21±7.93 a *γ*	0.72±0.19 a *γ*	0.07±0.06 a *γ*	ULD
	Average*	**43.54±4.56**	**112.86±3.78**	**0.68±0.06**	**0.12±0.04**	-
	Average*	***39.17±1.11***	***101.08±0.89***	***0.60±0.03***	***0.13±0.01***	-
F (Fisher factor)		2.875	13.614	2.432	0.402	-
Sig.		*	***	*	ns	-
Location	*F*	2.712	10.051	3.517	0.221	-
	Sig.	ns	**	*	ns	-
Variety	*F*	2.006	20.840	1.346	0.268	-
	Sig.	ns	***	ns	ns	-
Location x Variety	*F*	3.363	11.188	2.620	0.530	-
	Sig.	*	***	*	ns	-

Average value ± standard deviation (n=3). Greek letters is significance of difference $P \leq 0.05$ for the same variety grown in different areas. The difference between any two values, followed by at least one common letter, is insignificant. Significance of area, variety, and interaction of these factors area x variety was tested for $P \leq 0.05$ (*), $P \leq 0.01$ (**), and $P \leq 0.0001$ (***); ULD = under limit of detection.

MLA = maximum limit allowed (O.I.V.) and Decision no. 1134 of October 10 for approval norms for the application of the law on vine and wine system common organization of the market in vine, no. 244/2002.

At the opposite the lowest concentration of Ca in wine was recorded in wine from varieties Fetească albă (80.60 mg/L from Șimleul Silvaniei and 60.98 mg/L from Zalău), Fetească regală (51.45 mg/L from Șimleul Silvaniei) and Pinot gris variety (88.10 mg/L from Șimleul Silvaniei). The differences between variants were statistically assured ($F = 13.614$, $p \leq 0.000$).

Accumulation of Mg in wine was a very significant influenced by variety fator ($F = 20.840$, $p \leq 0.000$) and interation from location x variety ($F = 11.188$, $p \leq 0.000$), in case of variety this factor has a significant influenced on this character.

The results present by Iochims dos Santos et al., (2010) show values lower than those shown in this study (58 mg/L) and comparable to those obtained by Galgano et al., (2008) (116 mg/L), Pérez et al., (2011) (112.5 mg/L), Kment et al., (2005) (75.4 mg/L), Paneque et al., (2010) (65.9 mg/L).

Regarding the Cu concentration in wine (Table 3), it can be seen that the highest concentration of Cu was recorded in all varietes study, Fetească albă (0.83 mg/L from Șimleul Silvaniei), Fetească regală (0.62 mg/L from Șimleul Silvaniei; 0.64 mg/L from Halmeu), Riesling Italian (0.85 mg/L from Șimleul Silvaniei), and Pinot griș (0.59 mg/L from Șimleul Silvaniei; 0.73 mg/L from Zalău; 0.72 mg/L from Halmeu). The lowest concentration was recorded in wine made form Fetească albă variety (0.17 mg/L from Halmeul area) and Fetească regală (0.48 mg/L from Zalău area). Notice that in this case factor location ($F = 3.517$, $p = 0.046$) and and interation from location x variety ($F = 2.620$, $p = 0.043$), has a significant influence, but variety factor was not any influence on this charater.

Comparing the results for Cu with the maximum set by the MLA (1 mg/L), it can be noted that all tested cultivars registered Cu concentration well below this limit.

As for Pb concentration found in the wine sample, from the data presented in Table 3 it can be seen that there are not statistical difference between variants ($F = 0.402$, $p = 0.941$), in this case the significance ($p = 0.941$) is much over the analyzed statistical threshold ($p \leq 0.050$).

Comparing the results for Pb with the maximum set by the MLA (0.1 mg/L), it can be noted that all tested cultivars registered Pb concentration well below this limit.

The results obtained for Pb concentration are comparable whit those obtained by Avram et al., (2014) (27.36 µg/L), Dugo et al., (2005) (169.3±35.2 $\mu g/L^{-1}$), Zacharia et al., (2013) (0.019±0.02 mg/dm^3), Gena et al., (2013) (42.83±35.38 $\mu g/L^{-1}$).

Cd it is below the detection limit of the device as well as the method of analysis.

Pearson correlation coefficients of qualitative characteristics and content of macro-, microelements and heavy metals in wine

To reveal if the qualitative characteristic of wine are influenced by the concentration of micro-, macroelements from wine, in this sense we have been performed Person correlations, between qualitative characteristics of wine (alcohol, total acidity, residual sugar and dry extract) and values of metals from wine (Na, Mg, Cu, Pb, Cd).

Values greater than 0.5 represent a strong correlation between variables. A positive correlation means that, when a variable increases, correlated variables increase also, while a negative correlation menas an increase in the primary variable causes a decrease in the correlated variables.

They have obtained a large number a strong relationships between the qualitative characteristics of wine and concentration of micro-, macroelements from wine Mg&Total Acidity (0.864**); Mg&Residual Sugar (0.861**); Pb&Residual Sugar (0.837**); Pb&Dry Extract (0.772*); Mg&Na (0.726*); Pb&Mg (0.694*).

In other words, the qualitative characteristics of wine are directly influenced by the concentration of micro-, macroelements from wine. The most important aspect is the concentration of these metals, or the quantly in which are found in wine.

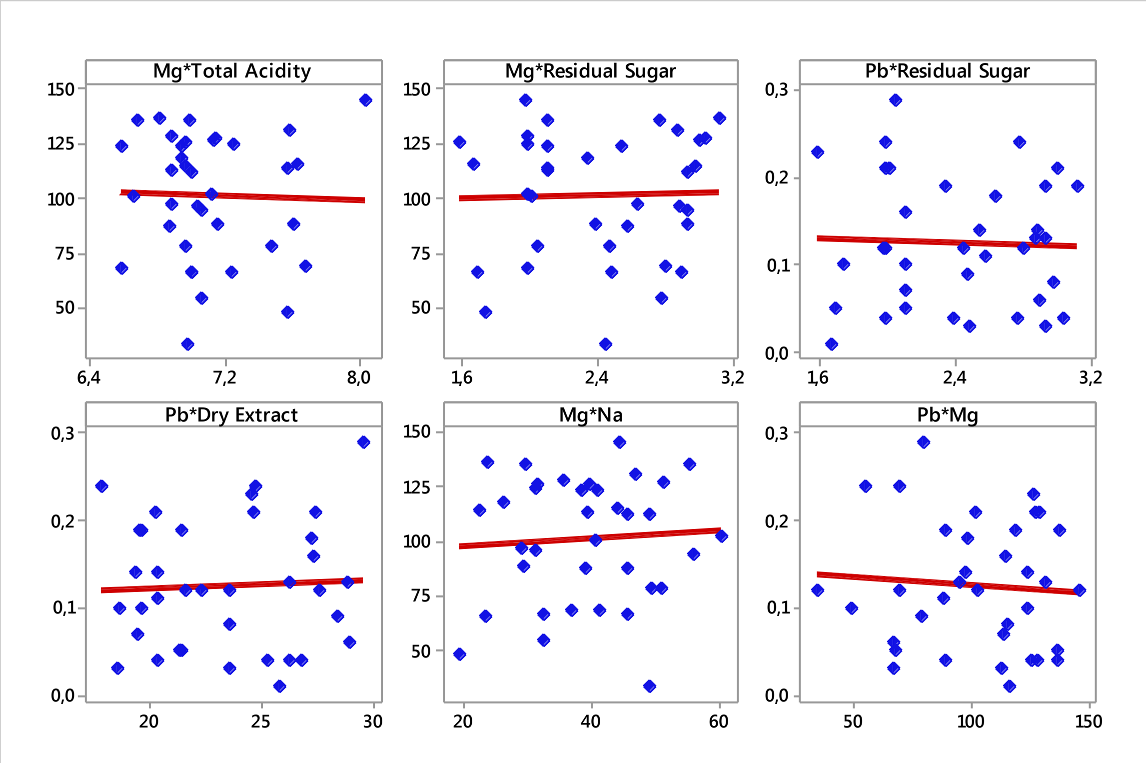

Fig. 1: Pearson correlation coefficients of qualitative characteristics and content of macro-, microelements and heavy metals in wine

4. CONCLUSION

Based on the results of the qualitative characteristics from wine we can say that the wine is a dry wine, slightly acidic, with specific taste variety. By comparing the values for micro-, macroelements and heavy metals in wine found in literature with the cocentration level of Na, Mg, Cu, Pb, Cd in young white wines obtained in Silvaniei vineyard (NW Romania) we can see that all four wines were similar with the values found in some European countries. Na, Mg, Cu, Pb and Cd in Romanian wine were below the recommended health limits of the International organization of Vine and Wine. Person῾s correlation analysis revealed a number of strong correlation between the qualitative characteristics of wine and concentration of micro-, macroelements from wine and also between metals.

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