

Inductively coupled plasma-mass spectrometry (ICP-MS) characterization of some white wines from Dealu Bujorului Vineyard by their mineral content

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Abstract. Wine is a complex matrix, which, besides water, alcohol and sugar contain a great variety of components, organic as well as inorganic. Numerous studies have shown that a moderate consumption of wine, especially red wine, improves health and enhance longevity when it is combined with a balanced diet. Daily consumption of wine in moderate quantities contributes significantly to the requirements of the human organism for essential elements such as: Ca, Mg, K, Cu, Mn, Mo, Ni, Se, Co, Fe, F, I and Zn. On the other hand, several metals, such as As, Pb and Cd are known to be potentially toxic for human organism. The present work is aimed to establish the metal content of wines from Dealul Bujorului vineyard (S-E Romania) due to which we have not found information about the metal content of Romanian wines (Dealul Bujorului vineyard) using ICP-MS method for the determination of metals content from the published literature. The wine samples used in this experiment were obtained from the wines produced from Fetească Albă, Italian Riesling and Sarba from the wine production of the years 2013, 2014 and 2015 at the Dealul Bujorului Vineyard. The wine samples resulted from micro-wine production. Regarding the major elements in wine, Feteasca Albă variety has recorded the highest concentrations (81.86±3.72 mg/L Ca [2014]; 153.29±3.03 mg/L Mg [2014]; 54.79±4.61 mg/L Na [2014]), while the Sarba variety has recorded the highest concentrations of K (275.78±10.90 mg/L [2014]) and Li (13.48±0.10 mg/L [2014]). In all tested wine samples, the toxic metals contents were found in quantities below the limits imposed by legislation. Using the principal components analysis (PCA) it was possible to group metals from wine according to their concentration, the significant variables in relation to this separation being the K, Li, A, Ba, Cs, Sr, Co (PC1) and Na, V, La (PC2). Key Words: ICP-MS method, metals, wines.

Rezumat. Vinul este o matrice complexă care, pe lângă apă, alcool și zahăr mai conține și o varietate de componente, atât organice cât și anorganice. Numeroase studii au demonstrat că un consum moderat de vin, în special de vin roșu, este benefic sănătății și longevității, atunci când este combinat cu o dietă echilibrată. În cantități moderate, consumul zilnic de vin contribuie la necesarul organismului de elemente esențiale precum: Ca, Mg, K, Cu, Mn, Mo, Ni, Se, Co, Fe, F, I și Zn. Pe de altă parte, metale precum As, Pb și Cd sunt cunoscute ca potential toxice pentru organismul uman. Scopul prezentei lucrări este acela de a stabili conținutul de metal în vinurile din podgoria Dealul Bujorului (S-E României), folosind metoda ICP-MS, datorită inexistenței acestor informații în literatura de specialitate existentă. Probele de vin folosite în acest experiment au fost obținute din vinurile produse din Fetească Albă, Riesling Italian și Şarba, din anul de producție 2013, 2014 și 2015 în podgoria Dealul Bujorului. Probele de vin provin din producția micro. În ceea ce privește elementul predominant al vinului, soiul Fetească Albă a înregistrat cele mai mari concentrații (81.86±3.72 mg/L Ca [2014]; 153.29±3.03 mg/L Mg [2014]; 54.79±4.61 mg/L Na [2014]), în timp ce soiul Șarba a înregistrat cele mai mari concentrații de K (275.78±10.90 mg/L K [2014]) și (13.48±0.10 mg/L Li [2014]). În toate probele testate, conținutul de

metale toxice a fost sub limita impusă de lege. Folosirea analizei componentelor principale (ACP) a făcut posibilă gruparea metalelor din vin în funcție de concentrație, variabila semnificativă în relație cu această separare a fost K, Li, A, Ba, Cs, Sr, Co (PC1) și Na, V, La (PC2). **Cuvinte cheie**: metoda ICP-MS, metale, vinuri, minerale.

Introduction. Wine is a complex matrix, which, besides water, alcohol and sugar, contains a great variety of components, organic as well as inorganic. The composition of wine is influenced by many factors related to the specific production areas: soil and climate conditions, grape varieties, culture, winemaking, and also transport and storage of wine (Sperkova & Suchanek 2005; Augagneur et al 1996).

Numerous studies have shown that a moderate consumption of wine, especially red wine, improves good health and longevity when it is combined with a balanced diet (Doll et al 1994; Gronbaek et al 1995; Klatsky et al 1992; Lara et al 2014). Daily consumption of wine in moderate quantities contributes significantly to the requirements of the human organism for essential elements such as: Ca, Mg, K, Cu, Mn, Mo, Ni, Se, Co, Fe, F, I and Zn (Eschnauer & Neeb 1988). On the other hand, several metals, such as Ca, Pb and Cd are known to be potentially toxic for human organism. Therefore the analysis for target elements in wines is of special interest due to their toxicity in case of excessive intake, and not at least becuse the effect they may have on the organoleptic properties of the final product (Lara et al 2014).

The presence of metals in wines is of special concern, particularly within the technological, sensory and food safety scope. Over the last years, aspects associated with metals contaminant evolution throughout the winemaking process, exogenous and endogenous presence, contamination source, levels of occurrence and development of analytical methods, have been deeply investigated in order to prevent undesirable metal contaminations (Médina et al 2000; Katalinic et al 2004; Catarino et al 2006, 2008, 2009; Dalipi et al 2015; Karataş et al 2015; Bora et al 2013, 2014, 2015a).

Modern societies appear to consume large amounts of alcoholic products (especially wine and beer) (Mena et al 1996; Galani-Nikolakaki et al 2002), sometimes increasing the daily intake of heavy metals above the maximum permissible levels. When wine are consumed in large quantities the toxic effects of their pollutants may have an additive effect to induction of alcoholism, example is the presence of lead in wines (Roses et al 1997; Lopes et al 1997).

The mineral constituents of wine can be assessed by several analytical methods. However, most of the methods require extensive sample preparation. Atomic spectrometry techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) (Almeida et al 2002; Castiñeira et al 2001; Šelih et al 2014; Grindlay et al 2009), ICP atomic emission spectrometry (ICP-OES) (Martin et al 2012; Sen & Tokatli 2013), electrothermal atomic absorption spectrometry (ETAAS) (Grindlay et al 2009; Martin et al 2012; Sen & Tokatli 2013; Alkiş et al 2014) and also flame atomic absorption spectrometry (FAAS) (Schiavo et al 2008; Bora et al 2015b) have been widely used for elemental analysis of wine. A fast and simple method was used for the determination of metal and mineral content from wine samples namely by inductively coupled plasma with mass spectrometry (ICP-MS).

Mineral content of wines depend on several factors, including soil, environmental conditions and viticultural, variety of grapes and enological practices. The quantification of some elements is of interest because of their toxicological or physiological properties, and can lead to wine spoilage (Avram et al 2014).

Depending on their concentration in wine, the mineral content are divided into three groups: (1) macroelements or major elements (Ca, Mg, K, Na and Li) which have a concentration greater than 10 mg/L; (2) micro-elements or oligo-elements (AI, Cu, Fe, Mn, Zn, Rb, Sr, As, Ba) having concentration between 0.1-10 mg/L and (3) trace elements (Pb, Cd, Cs, Hg) whose concentration are below 0.1 mg/L (Grindlay et al 2011; Tenore et al 2011; Avram et al 2014).

Lithium is an element seldom determined in wines, and lithium content is influenced essentially by soil type, however, higher values of lithium were reported for aged wines because of its extraction from glass (Ough & Amerine 1988). Determination

of lithium levels is important because of their use for the chemometric differentiation of wines from various geographic origins (Núñez et al 2000).

Several studies have demostrated that the ⁸⁷Sr/⁸⁶Sr ration is an optimal geographic footprint for food and animal products because Sr is actively involved in the metabolism of the plants (Fortunato et al 2004; Crittenden et al 2007; Voerkelius et al 2010; Schellenberg et al 2010; Asfaha et al 2011). Variations in the ⁸⁷Sr/⁸⁶Sr ration in wine have been used to differentiate the geographic origin of wine from wine-producing countries such as Argentina (Di Paola-Naranjo et al 2011), France (Lurton et al 1999; Barbaste et al 2002), Germany (Hocq & Dubé 1994; Wolff-Boenisch et al 1998), Italy (Boari et al 2008; Marchionni et al 2013; Durante et al 2015; Petrini et al 2015), Romania (Dehelean & Voica 2011) and South Africa (Vorster et al 2010).

The arsenic content in wine may result from a number of sources, including naturally-occurring arsenic in soil, industrial messions, and from the historical use of arsenic in a wide range of agricultural practices (Handson 1984; Moreno et al 2000; Rodrigues et al 2011; Tariba 2011; Hopfer et al 2015).

Arsenic concentration from environmental media, such as groundwater used for wine making, have also been reported to impact the final arsenic concentration in wine (Hopfer et al 2015; Kunkee & Eschnaur 2002). These practices include also the use of bentonite as filtering agent, grape pressing processes, contact with juice lees, and the contact whit metals in the production equipment (Kunkee & Eschnaur 2002; Barbaste et al 2003; Bertoldi et al 2013; Hopfer et al 2015).

Naturally, the wine contains arsenic in trace amounts, up to a maximum of 0.02 mg/L. The white wines from the wine center Valea Călugărească have an arsenic content between 2.6-7.6 μ g/L. The concentration of arsenic is different depending on the variety and on the harvest year (Avramescu 1994).

Lead is highly toxic to the organic structures, as it tends to accumulate itself in the body and cause the disease illness known as the "saturnism". The toxic effects of lead organic compounds are more important than the inorganic ones. The wine contains very small amounts of lead, a 60 μ g/L average, with about 45-50% less than the must. By sulphitation and settling processes of the must before fermentation and after alcoholic fermentation, the concentration of lead in wine decreases without reaching the toxicity limit (Târdea 2007).

The present work is aimed at establishing the metal content in wines from Dealul Bujorului vineyard (S-E Romania) due to which we have not found from the literature information about the metal content of Romanian wines (Dealul Bujorului vineyard) using ICP-MS method for the determination of metals content.

Material and Method

Study area. Dealu Bujorului vineyard is located in the Galati County, Romania. This region has a long tradition in culture of vine, vineyard Dealu Bujorului was developed with the establishment of Research and Development Station for Viticulture and Oenology Bujoru, from Târgu Bujoru City. In Dealu Bujorului vineyard the predominant soil is levidated chernozem having a clayey sand texture with a pH between 7.4 and 8.1, although moisture deficit, natural conditions offer viable ecosystem for the development of vineyard.

The study area is 2.10 ha and is consisting of: Fetească Albă (3000 of vine hubs; planting data 23.05.2012) (0.72 ha cultivated area, 2 m distance between rows and 1.2 m distance between vine); Italian Riesling (2667 of vine hubs; planting data 01.04.1978) (0.66 ha cultivated area, 2 m distance between rows and 1.2 m distance between vine). Fetească Albă (3000 of vine hubs; planting data 23.05.2012) (0.72 ha cultivated area, 2 m distance between rows and 1.2 m distance between vine). Fetească Albă (3000 of vine hubs; planting data 23.05.2012) (0.72 ha cultivated area, 2 m distance between rows and 1.2 m distance between vines). Vines were pruned according to the Guyot system and were grown on espaliers.

The wine samples used in this experiment were obtained from the wines produced from Fetească Albă, Italian Riesling and Şarba from the wine production of the years 2013, 2014 and 2015 in the Dealul Bujorului Vineyard. The wine samples resulted from micro-wine production.

Microvinification process. In order to evaluate the quality of white wines obtained in the 2013, 2014 and 2015 crop from Dealu Bujorului vineyard, for micro-vinifications process was carried out for each treatment (Sampaio et al 2007). Grapes were harvested on September 25-26, 2013, 2014 and 2015. Ten kilograms of grape were destemmed and crushed, then transferred to a microfermentor (7 L cylindrical glass container, covered with aluminum foil to limit the effect of the light over the must), equipped with a fermentation airlock.

Fermentation took place at 23-24°C and at a humidity of 56-60%. Afterwards wine was clarified by means of bentonite (40 g/L 1:10 dilution) and combined with SO₂ up to 100 g/L. Then wines were allowed to cool for 30 days at -6°C for cold stabilization, then stored at 4-6°C until the analyses. The wine samples were stored in glass bottles until analysis.

ICP-MS analysis. The determination of 17 elements was performed on mass spectrometer with inductively coupled plasma, (ICP-MS) iCAP Q Thermo scientific model, based polyatomic species before they reach the quadrupole mass spectrometer, using a PFA micro flow concentric nebulizer.

The argon used was of 99.99% purity. The instrument was optimized (daily performance) to give maximum sensitivity for M^+ ions and the double ionization and oxides monitored by the means of the rations between Ba^{2+}/Ba^+ and Ce^{2+}/CeO^+ , respectively, these always being less than 2%. The experimental conditions was: 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 (2.55±1.00°C). Accuracy was calculated for the elements taken into consideration (0.5-5.0%).

Chemical analysis. For quantitative determination of elements, a Certipur multielement standard solution XXI (10 mg/L [100 mL]) was used, for calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), lithium (Li), arsenic (As), barium (Ba), caesium (Cs), lead (Pb), cadmium (Cd), strontium (Sr), cobalt (Co), lanthanum (La), cerium (Ce), molybdenum (Mo).

For mercury (Hg) was used Mercury standard (10 mg/L [100 mL]). The solution used for calibration was from Merck KGaA, Darmstadt, Germany.

For quality control purpose, blanks and triplicates samples (n=3) we analyzed during the procedure. The variation coefficients were under 5% and detection limits (ppb) were determined by the calibration curve method.

LoD (limit of detection) and LoQ (limit of quantification) 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, and s - slope of the calibration curve). The results obtained are shown in Table 1.

Samples preparation for determination of metals from wine using ICP-MS. For the determination of metals in wine samples was used an amount of 0.2 mL and was placed into 8 mL (7 mL HNO₃ 69% + 1 mL H₂O₂), after 15-30 minutes the mineralization was performed using a microwave system Milestone START D Microwave Digestion System set in three steps (Table 2). After mineralization, the samples were filtered through a 0.45 mm filter and brought to a volume of 100 mL, for dilution of samples was used ultrapure water (Milli-Q Integral ultrapure water-Type 1).

Та	ble 1	
Instrumental conditions for the determination of each element (ICP-MS technique)	

Elomont	Correlation	LoD	BEC	LoQ
Liement	coefficient	(ppb) *	(ppb) * *	(ppb)***
Са	0.9999	1.8256	51.7280	6.0792
Mg	0.9998	2.7325	21.6650	9.0992
K	0.9998	2.1860	31.7280	7.2794
Na	0.9999	3.9808	32.1210	13.2560
Li	0.9998	0.0445	0.1010	0.1481
As	0.9999	0.2291	0.1900	0.7629
Ba	0.9999	0.1366	0.4030	0.4548
Cs	0.9999	0.1045	0.2145	0.3479
Pb	0.9999	0.1080	0.8500	0.3596
Cd	0.9999	0.0467	0.0470	0.1555
Hg	0.9999	0.1236	0.1278	0.4115
Sr	0.9998	0.2807	0.8420	0.9347
Со	0.9999	0.0365	0.1520	0.1215
V	0.9998	0.1970	0.3860	0.6560
La	0.9999	0.2964	0.3456	0.9870
Ce	0.9999	0.2145	0.2364	0.7142
Мо	0.9999	0.0123	0.1479	0.0409

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

Table 2

Working parameters in the microwave (Milestone START D Microwave Digestion System) for disaggregation of wine samples

			Wine		
Step	Time	Ventilation	Temperature (⁰ C)	Pressure (Pa)	Power (W)
I	00:10:00	-	200	-	1000
П	00:15:00	-	200	-	1000
	00:60:00	+	38	-	0

Milestone START D Microwave Digestion System Device user manual.

Statistical interpretation. The statistical interpretation of the results was performed using the Duncan test, SPSS Version 23 (SPSS Inc., Chicago, IL., USA). The statistical processing of the results was primarily performed in order to calculate the following statistical parameters: arithmetic average, standard deviation, average error. This data was interpreted with the analysis of variance (ANOVA) and the average separation was performed with the DUNCAN test at $p \le 0.05$. The principal component analysis (PCA) was performed using the SPSS Version 23 (SPSS Inc., Chicago, IL., USA).

The analytical data were also processed using the linear correlation matrix and principal components analysis techniques. Principal components analysis was applied to all samples of white considering the variables mineral content. The principal components were determined and in order to group the samples for similarity components that accounted for over 70% of the total variation were considered. Scatter plots were obtained to visualize the dispersion of the treatments according to the scores of the principal components.

Results and Discussion

Major elements. Table 3 presents the concentrations of major elements (Ca, Mg, K, Na, Li) in the selected wine samples. Calcium (Ca) is a natural component of wine, it accumulates in grapes up to their ripening.

				Total metal concentrations (mg/L)					
				Са	Mg	К	Na	Li	
Area	Vineyard	Variety	Year	M.P.L	M.P.L	M.P.L	M.P.L*	M.P.L	
				-	-	-	(60 mg/L)**	-	
		Fotoscă	2013	76.67±9.28 ^{abc} a	130.73±6.34 ^b β	170.17±6.88 ^d γ	53.09±2.32 ^{ab} a	11.69±1.24 ^{bc} a	
			2014	81.86±3.72 ^a a	153.29±3.03 ^a a	240.83±8.33 ^b a	54.79±4.61 ^a a	10.11±0.43 ^{cd} αβ	
		Alba	2015	71.98±3.13 ^{abc} a	110.54±1.54 ^e γ	$202.27 \pm 4.11^{c} \beta$	54.39±2.76 ^a a	10.12±0.86 ^d αβ	
		Italian	2013	83.13±4.93 ^a a	119.76±6.69 ^{cd} a	239.11±5.99 ^b β	48.91±2.76 ^{bc} a	12.50±0.70 ^{ab} a	
Târqu	Doalu	Diocling	2014	67.87±5.67 ^c β	117.58±6.13 ^{de} a	204.70±5.43 ^c a	44.75±2.14 ^c a	12.18±0.22 ^{ab} a	
Pulor	Puiorului	Riesing	2015	69.58±8.85 ^{bc} β	127.80±5.56 ^{bc} a	242.41±7.77 ^b β	47.24±0.82 ^c a	12.11±1.34 ^{ab} a	
Бијо	Bujululu	Şarba	2013	80.45±3.64 ^{ab} a	100.15±2.01 ^f β	277.65±7.64 ^a a	57.44±2.84 ^a a	11.26±0.90 ^{bc} β	
			2014	73.01±8.58 ^{abc} a	129.14±6.58 ^b a	275.78±10.90 ^a a	55.73±1.07 ^a a	13.48±0.10 ^a a	
			2015	76.96±1.75 ^{abc} a	122.69±3.39 ^{bcd} a	252.16±3.91 ^b β	57.14±2.78 ^a a	9.21±0.66 ^d γ	
		F. Sig.		2.397	26.416	75.169	8.749	8.022	
				p=0.059	p≤0.000	p≤0.000	p≤ .000	p≤0.000	
		F.		0.874	19.156	187.757	32.468	9.870	
Variety		Sig.		p=0.434	p≤0.000	p≤0.000	p≤0.000	p=0.001	
		C C		ns	* * *	* * *	* * *	* *	
		F.		3.565	27.255	6.238	0.704	9.996	
Years		Sig.		p=0.050	p≤0.000	p=0.008	p=0.508	p=0.001	
				*	* * *	* *	ns	* *	
Variaty y		F.		2.573	29.626	53.340	0.911	6.110	
Voore		Sig.		p=0.073	p≤0.000	p≤0.000	p=0.478	p=0.003	
Years		-		ns	* * *	* * *	ns	* *	

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

Romans represent the significance of the variety difference ($p \le 0.005$). Greeks represent the significance differences of the same variety cultivated in other years ($p \le 0.005$). The difference between any two values, followed by a common letter is insignificant.

*M.P.L - maximum permissible limit.

** OIV, 2005.

The presence of calcium in wine in large quantities is due to some exogenous sources such as storage of wine in concrete tanks, treatment with calcium bentonite, filtration with alluvial infusorial soil (diatomite), de-acidification of calcium carbonate. The wines that exceed the calcium content of 100 mg/L are prone to the formation of deposits of calcium tartrate (TCa). Calcium precipitation in wine is influenced by the wine pH and temperature. Low values of pH 2.9-3.2 and low temperature favors the formation of the crystals TCa as uthe scale of tartrate anions rise (T2-) which combines with the calcium in wine. High temperature favors the formation of calcium malate (Târdea 2007; Bora 2015b).

The highest concentration of Ca was recorded at Fetească Albă (81.86±3.72 mg/L [2014]) and Riesling Italian (83.13±4.93 mg/L [2013]), between these varieties there is no statistical difference. The Sarba variety (80.45±3.64 mg/L (2013); 73.01±8.58 mg/L (2014); 76.96±1.75 mg/L [2015]) and Fetească Albă (76.67±9.28 mg/L [2013]; 71.98±3.13 mg/L [2015]) have recorded an average Ca content compared to the other analyzed varieties. The lowest levels were recorded in the Italian Riesling variety (69.58±8.85 mg/kg [2015]; 67.87±5.67 mg/L [2014]). From a statistical point of view, there was no difference between the analyzed variants (F=2.397; p=0.059). From the polyfactorial analysis we see that the factor variety (F=0.874; p=0.434) and the interaction between the two factors (Variety x Year) (F=2.397; p=0.059) had no influence on the accumulation of calcium in wine; while the factor (Years) (F=2.573; p=0.073) had a significant influence on this character (Table 3).

The magnesium concentration in wine ranges from 0.048-0.78 g/L (Jârdea 2007; Bora et al 2016), it activates the enzymes that perform the phosphorylation of sugars in the processes of alcoholic fermentation (Jârdea 2007). The highest concentration of magnesium was registered in Fetească Albă (153.29 \pm 3.03 mg/L [2014]; 130.73 \pm 6.34 mg/L [2013]), followed by the Şarba variety 129.14 \pm 6.58 mg/L [2014]). The lowest concentrations of this macroelement were recorded Fetească Albă (110.54 \pm 1.45 mg/L [2015]) and Sarba (100.15 \pm 2.01 mg/L [2013]). Statistically, between the analyzed variants was no highly significant difference (F=26.416, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=19.156, p≤0.000) had the greatest influence on the accumulation of calcium in wine, followed by the interaction between the two factors (Variety x Year) (F=29.626, p≤0.000). Year factor (F=27.255, p≤0.000) had a very significant influence on this character.

The grapevine consumes large amounts of potassium for its mineral nutrition, which can be found in must and wine. It gives organoleptic finesse, while the low potassium wines have a harsh taste (Jârdea 2007; Jârdea et al 2001). The highest concentration was recorded in the Sarba variety (277.65 \pm 7.64 mg/L [2013]; 275.78 \pm 10.90 mg/L [2014]; 252.16 \pm 6.91 mg/L [2015]), followed by Fetească Albă (240.83 \pm 8.33 mg/L [2014]) and Italian Riesling (239.11 \pm 5.99 mg/L [2013]; 242.41 \pm 7.77 mg/L [2015]). The lowest concentrations of this macroelement were recorded in the Feteasca Albă variety (202.27 \pm 4.11 mg/L [2015], 170.17 \pm 6.88 mg/L [2013]). From the statistical point of view, between the analyzed variants, no significant difference was recorded (F=75.169, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=187.757, p≤0.000) had the greatest influence on the accumulation of calcium in wine, followed by the interaction between the two factors (Variety x Year) (F=53.340, p≤0.000), while the factor Year (F=6.238; p=0.008) had a distinct significant influence on this character (Table 3).

The Şarba variety recorded the highest concentration of K regardless of the year of culture, which demonstrates that this variety of grapevine favors the accumulation of this macro element in comparison with the other studied varieties. The year of culture had a great influence on the accumulation of this element.

When compared to K, Na is present in grapes in very low concentrations, of several tens of milligrams, because the vines consume insignificant amount of sodium from the soil. Taking into account the geographical area, the vineyards from the coastline with halomorphe soils and the vineyards with volcanic soils are richer in sodium; as well as the wines produced in the irrigated vineyards and the vineyards on their own roots (sandy land) (Bora et al 2016).

Regarding the Na concentration in the samples of wine, the highest concentration was recorded in Fetească Albă (54.79±4.61 mg/L [2014]; 54.39±2.76 mg/L [2015], followed by the Sarba variety (57.44±2.84 mg/L [2013]; 55.73±1.07 mg/L [2014]; 57.14±2.78 mg/L [2015]). These variants are equal in terms of statistics. The lowest levels were registered in the Italian Riesling variety (44.75±2.14 mg/L [2014]; 57.24±0.82 mg/L [2015]). From the statistical point of view, there is no significant difference between the analyzed variants (F=8.749; p≤0.000). From the polyfactorial analysis we can see that the factor Variety (F=32.468, p≤0.000) had the greatest influence on the accumulation of calcium in the wine, while the factor Year (F=0.508; p=0.508) and the interaction between the two factors (Variety x Year) (F=0.911; p=0.478) had no influence on this character (Table 3).

Reporting the results to national legislation, we note that the concentrations of sodium are below the maximum limit allowed by the applicable law (60 mg/L).

The behavior of lithium in wine is similar to that of alkaline-earth metals and especially of magnesium. By the aging of the bottled wine, and due to the fact that a reducing environment is created, lithium is expelled out of the wine.

The highest concentration of this element was registered in the wine produced from the variety Sarba (13.48±0.10 mg/L [2014]), followed by the Italian Riesling (12.50±0.70 mg/L [2013]; 12.18±0.22 mg/L [2014]; 12.11±1.34 mg/L [2015]), these varieties are equal in terms of statistics. The lowest concentrations of lithium were recorded in the Fetească Albă variety (10.12±0.86 mg/L [2015]) and Şarba (9.21±0.66 mg/L [2015]). Statistically, there is no significant difference between the analyzed variants (F=8.022; p≤0.000). From the polyfactorial analysis we see that the factor Years (F=9.996; p=0.001) had the greatest influence on the accumulation of lithium in wine, followed by factor Variety (F=9.870; p=0.001) and by interaction between the two factors (Variety x Year) (F=6.110; p=0.003), they had a distinct significant influence on this character (Table 3).

Minor elements content. Table 4 presents the concentrations of Ba, Cs, Sr, Co, V, La, Ce and Mo in the analyzed wine samples. Although Ba is reported to be commonly present in plants, it apparently is not an essential component of plant tissues. Plants may take up barium quite easily from acid soils; Weinberg (1977) reported a high affinity of Ba²⁺ to be bound to the surface of yeast. There are, however, only a few reports on toxic barium concentration in plants. Chanudry et al (1977) gave 1 to 2% (DW) barium in plants as highly toxic, while Shacklette et al (1978) stated that 220 ppm (AW) is moderately toxic. In the wine varieties produced in Romania, the concentrations of barium ranged between values of 145.74-311.46 µg/L (Fetească Albă) and 87.46-150.50 µg/L (Italian Riesling) (Avram et al 2014).

Fetească Albă (189.28±4.67 µg/L [2013]; 168.20±5.82 µg/L [2014], (270.63±7.86 µg/L [2015]), while the Şarba variety recorded the lowest concentrations (105.17±8.56 µg/L [2013] (102.92±3.95 µg/L [2014)) of Ba (Table 4). Among the analyzed varieties are very significant differences (F=285.893, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=725.390, p≤0.000) had the greatest influence on the accumulation of barium in wine, followed by factor Year (F=329.945, p≤0.000), and the interaction between the two factors (Variety x Year) (F=44.118, p≤0.000), had a very significant influence on this character.

Regarding the concentration of strontium from the wine samples, the highest concentrations were recorded in the wine produced from Fetească Albă (275.25±12.36 μ g/ L [2013] followed by the same variety but another years of culture, i.e. 2014 and 2015 (325.20±11.40 μ g/L [2014]; 295.49±7.26 μ g/L [2014]); while the Italian Riesling variety (125.75±5.98 μ g/L [2013]), followed by Şarba (143.05±2.92 μ g/L [2013]; 154.51±10.01 μ g/L [2014]; 173.35±5.90 μ g/L [2015]) recorded the lowest concentrations of strontium (Table 4). Among the analyzed varieties are very significant differences (F=239.274, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=660.408, p≤0.000) had the greatest influence on the accumulation of strontium in wine, followed by factor Years (F=165.680, p≤0.000), and the interaction

between the two factors (Variety x Year) (F=65.504, $p \le 0.000$), had a very significant influence on this character.

Co is an essential element, potentially toxic in case of excessive intake (Galgano et al 2008; Catarino et al 2009). The concentrations of cobalt that have been found in grape berries and musts are lower than 3 mg/kg (dry weight) (Tokalioglu et al 2004) and 4 mg/kg (Catarino et al 2006). According to monitoring studies carried out all over the world, the cobalt concentration in wines does not normally exceed 15 μ g/L. Greek wine, from different areas, were analyzed and cobalt concentration always was lower than 8 μ g/L (Soulis et al 1984). A large number of samples of white wine (127) from Germany showed that the cobalt concentration was between values of 0.4 μ g/L and 15 μ g/L (Gómez et al 2004). As result of contamination cobalt concentration in wine can increase due to bentonite used as a technological aid for clarification purposes (Nicolini et al 2004; Catarino et al 2008). Enrichments occur also from the attack alloys by cobalt (Curvelo-Garcia 1988) and in the bed filtration of the wine (Eschnauer et al 1989).

The lowest concentrations of this metal were recorded in the wine produced from the Italian Riesling varieties $(2.31\pm0.87 \ \mu g/L \ [2014]; 3.42\pm1.05 \ \mu g/L \ [2015])$ followed by Şarba variety $(4.12\pm0.47 \ \mu g/L \ [2013]; 2.93\pm0.63 \ \mu g/L \ [2014]; 3.19\pm0.64 \ \mu g/L \ [2015])$, these variants are equal in terms of statistics. While Fetească Albă $(6.41\pm1.22 \ \mu g/L \ [2014]; 6.77 \pm 0.60 \ \mu g/L \ [2015]$ and Italian Riesling $(5.95\pm1.37 \ \mu g/L \ [2013])$ recorded an average content reported to the minimum and maximum concentrations of this research. Among the analyzed varieties, the differences are very significant $(F=44.513, \ p\leq0.000)$. From the polyfactorial analysis we see that the factor Variety $(F=44.513, \ p\leq0.000)$ had the greatest influence on the accumulation of cobalt in wine, followed by factor Years $(F=16.001, \ p\leq0.000)$, and the interaction between the two factors (Variety x Year) $(F=1.282; \ p\leq0.000)$ had a very significant influence on this character.

The lanthanides content of the wine is determined by the geographically equipping the soil formation rocks (Done 2006).

Food represents the major source of exposure to vanadium for the population (Barceloux 1999). Actually it is normally present at concentration levels between 1 μ g/L and 5 μ g/L in drinks and fruit juices (Filik & Aksu 2012), from 4 μ g/L to 41 μ g/L in tea infusions (Dundar & Saglam 2004), and up to 90 μ g/L in wines (Teissèdre et al 1998) (Table 5).

The wine produced from the Italian Riesling variety (799.83±2.19 µg/L [2014]; 670.24±4.59 µg/L [2015]; 633.13±6.24 µg/L [2013]) and Fetească Albă variety (619.75±6.40 µg/L [2015]) recorded the highest concentrations of vanadium. In contrast, the lowest concentrations were registered in the wine produced from Fetească Albă (526.97±5.01 µg/L [2014]; 449.70±15.90 µg/L [2013]) and the wine produced from the Şarba variety (397.73±7.02 µg/L [2015]). There are very significant differences among the analyzed varieties (F=788.454, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=1850.342; p≤0.000) had the greatest influence on the accumulation of vanadium in wine, followed by the interaction between the two factors (Variety x Year) (F= 512.291, p≤0.000) which also had a very significant influence on the accumulation of vanadium. The factor Years (F=278.891, p≤0.000) had a very significant influence on this character (Table 4).

Table 4

				Total metal concentrations (μg/L)								
Aroa	Vinovard	Varioty	Voar	Ba	Cs	Sr	Со	V	La	Ce	Мо	
Area	vineyaru	variety	rear	M.P.L	M.P.L	M.P.L	M.P.L	M.P.L	M.P.L	M.P.L	M.P.L	
				-	-	-	-	-	-	-	-	
		Fotoasca	2013	189.28±4.67 ^b β	$7.14 \pm 0.72^{d} \gamma$	275.25±12.36 ^c β	9.11±1.47ª a	449.70±15.90 ^g γ	3.15±0.56 ^c β	6.55 ± 0.90^{bc}	BDL***	
		Δlhă	2014	168.20±5.82 ^c γ	15.61±0.87ª a	325.20±11.40 ^a a	6.41±1.22 ^b β	526.97±5.01 ^f β	1.91±0.67 ^{ef} γ	7.50 ± 0.34^{a}	0.11 ± 0.02	
		Alba	2015	270.63±7.86 ^a a	13.48±1.17 ^b β	295.49±7.26 ^b β	$6.77 \pm 0.60^{b} \beta$	619.75±6.40° a	4.30±0.27 ^b a	4.89±0.34 ^d	BDL	
		Italian	2013	125.41±3.05 ^f γ	11.27±0.84 ^c a	125.75±5.98 ^g γ	5.95±1.37 ^b a	633.13±6.24 ^c γ	6.51±0.83 ^a a	7.20 ± 0.23^{ab}	BDL	
Târqu	Dealu	Riesling	2014	133.74±1.72 ^f β	13.14±0.56 ^b a	283.02±5.52 ^{bc} a	2.31±0.87°β	799.83±2.19 ^a a	4.16±0.56 ^b β	3.48±0.43 ^e	BDL	
Buior	Buiorului	alu Klesiliy rului	2015	158.84±4.97 ^d a	11.24±1.51 ^c a	187.97±10.22 ^d β	$3.42 \pm 1.05^{\circ} \beta$	670.24±4.59 ^b β	6.47±0.35 ^a a	6.56±0.51 ^{bc}	BDL	
bajor bajorate	Bajoralar	ijorului	2013	105.17±8.56 ^g β	5.28±0.62 ^e β	143.05±2.92 ^f β	4.12±0.47 ^c a	566.27±6.89 ^d a	2.49±0.17 ^{cd} a	3.15±0.12 ^e	BDL	
			Şarba	2014	102.92±3.95 ^g β	8.28±1.03 ^d a	$154.51 \pm 10.01^{f} \beta$	2.93±0.63 ^c a	$552.03 \pm 2.19^{e} \beta$	3.04±0.49 ^c a	$6.15 \pm 0.44^{\circ}$	BDL
			2015	148.65±2.81 ^e a	7.51±0.91 ^d a	173.35±5.90 ^e a	3.19±0.64 ^c a	397.73±7.02 ^h γ	1.13±0.12 ^f β	3.09±0.47 ^e	0.13 ± 0.02	
			F.	285.893	38.755	239.274	15.770	788.454	42.251	43.530		
			Sig.	p≤0.000	p ≤ 0.000	p ≤ 0.000	p ≤ 0.000	p ≤ 0.000	p≤0.000	p ≤ 0.000		
		F.		725.390	80.434	660.408	44.513	1850.342	118.543	53.257		
Variety		Sig		p≤0.000	p≤0.000	p≤0.000	p≤0.000	p≤0.000	p 0.000	p≤0.000		
				* * *	* * *	* * *	* * *	* * *	* * *	* * *		
		F.		329.945	49.418	165.680	16.001	278.891	11.420	9.451		
Years		Sig		p≤0.000	p≤0.000	p≤0.000	p≤0.000	p≤0.000	p = 0.001	p = 0.002		
				* * *	* * *	* * *	* * *	* * *	* * *	* * *		
Variety		F.		44.118	12.586	65.504	1.282	512.291	19.520	55.706		
x Years		Sig	•	p≤0.000	p≤0.000	p≤0.000	p≤0.000	p≤0.000	p≤0.000	p≤0.000		
7 10013				* * *	* * *	* * *	* * *	* * *	* * *	* * *		

The concentrations of Ba, Cs, Sr, Co, V, La, Ce and Mo in wine samples (μ g/L) (Mean \pm standard deviation [n=3])

Romans represent the significance of the variety difference (p≤0.005). Greeks represent the significance of the same variety cultivated in other year's difference (p≤0.005). The difference between any two values, followed by a common letter is insignificant. *M.P.L - maximum permissible limit. BDL - below the detection limit (<0.001 μ g/L).

** OIV, 2005.

Lanthanum recorded the highest concentrations in the wine produced from Italian Riesling variety (6.51±0.83 µg/L [2013]; 6.47±0.35 µg/L [2015]), followed by Fetească Albă (4.30±0.27 µg/L [2015]), while the Şarba variety (1.13±0.12 µg/L [2015]) and Fetească Albă (1.91±0.67 µg/L [2014]) had the lowest concentrations of lanthanum. It can be seen that the studied varieties of vines recorded concentrations of lanthanum within wide limits (6.51±0.83 µg/L [2013] Italian Riesling and 1.13±0.12 µg/L [2015] Şarba). Among the analyzed varieties are very significant differences (F=42.251, p≤0.000). When performing the polyfactorial analysis, we see that the factor Variety (F=118.543, p≤0.000) had the greatest influence on the accumulation of lanthanum in wine, followed by the interaction between the two factors (Variety x Year) (F=19.520, p≤0.000) which also had a very significant influence on the accumulation of vanadium. The factor Years (F=11.420, p≤0.000) had a very significant influence on this character (Table 4).

Regarding the concentration of Ce in the wine samples, based on the results we can say that Fetească Albă (7.50±0.34 µg/L [2014]) and the Italian Riesling varieties (7.20±0.23 µg/L [2013]) accumulated the highest concentration in the analyzed samples of wine; while the Italian Riesling variety ($3.48\pm0.43 \mu g/L$ [2014]) and Şarba ($3.15\pm0.12 \mu g/L$ [2013]; $3.09\pm0.47 \mu g/L$ [2015]) had the lowest concentration of cerium in wine samples. Among the analyzed varieties are very significant differences (F=43.257, p≤0.000). From the polyfactorial analysis we see that the factor Variety (F=53.257, p≤0.000) had the greatest influence on the accumulation of Ce in wine, followed by the interaction between the two factors (Variety x Year) (F=55.706, p≤0.000) which also had a very significant influence on the accumulation of vanadium. While the factor Years (F=9.451; p=0.002) had a significant distinct influence on this character.

In the case of Mo the majority of analyzed wine samples displayed a content below the limit of detection (LOD<0.001 μ g/L). The wine produced from Fetească Albă (0.11±0.02 μ g/L [2013]) and Şarba (0.13±0.02 μ g/L [2015]) showed concentrations above the detection limit.

In the case of cerium and molybdenum concentration, they are comparable to those obtained by Avram et al (2014) with 3.80 μ g/L Ce (Sauvignon Blanc from Muntenia) and 11.34 μ g/L Ce (Sauvignon Blanc from Oltenia) and the concentrations of molybdenum, in this research are lower than those obtained by Avram (2014) (41.30 μ g/L Mo) (Fetească Albă from Muntenia) and (77.08 μ g/L Mo) (Sauvignon Blanc from Oltenia).

Toxic metals. The levels of certain contaminant elements, such as As, Cd, Pb at different stages of the winemaking are of great concern because of their toxicological potential and legal requirements. Some upper limits for the metal concentrations in wine are given by the International Organization of Vine and Wine (OIV 2005). The upper limits are: 0.01 mg/L for Cd and 0.2 mg/L for Pb and As.

Regarding As concentration, the highest amount were recorded at wines from the Fetească Albă variety (18.41±2.70 mg/L [2014]), followed by Şarba (11.09±0.72 mg/L [2015]) and Fetească Albă (12.74±0.25 mg/L [2015]), these variants are equal in terms of statistics. In contrast, the lowest concentrations were recorded in Fetească Albă (5.71 ± 1.09 mg/L [2013]), followed by the Italian Riesling variety (3.92 ± 0.85 mg/L [2013]). The cast of these results confirm the data from national and international literature on the influence of arsenic accumulation of factors variety and year. Statistically, between the analyzed variants is no highly significant difference (F=43.373, p≤0.000). From the polyfactorial analysis we see that the factor Year (F=83.007, p≤0.000) had the greatest influence on the accumulation of arsenic in wine, followed by factor Variety (F=51.750, p≤0.000) and the interaction between the two factors (Variety x Year) (F=19.367, p≤0.000), had a very significant influence on this character (Table 4).

					Total metal concentrati ons (µg/L)				
4000	Vincuard	Variaty	Voor	As	Pb	Cd	Hg		
Area	vineyaru	variety	real	M.P.L	M.P.L	M.P.L*	M.P.L*		
				0.2 (mg/L)	(0.2 mg/L)	(0.01 mg/L)**	-		
			2013	5.71±1.09 ^{de} γ	21.85±1.63 ^{ab} a	BDL***	0.66 ± 0.11		
		Feteasca Albă	2014	18.41±2.70 ^a a	12.04±0.50 ^e β	BDL	0.71 ± 0.06		
			2015	12.74±0.25 ^b β	25.80±4.93 ^a a	BDL	BDL		
		_	2013	3.92±0.85 ^e β	18.42±0.90 ^{bc} a	0.12±0.01	0.58 ± 0.03		
		Italian Riesling	2014	8.66±0.78 ^c a	20.32±3.88 ^{bc} a	BDL	BDL		
Târgu Bujor Dealu	Dealu Bujorului		2015	8.19±0.39 ^c a	16.83±0.45 ^{cd} a	BDL	0.19 ± 0.20		
			2013	7.12±0.72 ^{cd} γ	19.64±1.81 ^{bc} a	0.13 ± 0.05	0.42 ± 0.07		
		Şarba	2014	9.07±0.59 ^c β	13.49±1.10 ^{de} β	BDL	BDL		
			2015	11.09±0.72 ^b a	19.25±0.66 ^{bc} a	BDL	BDL		
		F.		43.373	9.738				
		Sig.		p≤0.000	p≤0.000				
		F.		51.750	2.508				
Variety		Sig.		p≤0.000	p = 0.109				
				* * *	ns				
Years		F.		83.007	14.273				
		Sig.		p≤0.000	p≤0.000				
				* * *	* * *				
Variaty		F.		19.367	11.086				
Vorrs		Sig.		p≤0.000	p≤0.000				
rears				* * *	* * *				

The concentrations of toxic elements in wine samples (μ g/L) (Mean ± standard deviation [n=3]).

Romans represent the significance of the variety difference ($p \le 0.005$). Greeks represent the significance of the same variety cultivated in other years difference ($p \le 0.005$). The difference between any two values, followed by a common letter is insignificant.

*M.P.L - maximum permissible limit.

BDL - below the detection limit (<0.001 μ g/L).

** OIV, 2005.

Regarding the concentration of lead from the analyzed samples of wine, it appears that wine produced from Feteasca Albă has accumulated the highest concentration of this heavy metal ($25.80\pm4.93 \mu g/L$ [2015]) followed the same variety but in the culture conditions of 2013 ($21.85\pm1.63 \mu g/L$). While Italian Riesling ($18.42\pm0.90 \mu g/L$ [2013] ($20.23\pm3.88 \mu g/L$ [2014]) and the Şarba variety ($19.64\pm1.81 \mu g/L$ [2013] ($19.25 0.66 \mu g/L$ [2015]) display no difference in terms of statistics. The wine obtained from Fetească Albă ($12.04\pm0.50 \mu g/L$ [2014]) and Şarba ($13.49\pm1.10 \mu g/L$ [2014]) recorded the lowest concentrations of lead. Very significant differences occur among the analyzed varieties (F=9.738; p≤0.000). From the polyfactorial analysis we see that the factor Years (F=14.273, p≤0.000) had the greatest influence on the accumulation of lead in wine, followed by the interaction between the two factors (Variety x Year) (F=11.086, p≤0.000) which also had a very significant influence; while the Variety factor (F=2.508; p=0.109) had no influence on this character (Table 4).

Cadmium is toxic to the organism, because it accumulates in the kidneys and liver. It induces artificial high blood pressure. Cadmium poisoning has been reported in Japan (1970) as the disease "Itai-Itai", its turmoil being localized mainly in the kidneys and is being characterized by the highly removal of calcium from the body (osteoporosis) (Jârdea 2007).

Mercury and its soluble compounds are toxic to organic structures. Mercury vapors become toxic by forming the methyl mercury ions CH_3Hg^+ and dimethyl mercury $(CH_3)_2Hg$ which affects the central nervous system and weakens the memory. The presence of mercury in wine is entirely accidental: pesticide residues from the grapes, prolonged contact of the must and wine with metals that contain alloys of mercury in their structure (Jârdea 2007) (Table 4).

Regarding the content of cadmium and mercury in the wine samples, it can be seen that these two metals with a noxious effect on the wine consumer, in most analyzed wine samples showed a content below the limit of detection (BLD<0.001 µg/L). In the case of cadmium, the wine produced from the variety Italian Riesling (0.12±0.01 µg/L [2013]) and Şarba (0.13±0.05 µg/L [2013]) have a low content compared to the maximum allowed by applicable law (0.01 µg/L Cd), in the case of mercury, its concentration varies within wide range (Şarba (0.71±0.06 µg/L [2015]) and Italian Riesling (0.19±0.20 µg/L [2015]), these results can not be discussed because statistically they were not insured; in other words, based on these results we can not say which of the analyzed grapevine varieties recorded a higher content of cadmium and mercury, and which recorded a lower content of these harmful metals (Table 4).

Principal component analysis (PCA). The principal components analysis (PCA), also known as the transformation Hotelling or processing Karhunen-Loeve is a technique of factor analysis in which the aim is to reduce the number of variables used initially by taking into account the reduced number of representative variables. PCA is the simplest analysis of the analysis based on own vectors. Due to the fact that in large data, the templates are very difficult to identify, PCA method is very useful because by reducing the number of sizes, the patterns can be identified without any loss of important information. PCA has applications in areas such as face recognition and image compression (Mihaly-Cozmuța 2016).

The PCA to the samples of Dealu Bujorului wines, using variables related to mineral content resulted in 14 principal components and demonstrated that four principal components can explain more than 81.354% of the variation obtained for the samples. The importance of each principal component (PC) is evaluated by the percentage of total variance that it explains. Table 5 shows that PC1 explains 26.935% din the total variance and PC2 explains 23.348, these being the components of greatest importance in this analysis.

Factor analysis showed that the variables with the highest contribution to the separation of the samples in relation to the first principal component, whit marked factorial loading >0.70 were k, Li, A, Ba, Cs, Sr and Co. For the second principal component, the variables with the greatest contributions were Na, V and La. In the third

principal component the variables with greatest contributions in terms of explaining the data were Mg, Pb and the principal component four Co.

Principal component	Eigenvalue	% Total variance	Cumulative eigenvalue	Cumulative %	KMO and Bartlett test*	Sig.*
1	3.771	26.935	26.935	22.713		
2	3.269	23.348	50.283	43.906	0.045	n<0.000
3	2.536	18.114	68.397	64.126	0.943	p30.000
4	1.814	12.956	81.354	81.354		

Estimation of eigenvalues and proportion of variance explained by the principal components obtained by the analysis of mineral content

Table 5

*Kaiser-Meyer-Olkin Measure of Sampling Adequacy.

The variables that contributed little to the study of the compositions from Dealu Bujorului wines were calcium, magnesium and cesium.

Scatter plots of the scores were obtained only in the case of the two principal components, highlighted as most important for the separation of the samples according to region of origin (Figure 2).



Figure 2. Principal components analysis of the determinations of metals for samples of wine. Variance explained: 26.935% (PC1) and 23.348% (PC2).

With exception of the potassium (-0.651) and lithium (-0.534), were found positively correlated metals with PC1 (arsenic (0.640), barium (0.823), cesium (0.637), strontium (0.888) and cobalt (0.609)). For PC2 whit exception of the sodium (-0.854) were found positively correlated metals lithium (0.496) vanadium (0.416) and lanthanum (0.839). The metals belonging to the PC1 can be distinguished from metals from PC2, among these, there is no correlation whatsoever.

Therefore, it can be concluded that the use of a chemometric method such as the PCA is very helpful in terms of metals discrimination based on their concentration. Moreover, this statistical approach enables monitoring the metal accumulation during a crop year, and also to make the differentiation of the vine varieties based on the accumulation of metals and heavy metals. Also, statistical processing of data provided information on the manner the metals interact, as well as how those metals are correlated with each other or not.

Using PCA it was possible to group metals from wine according to their concentration, the significant variables in relation to this separation being the k, Li, A, Ba, Cs, Sr, Co (PC1) and Na, V, La (PC2).

Conclusions. Three varieties of vines cultivated for obtaining high quality of white wine from Dealu Bujorului vineyard were analyzed. Their relatively large ranges of variation were due to the diversity of Romanian areas from which they are originating, with diverse quality of the soil but also as a result of anthropic impact. As detailed within the analysis of measured data, the highest concentration of metals with anthropic impact may due to the viticultural practices, the use of plant protection products (Ca, Mg, K, Na and Li) or as consequence of the use of pesticides and fungicides during the grapes development (Cu, Cd, Mn, Pb, Hg and As).

Several factors, like environmental ecoclimatic conditions, agricultural practices, climatic changes and winemaking processes, may change markedly the multi-element composition of the wine, and also may endanger the relationship between soil and wine composition. In this research, based on polyfactorial analysis, we can say that the variety of wine and years of culture had a significant influence on accumulation of elements.

Using PCA it was possible to group metals from wine according to their concentration, the significant variables in relation to this separation being the k, Li, A, Ba, Cs, Sr, Co (PC1) and Na, V, La (PC2).

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