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ICP-MS CHARACTERIZATION OF SOME ROUMANIAN WHITE WINES BY THEIR MINERAL CONTENT

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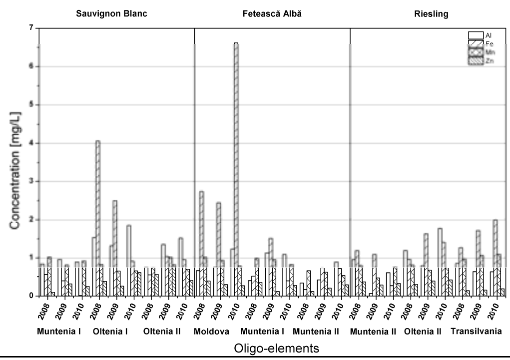
Twenty-seven Roumanian white wines from different wine-making areas produced in three different years were investigated regarding their metal content and isotopic ratios $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$ and $^{87}Sr/^{86}Sr$. All determinations were performed by ICP-Q-MS. Twenty-five metals were identified, K being the most abundant. Relative important concentration of Cr and Ni are due to technological procedure. The As, Cd, Pb were detected in all analyzed wines, but the concentrations are under legal limits. The $^{87}Sr/^{86}Sr$ isotope ratio can be used as a tracer of wine's origin, while the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios are commonly used as tracers to differentiate natural and anthropogenic Pb.



INTRODUCTION

Wine is a very complex product, which along with water and alcohol contains a great variety of both inorganic and organic substances.[1] The presence of trace elements in wine is generally related with soil composition and properties as well as with plant uptake processes, although it can be changed by wine-producing practices.[2,3]

The study of the mineral content of wines is of great interest due to its influence on their stability (copper and iron), due to their toxicological risks, and because some of them are regulated by law. Another major interest resides in the fact that mineral content can be used to characterize the wines by their geographical origin, minerals being the most appropriate 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.[1,4-6] This differentiation can be carried out by using major, trace and ultra-trace elements.[1,5]

The identification of the geographical origin of wines is of great interest for wine consumers and producers, since it may provide determinant criteria for wine price and guarantees of quality.[7] In this sense, the knowledge of the mineral content can be useful to prevent fraud and to guarantee origin.[5] The main purpose of the Regulatory Councils is to prevent fraud by guaranteeing the

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origin and quality of wines; to obtain a quality label, a useful tool is the knowledge of the values of several chemical descriptors that allow a link to be established between the wine samples and their geographical origin. Among them, mineral content has been studied with this goal in mind.[1]

Even though certain agricultural practices (fertilization, fungicide treatments), vinification processes and variability of environmental conditions may complicate the fingerprinting of wine provenance, recent studies have shown that trace elements are good indicators of wine origin and that their concentrations can be used as criteria for guaranteeing authenticity.[2] Further understanding of the factors controlling the variability of trace element contents in wine samples is therefore necessary.[3]

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique suitable for the analysis of young-finished, red-white, table-fortified wines and even sweet wines made of over-ripe grape samples in (semi)quantitative mode providing high selectivity, sensitivity and lower detection limits than other multi-element techniques.[8] A number of papers have been published reporting the use of ICP-MS methods for determine trace metals and rare earth elements in wine fingerprints.[9-13]

Recently, ICP-MS have increasingly been used in isotope ratio measurement.[14,15] Although ICP-MS analysis cannot achieve the precision and accuracy in isotope ratio determination attained in thermal ionization mass spectrometry (TIMS), several advantageous features make the use of ICP-MS a suitable alternative: fast sample throughput, low sample analysis cost, instrument robustness and simplified sample preparation.[16,17]

Measurements of isotope ratios of elements with variable isotopic abundances may be useful for the protection of prestige wines. This variation may be explored in order to determine the origin of a wine. Trace element concentrations in wines depend, among others factors, on geographical origin. Elements are taken up by roots of plants, passing to the grapes in the same isotopic proportions as they occur in the soil. Thus, the $^{87}Sr/^{86}Sr$ (isotope ratio) can be used as a tracer of wine origin if a significant correlation between the value of this parameter in the soil and in a wine is observed and if significantly different values are present in wines of different provenance region.[18]

Lead is composed of four stable isotopes, three of which are of radiogenic origin. The radioactive decay of ^{238}U; ^{235}U and ^{232}Th generates, respectively, ^{206}Pb; ^{207}Pb and ^{208}Pb. The most stable isotope, ^{204}Pb, is non-radiogenic. The respective proportions of these lead isotopes, originated from the genesis of the rocks and ore deposits, vary with geological ages and consequently with geographical locations. Stable isotope ratio analysis can yield information about the origin of lead in a given sample.[19] $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$ are commonly used as tracers to differentiate natural and anthropogenic Pb.[20]

In the present paper twenty-seven wine assortments from Romania were investigated from the point of view of their metal content and isotopic ratios $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{86}Sr/^{87}Sr$.

EXPERIMENTAL

Wine samples

Twenty-seven commercial bottled Roumanian white wine samples were investigated in this study. The wines were produced by different vineyards from four most important wine-making Romanian areas: Oltenia (Oprişor and Vânju-Mare vineyards), Muntenia (Halewood and Ceptura vineyards), Moldova (Huşi vineyard) and Transylvania (Jidvei vineyard). The studied wine sorts were Sauvignon Blanc, Fetească Albă and Riesling produced in three consecutive years: 2008, 2009 and 2010 (Table 1).

Samples preparation

For ICP-MS analysis the wines samples were mineralized and diluted to avoid clogging the nebulizer. According to W. Diegor[21] *et al.*, 2.5 mL ultrapure nitric acid was added to the 2.5 mL of wine in a Teflon container which was then sealed. Six such vessels were inserted in a device consisting of six cylinders of stainless steel mount between two flanges, ensuring a pressure-resistant armor. The entire system was placed in an oven at 200°C for 12 hours. Ultrapure water was added to the colorless resulted solutions up to a volume of 50 mL, and then the samples were diluted 1:20 v/v.

ICP-MS Analysis

All measurements were performed with an ICP-MS Perkin-Elmer Elan DRC (e), equipped with a nebulizer Meinhard and a cyclonic spray chamber. The ELAN DRC (e) uses chemical resolution to eliminate plasma – based polyatomic species before they reach the quadrupole mass spectrometer. This ion molecule chemistry uses a reaction gas to "chemically scrub" polyatomic or isobaric species from the ion beam before they enter the analyzer, resulting in improved detection limits for traditional difficult elements, including As, Cr, Fe, Se and other.

The experimental conditions were: argon flow on nebulizer - 0.86 L/min; auxiliary gas flow - 1.2 L/min; argon flow in plasma - 15 L/min; lens voltage - 7.25 V; RF power in plasma-1100 W; CeO/Ce = 0.027; Ba^{++}/Ba^{+} = 0.025. Accuracy was calculated for the elements taken into consideration (0.5–15%).

The strontium isotope ratio was measured in the scan mode peak hopping, mode standard, using 25 sweeps (reading 3, replicates 6) at a dwell time of 50 ms and an integration time of 3750 ms. The corrections for Sr86 and Sr87 were: -1.505657 Kr83 and -0.385617 Rb85 respectively. The lead isotope ratios were measured in the scan mode peak hopping, mode standard, using 40 sweeps (reading 3, replicates 6) at a dwell time of 50 ms and an integration time of 6000 ms.

RESULTS AND DISCUSSION

Metal content

Mineral content of wines depend on several factors, including soil, variety of grape, environmental conditions and viticultural and enological practices. The determination of some elements is of interest due to their toxicological or physiological properties, while others can lead to wine spoilage.[22]

Depending on their concentration in wine, the elements are divided into three groups: macro-elements or major elements (Na, Mg, K and Ca) which have a concentration greater than 10 mg/L; micro-elements or oligo-elements (Al, Cu, Fe, Mn, Zn, Rb, Sr, etc.) having concentrations between 0.1-10 mg/L and trace elements (Pb, Cd, Cs, etc.) whose concentrations are below 0.1 mg/L.[23,24]

The obtained concentration of major elements in analyzed wine samples are presented in Table 1 and they are ranged as following: for Na between 13.84-95.88 mg/L, for K between 145.22-301.84 mg/L, for Ca between 38.74-77.36 mg/L, for Mg between 56.38-118.68 mg/L.

Among the major elements, potassium showed the highest concentrations, followed by magnesium, calcium and sodium, values in accordance with literature data.[24-26]

Table 1

Major element concentration in the investigated white wine samples

Code	Wine varieties	Wine region	Production year	Major element concentration [mg/L]			
				Na	Mg	K	Ca
W_1	Sauvignon Blanc	Muntenia (Vineyard I) (Halewood, Dealurile Munteniei)	2008	52.10	106.42	145.22	63.60
W_2			2009	59.30	109.54	230.70	77.36
W_3			2010	60.46	113.64	276.18	69.40
W_4		Oltenia (Vineyard I) (Oprişor, Dealurile Olteniei)	2008	28.10	83.94	175.38	62.54
W_5			2009	36.98	100.24	215.24	74.16
W_6			2010	43.28	85.46	180.74	68.00
W_7		Oltenia (Vineyard II) (Mehedinţi,Vânju-Mare)	2008	31.30	113.24	251.40	63.72
W_8			2009	37.76	100.90	268.22	75.44
W_9			2010	39.58	106.08	257.98	72.82
W_{10}	Fetească Albă	Moldova (Dealurile Huşilor)	2008	25.42	103.12	267.20	44.28
W_{11}			2009	95.88	100.94	301.84	70.06
W_{12}			2010	38.94	95.50	261.18	54.46
W_{13}		Muntenia (Vineyard I) (Halewood, Dealurile Munteniei)	2008	45.18	102.24	168.36	64.82
W_{14}			2009	52.70	104.78	188.30	73.84
W_{15}			2010	61.60	118.68	230.18	67.78
W_{16}		Muntenia (Vineyard II) (Ceptura, Dealurile Munteniei)	2008	29.00	106.70	179.94	49.32
W_{17}			2009	27.82	109.82	254.72	40.52
W_{18}			2010	30.68	104.84	265.46	54.66
W_{19}	Riesling	Muntenia (Vineyard II) (Ceptura, Dealurile Munteniei)	2008	31.64	115.22	148.70	60.58
W_{20}			2009	18.08	56.38	147.40	38.74
W_{21}			2010	27.70	82.76	147.82	61.78
W_{22}		Oltenia (Vineyard II) (Mehedinţi, Vânju-Mare)	2008	29.36	108.14	179.54	70.34
W_{23}			2009	27.98	105.22	210.26	72.90
W_{24}			2010	29.84	84.04	216.08	65.28
W_{25}		Transylvania (Jidvei)	2008	27.64	87.96	208.80	60.34
W_{26}			2009	16.46	80.22	176.62	56.74
W_{27}			2010	13.84	74.04	182.88	61.40

Potassium (K) plays an important role in balancing the pH, organoleptic quality and stability of wine. In the analyzed wines samples the average content of K was 212.45±14.85 mg/L, while the averages on assortments being: 222.34±15.60 mg/L in Sauvignon Blanc (W_1-W_9), 235.24±16.50 mg/L in Fetească Albă (W_{10}-W_{18}), and 179.78±12.60 mg/L in Riesling (W_{19}-W_{27}). It can remark somewhat lower value of potassium content for the Riesling and close values for the averages of other two varieties. This behaviour seems to be caused by the fact that in vineyards II of Muntenia and Oltenia potassium levels appear to be in a consistently way lower than that obtained for Sauvignon Blanc and Fetească Albă in the same vineyards. Another fact that can be noted is the increasing evolution trend from year to year of the values in potassium content for Sauvignon Blanc and Fetească Albă varieties from most vineyards of Muntenia, while the values obtained for Riesling are almost constant in these three years. A similar trend is observed for Riesling from the vineyard of Oltenia region, whilst for Sauvignon Blanc from the vineyards of Oltenia region the maximum content of potassium are present in the sample from the year 2009. At first glance the absorption of potassium from the soil seems to be different depending on the grape variety. However, despite the relatively limited number of wine samples studied, it can be concluded that the obtained values depend crucially on the particular metal content of the soil, and, of course, on the amount of fertilizer used locally from year to year and on the winemaking practices. It is well known from literature data that the potassium level in wine is mainly influenced by fertilizer used for cultivation[2,23] and the quantity of potassium metabisulfite ($K_2S_2O_5$) usually added during the winemaking process for its antibacterial and antioxidant properties.[2,27]

Magnesium (Mg) and **calcium (Ca)** also occur in substantial concentrations in wine. Mg is an essential micronutrient in plants being an essential element in the chlorophyll molecule and, together with calcium, contributes to the structure of cell walls.[25] Magnesium content is quite stable in the analysed wines. In most samples, the concentrations varied in the range of 80.22 - 118.68 mg/L, excepting only two values for Riesling samples (56.38 mg/L for W_{20} and 74.04 mg/L for W_{27}). The average value of magnesium content for Riesling sort is 88.22±5.30 mg/L (W_{19}-W_{27}), lower than the relatively close obtained averages for Sauvignon Blanc (102.16±6.13 mg/L for W_1-W_9) and Fetească Albă (105.18±6.31 mg/L W_{10}-W_{18}). This trend is similarly to that observed for potassium. It can also note that, unlike the dispersed evolution of potassium concentrations, magnesium content varies generally between significantly lower limits. Generally, the level of Mg appears to have correlated amplitudes with those of K, excepting the Riesling produced in Oltenia (vineyard II) where the level of K increases whereas the level of Mg decreases. This fact may be due to the use of different fertilizers (in some areas deficiencies regarding a particular metal can be developed) and to winemaking practices.

The range of average values of *calcium* content is also relatively small, being: 69.67±4.87 mg/L for Sauvignon Blanc (W_1-W_9), 57.75±4.04 mg/L for Fetească Albă (W_{10}-W_{18}), and 60.90±4.26 mg/L for Riesling (W_{19}-W_{27}), respectively. Although this metal is a natural constituent of grapes, its concentration may be influenced by the addition of calcium carbonate in the wine for balancing its acidity.[1,25] Calcium oxide (lime) as a constituent of fungicides used for spraying of vines may also contribute to the Ca content of wine.[25] Therefore, small variations in the content of Ca may be due to such practices which can differ depending on the vineyard.

Sodium (Na) concentration was in most samples below the maximum allowed (60 mg/L),[28] being in the range of 13.84-52.70 mg/L. One exception is the Sauvignon Blanc from Muntenia I, in which the sodium content is close to the maximum admissible concentration (60.46 mg/L). Another exception is Fetească Albă, where the values are exceeded the admitted value, the highest value being in the sample from Moldova region (95.90 mg/L). This could be explained by wines contamination with Na due to the use of fining agents, such as bentonite[2,23] or to the addition of sodium salts, such as sulphate or sorbate.[29]

As regards micro- and trace elements, Tables 2-4 and Figs. 1 and 2 show the concentration of twenty-one metals determined in the analyzed wines samples. The levels of certain contaminant elements, such as Cu, Zn, 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.[28] The upper limits for Cd, Cu, Pb, Zn and As are 0.001, 1.0, 0.2, 5.0 and 0.2 mg/L, respectively.

Table 2

Metal concentration for Sauvignon Blanc wine varieties

Metal	Wine sample/Metal concentrations [µg/L]								
	Muntenia I			Oltenia I			Oltenia II		
	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8	W_9
Ti	27.99	288.18	234.36	75.18	339.32	4.72	171.86	44.26	58.82
V	159.54	522.56	240.68	417.00	942.82	831.28	79.22	101.54	110.60
Co	2.50	4.52	3.90	3.74	4.94	6.86	2.08	9.14	2.44
As	5.24	11.90	7.50	12.62	21.12	13.74	3.52	3.52	5.10
Mo	10.28	49.16	16.84	40.80	77.08	0.76	3.18	2.60	7.94
Cs	6.24	9.30	17.78	14.56	13.30	13.42	6.14	4.32	5.12
Ba	156.14	162.76	152.56	76.58	102.38	124.66	130.42	139.42	110.50
W	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	35.90	33.30	19.24	14.6	9.86	17.72	15.36	7.74	5.60
Cd	<0.001	0.22	<0.001	<0.001	0.12	<0.001	<0.001	<0.001	<0.001
La	2.00	4.28	3.14	1.58	3.30	16.74	0.62	0.10	3.38
Ce	3.80	9.52	6.20	4.44	7.12	35.48	2.30	0.48	11.34
Hg	0.56	0.22	0.28	0.44	0.22	0.34	<0.001	0.30	0.22
Sr	355.80	280.30	319.60	169.50	139.80	154.90	147.50	171.40	164.40

Table 3

Metal concentration for Fetească Albă wine varieties

Metal	Wine sample/Metal concentrations [µg/L]								
	Moldova			Muntenia I			Muntenia II		
	W_{10}	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}	W_{16}	W_{17}	W_{18}
Ti	169.30	22.44	146.50	185.22	276.76	217.26	20.62	93.14	38.80
V	14.46	13.72	17.28	57.70	400.54	277.16	72.62	24.56	128.36
Co	4.24	4.10	6.60	1.48	2.48	1.96	2.70	3.22	2.92
As	1.56	<0.001	3.24	0.98	9.78	7.36	0.98	1.12	3.52
Mo	15.72	<0.001	<0.001	1.70	41.30	21.04	2.56	<0.001	16.80
Cs	8.44	9.40	20.42	4.26	5.68	8.98	11.54	11.70	14.54
Ba	180.24	191.20	311.46	113.94	231.86	145.74	149.30	122.42	150.68
W	3.08	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	10.76	5.24	18.18	48.30	36.66	26.88	5.10	6.88	5.04
Cd	<0.001	<0.001	<0.001	<0.001	0.16	<0.001	<0.001	<0.001	<0.001
La	1.04	2.68	0.78	0.84	1.06	2.86	0.56	<0.001	<0.001
Ce	2.44	7.24	1.94	3.20	3.82	6.16	1.50	<0.001	<0.001
Hg	0.50	0.34	0.60	<0.001	0.22	0.44	0.38	<0.001	0.66
Sr	234.70	588.40	190.70	329.70	246.60	265.40	208.12	182.10	193.70

Table 4

Metal concentration for Riesling wines varieties

Metal	Wine sample/Metal concentrations [µg/L]								
	Muntenia II			Oltenia II			Transylvania		
	W_{19}	W_{20}	W_{21}	W_{22}	W_{23}	W_{24}	W_{25}	W_{26}	W_{27}
Ti	24.72	1.34	161.90	187.50	8.34	200.68	11.08	145.04	165.56
V	84.70	51.76	96.50	46.34	55.36	99.78	21.02	14.04	18.36
Co	6.16	3.40	4.68	1.90	2.02	2.30	1.52	1.68	1.76
As	2.26	2.98	2.54	2.12	1.82	2.54	0.12	0.26	<0.001
Mo	8.18	3.14	5.88	4.88	7.32	9.82	3.54	<0.001	6.68
Cs	12.06	8.72	12.82	5.38	4.16	3.36	53.50	40.84	38.08
Ba	98.44	87.46	123.70	111.26	134.64	126.08	150.50	125.64	119.00
W	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	160.98	2.26	10.50	8.80	7.98	5.66	16.28	11.26	19.28
Cd	0.18	0.28	0.48	0.72	<0.001	<0.001	<0.001	2.78	0.40
La	2.20	1.14	3.62	0.76	1.32	2.30	3.18	1.14	0.32
Ce	10.78	3.56	8.32	1.78	3.24	8.86	4.46	20.24	0.90
Hg	0.16	<0.001	0.58	0.34	0.10	0.16	0.38	<0.001	0.68
Sr	244.20	300.40	217.40	155.90	139.08	134.98	173.90	145.00	143.80

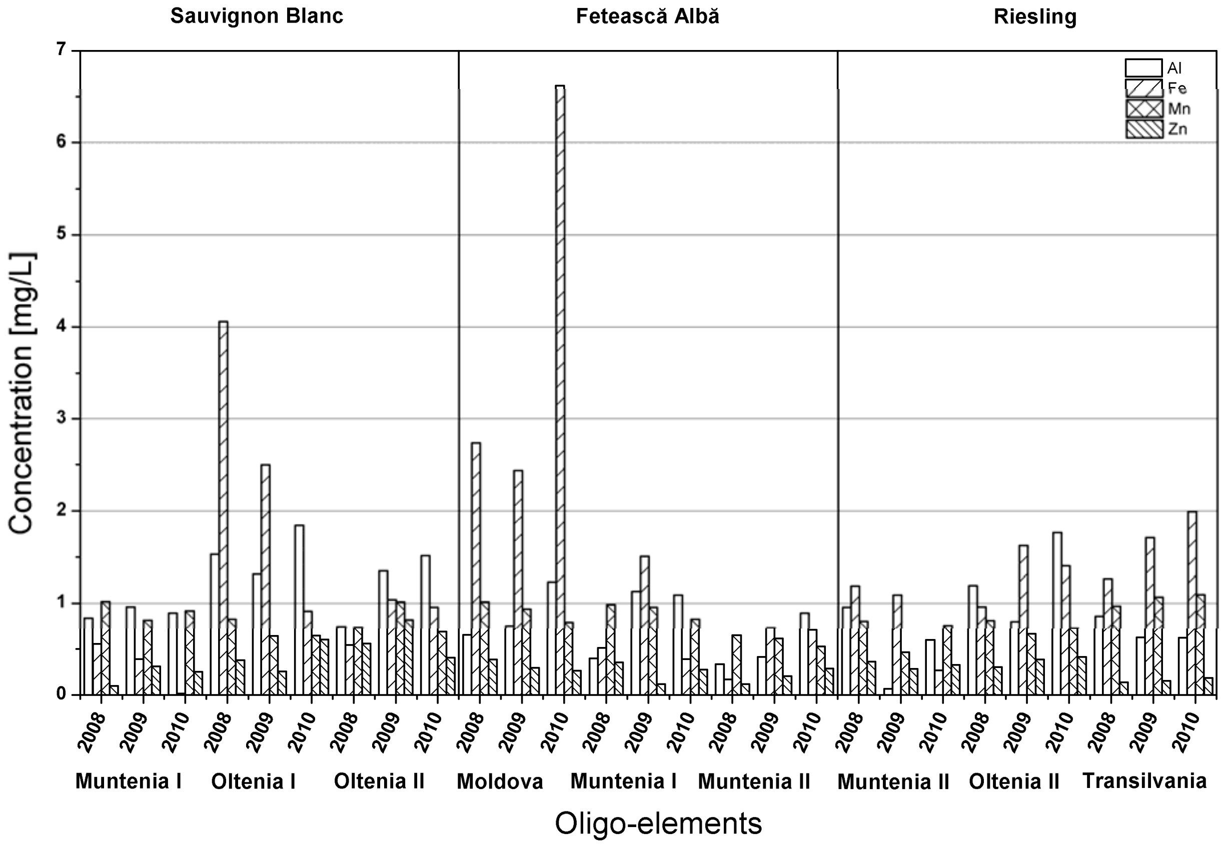

Fig. 1 – Distribution of the most abundant oligo-elements.

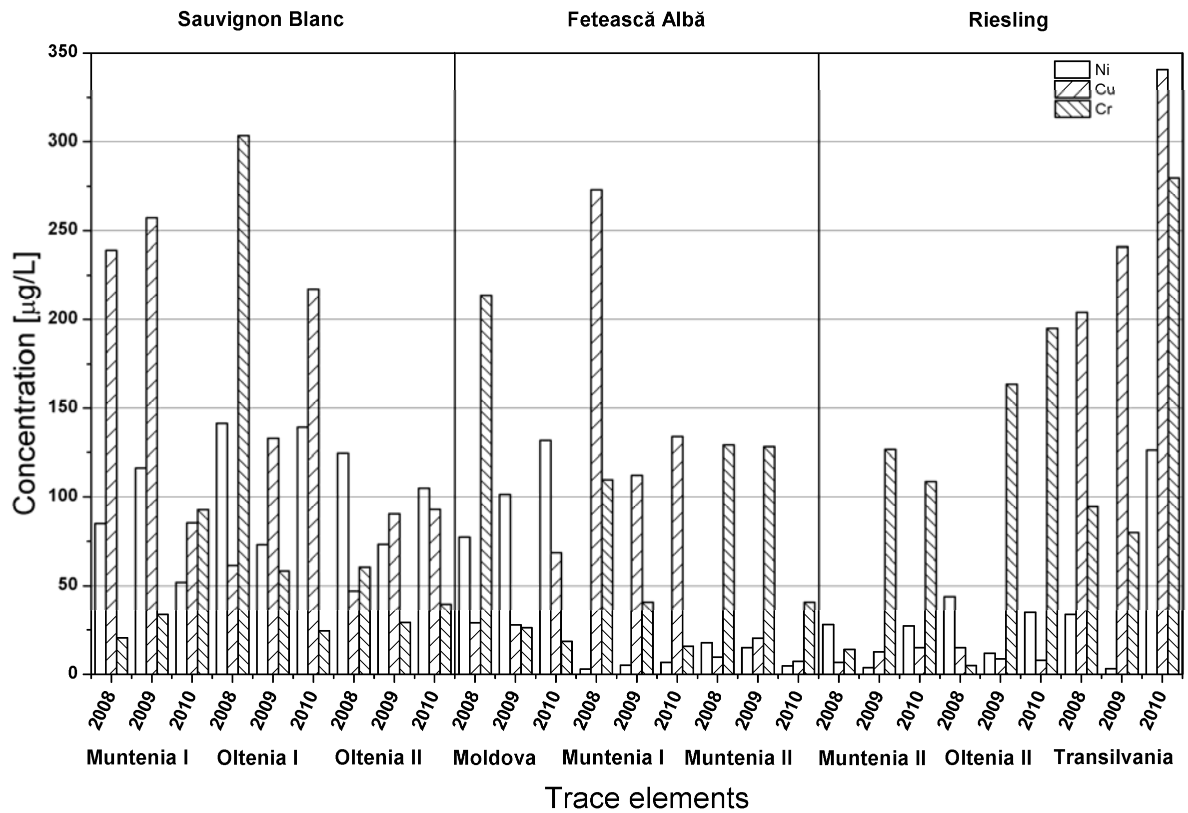

Fig. 2 – Distribution of Cu, Cr and Ni in the analyzed wine samples.

The elements considered to be of particular interest due to their effect on organoleptic properties of the wine, called micro-elements, such as Fe, Al, Mn, Zn and Cu are in lower concentrations. Total average concentrations of these elements obtained for the investigated wines were: 1.42±0.056 mg/L for Fe, 0.94±0.047 mg/L for Al, 0.81±0.048 mg/L for Mn, 0.32±0.016 mg/L for Zn and 0.10±0.007 mg/L for Cu. Figs. 1, 2 represent the concentrations of more abundant micro-elements in analyzed wine samples.

For the **iron (Fe)**, the range is quite different for analyzed wine varieties, so that for Sauvignon Blanc is 0.015-4.06 mg/L, for Fetească Albă is 0.17-6.62 mg/L and for Riesling is 0.27-1.99 mg/L. The highest values are obtained for Sauvignon Blanc produced in Oltenia I (W_4 - 4.06 mg/L), for Fetească Albă made in Moldova (W_{12} - 6.62 mg/L) and for Riesling produced in Transylvania (W_{27} - 1.99 mg/L). These extreme values might be due mainly to longer contact with the surfaces of equipment used in the winemaking.[24] In support of this statement seems to come also the fact that for Sauvignon Blanc assortment from Oltenia (vineyard I) the values obtained for wines from 2008 (4.06 mg/L) and 2009 (2.49 mg/L) are significantly higher than that obtained in the 2010 (0.91 mg/L). In addition, this value from 2010 is close to the average iron concentration in vineyard II in the same region, 0.85±0.031 mg/L. These large differences from year to year or even in the same vineyard can hardly be associated only with a variation of iron content in the soil, but of course, this also plays an important role along with a multitude of other factors.

The **aluminum (Al)** concentrations vary between 0.067-1.84 mg/L, with a maximum concentration obtained in wines produced in Oltenia vineyards. All the value is far below the allowed limit of 8 mg/L. The higher concentrations of Al found in wine samples may be associated with the use of fining and clarifying substances, such as bentonites added to wine for removing the suspended solids after fermentation and for reducing the turbidity, as well as due to the contact with aluminum surfaces.[23,30]

Manganese (Mn) in small amounts is a natural constituent of grapes and wine.[31] In this study, measured values are between 0.46 and 1.09 mg/L. Since Mn is less affected by the winemaking process, these small variations of concentrations can be caused by soil composition and the uptake capacity of grapes, which may differ depending on the variety.[27,31] The measured values show variations from vineyard to vineyard and from region to region. For example, in the case of Riesling assortment, the average concentration of Mn is 0.67±0.03 mg/L for the wines from Muntenia II, 0.73±0.04 mg/L for the wines from Oltenia II and 1.04±0.06 mg/L for the wines from Transylvania. Given the fact mentioned above, that Mn is a natural constituent in wine and does not depend on winemaking process, a detailed analysis of its concentration in parallel with an analysis of soil origin could lead to interesting results concerning authenticity of wine.

Variation of **copper (Cu)** content in analyzed wines samples is relatively large, the range of concentrations being: 46.92-257.16 µg/L for Sauvignon Blanc, 7.34-273.06 µg/L for Fetească Albă and 6.78-340.62 µg/L for Riesling. Higher amounts of Cu were obtained for the Riesling sort originating from Transylvania where the average for the three years is 261.82±17.80 µg/L, compared with an average of 11.51±0.82 µg/L obtained in Muntenia II and 10.55±0.75 µg/L in Oltenia II. Also, higher values were found for Sauvignon Blanc and for Fetească Albă from Muntenia I, where the average is 193.81±13.37 µg/L and 173.09±12.28 µg/L, respectively. Differences from year to year within the same vineyard can be major, as can be seen in Fig. 2. This situation seems to be due to the fact that copper is an element that is most affected by oenological practices and can decrease after fermentation, depending on wine and winemaking process, mainly because of the affinity yeast cells for Cu.[26,30] Since the origin of copper in wine is associated with vineyard sprays with copper sulphate or other copper-based fungicides to control the vine downy mildew,[25,32,33] this may be an additional reason, to the previously mentioned, for higher concentrations observed in some wines. Despite these high values, the content of all analyzed wines was below the maximum concentration allowed by the legislation to prevent formation of cupric cases - 1 mg/L.[2,24]

Zinc (Zn) and **nickel (Ni)** are essential elements for plant development, their content in wine deriving from plant uptake from soils. These elements can occur in soils due to effective contamination with respective metals, but mainly due to the use of certain pesticides and phytosanitary products that may be applied to protect the plants from harmful organisms or to prevent their effects and to eliminate unwanted plants.[3,34] The concentrations of Zn in the tested samples are shown in Fig. 1, the averages on assortment being: 409.32±20.06 µg/L for

Sauvignon Blanc, 256.87±12.84 µg/L for Fetească Albă and 283.66±14.46 µg/L for Riesling respectively. Higher values were obtained for Sauvignon Blanc sort, where Zn content was between 405.64 µg/L and 818.56 µg/L (Oltenia II), compared with the values obtained for Fetească Albă and Riesling assortments, where the concentration varies between 119.82-385.50 µg/L and 140.10-414.04 µg/L respectively. A higher value was observed also in Sauvignon Blanc sort produced in Oltenia I in 2010 (600.88 µg/L) compared with values obtained for the other two years 379.68 µg/L and 255.34 µg/L respectively. Variations from vineyard to vineyard or from year to year may be the result of the treatment of vineyards with pesticides or fertilizers, viticulture products used or of the longer contact with the materials used in the various operations of the vinification and conservation of wines.

The **nichel (Ni)** content in the analyzed wines shows also a large range of variation, as can be seen in Fig. 2. The obtained values are in the range of 52.02-141.44 µg/L for Sauvignon Blanc wines, 3.02-131.64 µg/L for Fetească Albă wines and 3.22-126.30 µg/L for Riesling wines. The more pronounced difference between the values obtained in different vineyards are observed, the wines from Muntenia region having a minimum content of nickel. Higher concentrations found in some wines for Zn and Ni may be highly due to the contamination by contact with stainless steel containers during winemaking.[3]

The **chrome (Cr)** content also has a large range of variation: for Sauvignon Blanc sort is between 20.44-303.40 µg/L, for Fetească Albă is between 15.68-213.56 µg/L and for Riesling is between 4.88-279.80 µg/L. The higher values in some samples may be due to the known fact that the amount of Cr in wine may increase during storage after a longer contact with stainless steel or glass utensils or following storage in bottles, being usually associated with metal oxides existing in bottles.[24,25,30,31]

The presence of **arsenic (As)** and **cadmium (Cd)** were detected in all analyzed wines, but the content are under the legal requirements. Arsenic concentrations were between <0.001-9.78 µg/L, except for a few samples, where higher concentrations were found. Thus, the concentration of As for Sauvignon Blanc assortment from Oltenia I is ranged between 12.62-21.12 µg/L. A higher concentration than 10 µg/L was also found in a sample of Sauvignon Blanc from Muntenia I (11.90 µg/L). A possible explanation may consist in the fact that the concentration of As depends both on the geochemistry of the soil as well as on the use of pesticides, fungicides and fertilizers containing arsenic compounds that may lead to an increase of its amount in soil and grapes and, therefore, in wine.[24,35]

The **cadmium (Cd)** concentration varied between <0.001-0.72 µg/L. For only one sample of wine (Rieslig from Transylvania) a higher concentration was found (2.78 µg/L). The Riesling is also the wine assortment where Cd was found more frequently, unlike Sauvignon Blanc and Fetească Albă where Cd concentration was below the detection limit in most samples. The amount of Cd present in wine may be due to agrochemical residues used as insecticides and fungicides containing cadmium or phosphate fertilizers which have higher concentrations of Cd.[30,34,35] A significant amount of Cd in wine may be due to the contact with equipment used in production and packaging process as well as oenological products used in winemaking.[30]

The determination of **lead (Pb)** in wine is important because of its well-known toxicity. The regular absorbtion of small amounts of lead may originate serious effects on human health, particularly in individuals of risk. The presence of lead in wine is due to two sources of contamination: natural, soil related, and that resulting from human activity. The later is related with atmospheric precipitation, pesticides, materials used to produce, transport and store the wine, etc.[36] The levels of Pb determined for all analyzed wines samples are lower than the upper limit established by the O.I.V. (International Organization of Vine and Wine O.I.V.), being within the range of 2.26-48.30 µg/L. Only one evident exception appear (Riesling sort from Muntenia II), where the measured concentration was of 160.98 µg/L, value close to the maximum allowed of 200 µg/L. Pb content in wine can increase as a result of corrosion of metals or alloys used in wine cellars,[26] and also due to the use of pesticides, fungicides and fertilizers during grapes development.[23]

Strontium and lead isotope ratio

The levels of total Sr detected in wines samples are presented in Tables 2, 3 and 4, the average content for each variety being: 0.21±0.012 mg/L for Sauvignon Blanc, 0.27±0.016 mg/L for Fetească Albă and 0.18±0.011 mg/L for Riesling.

It can be observed that the Sr concentrations are quite stable from year to year and on each vineyard, varying around a local average. Apparently, the concentration of Sr in wine is less influenced by vineyard practices and winemaking technology used, and seems to have a local fingerprint.

Strontium isotopes allow recognizing false declarations because the soils from different wine-producing regions almost always show different $^{87}Sr/^{86}Sr$ values. Horn[37] showed that the $^{87}Sr/^{86}Sr$ ratios for most wines fall into the estimated ranges for country rocks and respective soils. It is assumed that Sr isotopes abundances in wines could be directly linked to those in grapes and soil. In order to characterize a soil-vegetable system, it is necessary to consider all possible natural and anthropogenic strontium sources.

Isotopic ratios of $^{87}Sr/^{86}Sr$ for the investigated wines samples are presented in Table 5. For the $^{87}Sr/^{86}Sr$ isotope ratio the relative standard deviations (RSD_S) was between 0.4-8.3%. It can be observed that the average strontium isotope ratios for the samples from the same region in the three years have close values. It can be also viewed that for some samples the obtained ratios are the same values even though they are originating from different regions (i.e. W_8-Sauvignon Blanc and W_{20}-Riesling from 2009, W_1-Sauvignon Blanc and W_{22}-Riesling or W_{24} and W_{27}-Riesling from 2008). Some differences were found between the wines originating from different vineyards. In the vineyard I of Oltenia we obtained a minimum mean $^{87}Sr/^{86}Sr$ ratio of 0.80 ± 0.02 compared with the mean $^{87}Sr/^{86}Sr$ ratios of Muntenia II (0.82±0.02), Moldova (0.85±0.01), Oltenia II (0.87±0.04), Muntenia I (0.88±0.02) and Transylvania (0.89±0.04). A possible explanation for the higher mean $^{87}Sr/^{86}Sr$ isotope ratio for Transylvania wine can be the mineral consistency of the soil and its different geographical environment. In general, strontium isotope ratios in older rocks such as granite are typically higher, while sedimentary carbonate rich rocks as limestone have lower ratios.[38,39] The strontium isotope ratio in the bioavailable soil moisture however is low for igneous rock and could be as high as 0.75 for carbonate rich rocks.

For predictions of the $^{87}Sr/^{86}Sr$ ratio in wines, a thorough knowledge of the geological and pedological situation in the presumed regions is a prerequisite. In this respect it must be stated that the isotopic Sr compositions of wines do not only depend on natural Sr in soils. An important source of Sr is anthropogenic in origin and enters soils in the form of (phosphate) fertilizers, which are deployed in viticulture. As a further extraneous source of Sr in vines and wines, plant nutrition via aerosol uptake by leaves has to be considered because Sr from aerosol does not necessarily possess the same isotopic signature as Sr from local soil.[40] The $^{87}Sr/^{86}Sr$ isotope ratio may vary with the origin of the element, if anthropogenic contamination does not occur during the vinification, that Sr isotope ratio remain constant through the winemaking process.[41] To confirm this hypothesis, the Sr isotope ratio should be determined in vineyard soil. As wine processing changes from wine to wine, from winery to winery and from country to another, more studies are required before one is able to generalize the suitability of the $^{87}Sr/^{86}Sr$ isotope ratio as a tracer of wine origin.

As a conclusion, these results demonstrate that it is possible to distinguish between wines of different regions taking into account their strontium isotopic composition, which indicate its usefulness for wine provenance determination. Nevertheless, it was not possible to differentiate all the wines regions through strontium ratio only, which suggest that it must be complemented with other discriminating parameters.

The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios are commonly used as tracers to differentiate natural and anthropogenic Pb. In Central Europe, the lead isotopic ratio, as signatures of pollution sources, ranges from relatively high $^{206}Pb/^{207}Pb$ ratios (natural Pb, coals, fly ashes, $^{206}Pb/^{207}Pb$ = 1.17-1.22) to low $^{206}Pb/^{207}Pb$ values (gasoline, petrol combustion, $^{206}Pb/^{207}Pb$ = 1.06-1.14).[42]

Results of the determination of lead isotope ratios in the analyzed wines samples are given in Table 5. The precision values are in the range 0.8-9.5 % (average 5.3 %) for the $^{206}Pb/^{207}Pb$ ratio and 0.4-8.0 % (average 4.2 %) for the $^{208}Pb/^{206}Pb$ ratio. The wines from the Muntenia region (i.e. W_2, W_3 - Sauvignon Blanc, W_{13} W_{14},W_{15},W_{16} - Fetească Albă, W_{20},W_{21} - Riesling), the Oltenia region (W_5,W_6, W_7, W_8 - Sauvignon Blanc, W_{23} - Riesling), or the Transylvania region (i.e. W_{27} - Riesling) have a $^{206}Pb/^{207}Pb$ isotopic ratio between 1.17-1.21 that correspond to the contemporary urban air with particulate material. In the samples from Muntenia (W_1, W_{19}), Oltenia (W_4, W_{22}, W_{24}) and Transylvania (W_{25}) this ratio is more affected by automobile emissions ($^{206}Pb/^{207}Pb$ = 1.10-1.14).

Table 5

$^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ ratios for investigate wine samples

Wine sample	$^{206}Pb/^{207}Pb$±SD (RSD)	$^{208}Pb/^{206}Pb$±SD (RSD)	$^{87}Sr/^{86}Sr$±SD (RSD)
W_1	1.14±0.10 (8.7%)	2.10±0.15 (7.1%)	0.89±0.06 (6.8%)
W_2	1.21±0.07 (5.7%)	2.03±0.09 (4.4%)	0.91±0.02 (2.2%)
W_3	1.17±0.10 (8.5%)	2.06±0.05 (2.4%)	0.86±0.03 (3.5%)
W_4	1.11±0.05 (4.5%)	2.14±0.06 (2.8%)	0.79±0.04 (5.1%)
W_5	1.18±0.05 (4.2%)	2.04±0.06 (2.9%)	0.80±0.02 (2.5%)
W_6	1.19±0.09 (7.5%)	2.04±0.15 (7.3%)	0.80±0.003 (0.4%)
W_7	1.19±0.05 (4.2%)	2.11±0.09 (4.2%)	0.86±0.04 (4.6%)
W_8	1.17±0.04 (3.4%)	2.03±0.06 (2.9%)	0.81±0.04 (4.9%)
W_9	1.15±0.11 (9.5%)	2.10±0.15 (7.1%)	0.82±0.06 (7.3%)
W_{10}	1.15±0.01 (0.8%)	2.02±0.02 (0.9%)	0.85±0.006 (0.7%)
W_{11}	1.16±0.05 (4.3%)	2.08±0.07 (3.3%)	0.76±0.01 (1.3%)
W_{12}	1.18±0.03 (2.5%)	2.08±0.03 (1.4%)	0.94±0.02 (2.1%)
W_{13}	1.19±0.02 (1.7%)	2.06±0.04 (1.9%)	0.87±0.01 (1.1%)
W_{14}	1.17±0.02 (1.7%)	2.08±0.009 (0.4%)	0.86±0.007 (0.8%)
W_{15}	1.18±0.07 (5.9%)	2.06±0.09 (4.3%)	0.88±0.02 (2.3%)
W_{16}	1.18±0.07 (5.9%)	2.12±0.02 (0.9%)	0.80±0.01 (1.2%)
W_{17}	1.15±0.07 (6.5%)	2.10±0.16 (7.6%)	0.81±0.02 (2.5%)
W_{18}	1.16±0.05 (4.3%)	2.15±0.01 (0.4%)	0.84±0.02 (2.4%)
W_{19}	1.10±0.07 (6.3%)	2.16±0.10 (4.6%)	0.82±0.008 (1.0%)
W_{20}	1.19±0.04 (3.3%)	2.07±0.06 (2.9%)	0.81±0.008 (1.0%)
W_{21}	1.17±0.10 (8.5%)	2.11±0.17 (8.0%)	0.83±0.05 (6.0%)
W_{22}	1.14±0.09 (7.9%)	2.14±0.13 (6.0%)	0.88±0.01 (1.1%)
W_{23}	1.20±0.09 (7.5%)	2.05±0.13 (6.3%)	0.93±0.05 (5.4%)
W_{24}	1.14±0.07 (6.1%)	2.09±0.12 (5.7%)	0.92±0.07 (7.6%)
W_{25}	1.12±0.04 (3.6%)	2.09±0.04 (1.9%)	0.84±0.07 (8.3%)
W_{26}	1.15±0.10 (8.7%)	2.09±0.11 (5.2%)	0.92±0.02 (2.2%)
W_{27}	1.18±0.02 (1.7%)	2.08±0.02 (0.9%)	0.92±0.03 (3.3%)

CONCLUSIONS

Using ICP-MS technique 27 samples of commercial white wines were analyzed. In all tested samples, the toxic metals contents were found in quantities below the limits imposed by the legislation, namely by the International Organization of Vine and Wine (O.I.V.).

ICP-MS measurements have shown an important content of metals in studied wines. Their relatively large ranges of variation were due to the diversity of Romanian regions from which they are originating, with diverse quality of the soil, but also as a result of anthropical impact. As detailed within the analysis of measured data, higher content of certain metals with anthropic impact may be due to the viticulture practices, the use of fertilizers for cultivation (K, Ca, Cu) or as a consequence of the use of pesticides and fungicides during the development of grapes (Cd, Cu, Mn, Pb or Zn), the winemaking process, longer contact with processing equipment (Al, Cd, Cr, Cu, Fe and Zn) or addition of substances at different stages of wine production. Thus, contamination with Na, Ca or Al may be associated with the utilization of substances for wine clearing as bentonite.

The determined concentrations of metals are in agreement as magnitude order with the values reported by other authors.[22,35,43] The great variability in the concentration of some trace metals suggests the possibility to correlate the concentration pattern with the wine origin.

Several factors, like environmental contamination, agricultural practices, climatic changes and winemaking processes, may change markedly the multi-element composition of the wine and may endanger the relationship between wine and soil composition.

Much more reliable from this point of view are the $^{87}Sr/^{86}Sr$ isotopic ratios, as these values do not depend on the strontium concentration in wine and the anthropogenic contribution to this element seems to be of little importance.

The comparison of isotopic ratios and trace element concentrations obtained from wines with those determined from soils in which the grapes were cultivated could be used for wines authentication. A data base with such determinations would be very useful. Isotopic ratios $^{206}Pb/^{207}Pb$

can be precisely determined and even to differentiate between anthropogenic and lithogenic source of lead contamination.

A long-term detailed analysis of wines originating from the same vineyard, in parallel with an analysis of the soil and an oversight to the extent of the oenological practices used could contribute to identification with good accuracy of the parameters involved. Establishing a national database and its alignment with those already existing in other countries would contribute significantly to a refinement of the analysis, a better identification of fraud and, consequently, to the improvement in the quality of wines.

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