The determination of $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ isotope rations by ICP-MS for fingerprinting the South-East Romanian wines

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Abstract. Geographical origin of wine based on its chemical composition is one of the most challenging issues in relation to wine authenticity. In the last decade, many efforts have been made to identify the potential markers and develop reliable analytical methods to determine the wines authenticity. Among these "fingerprints", the isotopic rations play an increasingly important role. In this research, the determination of the $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ isotope rations in the wines from Dealu Bujorului vineyard (S-E) Romania using ICP-MS technique was performed. The wine samples resulted from micro-wine production. Regarding the concentration of lead in the analysed samples of wine, we can see that lead varies within a wide range (46.59±0.57 µg/L and 9.78±0.58 µg/L). Based on the statistical analysis is proven that the wine produced from Fetească Neagră (46.59±0.57 µg/L [2014]), (38.68±0.87 µg/L [2015]) followed by the wine produced from Fetească Albă (31.57±0.39 µg/L [2014], (31.96±1.41 µg/L [2015]) have recorded the highest concentration of this heavy metal. In contrast, the lowest concentration was recorded in the wines made from the variety of Băbească Neagră (9.78±0.58 µg/L [2014]) and from Cabernet Sauvignon (10.00±1.45 µg/L [2015]). Regarding the concentration of strontium from the samples of wine, and based on the results we can see that the concentration of this heavy metal varies within a wide range (418.87±18.03 µg/L and 129.60±5.12 µg/L). The highest concentrations were recorded in the wine produced from Fetească Neagră (418.87±18.03 µg/L [2014] and 387.38±8.36 µg/L [2015]), followed by Cabernet Sauvignon (323.35±10.22 µg/L [2014] and (360.95±15.94 µg/L [2015]). Regarding $^{206}Pb/^{207}Pb$ isotopic ration based on analyses we can say that Muscat Ottonel variety exhibited 1.1038±0.0175 (1.5886%) (2014) Băbească Gri variety 1.1079±0.0135 (0.2143%) (2014) and Șarba variety 1.0417±0.0160 (1.5404%) (2014). The higher mean of $^{87}Sr/^{86}Sr$ isotopic ration was obtained by the Merlot variety 1.3617±0.0517 (3.7979 %) (2015) and Burgund Mare Roze 1.3378±0.0240 (1.7939 %) (2015).
Key Words: fingerprinting, lead isotope ration, strontium isotope ration, ICP-MS.

Rezumat. Controlul originii geografice a vinului bazat pe compoziția sa chimică este una dintre problemele cele mai dificile în ceea ce privește autenticitatea vinului. In ultimul deceniu, s-au făcut eforturi mari pentru a identifica potențiali markeri și de a dezvolta metode analitice fiabile pentru a determina autenticitatea vinului. Printre aceste "amprente", rațiile izotopice joacă un rol din ce în ce mai important. În această lucrare a fost studiată determinarea rațiilor de izotopi $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ și $^{87}Sr/^{86}Sr$ în vinul de la podgoria Dealu Bujorului, (S-E) România folosind technica ICP-MS. Probele de vin au rezultat din producția de micro-vin. În ceea ce privește concentrația plumbului din probele de vin analizate putem observa că acest element variază între limite foarte largi (46.59±0.57 µg/L și (9.78±0.58 µg/L). Pe baza analizei statistice reiese că vinul obținut din soiul Fetească Neagră (46.59±0.57 µg/L [2014]; (38.68±0.87 µg/L [2015]) urmat de vinul obținut din soiul Fetească Albă (31.57±0.39 µg/L [2014]; (31.96±1.41 µg/L [2015]) au înregistrat cea mai mare concentrație al acestui metal greu. La polul opus cea mai mică concentrație a fost înregistrată la vinul obținut din soiul Băbească Neagră (9.78±0.58 µg/L [2014]) și vinul obținut din soiul Cabernet Sauvignon (10.00±1.45 µg/L [2015]). Privitor la concentrația stronțiului din probele de vin, pe baza rezultatelor putem observa că și concentrația acestui metal greu variază în limite foarte largi (418.87±18.03 µg/L și 129.60±5.12 µg/L). Cele mai mari concentrații au fost înregistrate la vinul obținut din soiul Fetească Neagră (418.87±18.03 µg/L [2014] și (387.38±8.36 µg/L [2015]), urmat de vinul obținut din soiul Cabernet Sauvignon

(323.35±10.22 µg/L [2014] respectiv 360.95±15.94 µg/L [2015]). În ceea ce privește rația izotopică $^{206}Pb/^{207}Pb$ pe baza analizelor, am obținut la soiul Muscat Ottonel 1.1038±0.0175 (1.5886%) (2014), la Băbească Gri 0417±0.0160 (1.5404%) (2014) și la Șarba 1.0417±0.0160 (1.5404 %) (2014). Valoarea medie mai mare de rație izotopică $^{87}Sr/^{86}Sr$ a fost obtinută de soiul Merlot 1.3617±0.0517 (3.7979%) (2015) și Burgund Mare Roze 1.3378±0.0240 (1.7939%) (2015).
Cuvinte cheie: prelevare amprente, rație de izotopi de plumb, rație de izotopi de stronțiu, ICP-MS.

Introduction. The globalization of food markets has raised consumer concerns for product quality and origin. The place of origin of foodstuff is regarded as value added information and as a guarantee of quality and authenticity of food (Martins et al 2013). Food authenticity is of major concern in the food industry because fraudulent practices such as the adulteration of food through addition of undeclared or harmful ingredients, deviant description on labels, or fake statements about the geographical origin of a food product, can have negative consequences and can even be a health hazard (Vorster et al 2010). Wine fraud in particular, is a common malpractice. In an attempt to combat this, wine authenticity is commonly addressed by a regulatory "wine of origin" system in many countries. The system, however, does not always succeed in preventing the different manifestations of wine fraud. Therefore wine fingerprinting by chemical means as a method of characterization has been studied as an alternative, to support the authenticity of a wine through verification its geographical origin. For wine in particular, geographical origin has a direct effect on its quality and commercial values, being one of the most studied products in terms of food authentication (Barbaste et al 2002; Almeida & Vasconcelos 2003).

Geographical origin of wine based on its chemical composition is one of the most challenging issues in relation to wine authenticity. In the last decade, many efforts have been made to identify potential markers and develop reliable analytical methods to determine the wines authenticity. Among these "fingerprints", isotopic rations play an increasingly important role (Almeida & Vasconcelos 2001; Barbaste 2001).

More recently, the study of isotopic ration of heavy metals elements such as Sr and Pb came into use in this field of application, providing additional information on the geographical origin, since plants inherit the isotopic signature of these elements from the pedological and geological environment (Horn et al 1993; Barbaste 2001; Rummel et al 2010).

Various approaches to wine authentication (Almeida & Vasconcelos 2001; Thiel et al 2004) by chemical analysis have been used including the analysis of organic wine components (Weber et al 1997; Yu et al 2007), multielement analysis (Coetzee et al 2005; Iglesias et al 2007; Taylor et al 2003; Kment et al 2005; Almeida & Vasconcelos 2003), rare earth element analysis (Rossano et al 2007; Jakubowski et al 1999) and isotope ratio analysis (Gremaud et al 2004; West et al 2007; Coetzee & Vanhaecke 2005; Mihaljevič et al 2006; Larcher et al 2003; Almeida & Vasconcelos 2004; Barbaste et al 2002). The determination of stable isotope rations of not only light elements, but also heavy metals (Rossmann et al 2000; Francke et al 2007), such as boron, hydrogen, carbon, nitrogen, oxygen, sulphur (Almeida & Vasconcelos 2004; Lemos et al 2002) and strontium and lead, has found application in the authentication of food and wine.

Strontium shows variations in isotope composition due to radioactive decay. Of strontium four stable isotopes ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, ^{87}Sr is radiogenic (Vanhaecke et al 1999) due to the β^- (β decay is a process whereby the atomic nucleus emits beta particles, electron or positron β^- when emits an electron and β^+ when emits a positron) decay of the long-lived ration nuclide ^{87}Rb (half-life $t_{1/2}$ = 48.8 x 10^9 y) to generate ^{87}Sr. The mean natural abundances (Chassery et al 1998) of ^{84}Sr, ^{86}Sr, ^{88}Sr remain constant, but ^{87}Sr gradually increases if ^{87}Rb is present in the soil, which is generally the case. The $^{87}Sr/^{86}Sr$ ration was shown not to be affected by biological isotope fractionation processes (Kawasaki et al 2002; Latkoczy et al 1998). Accurate determination of the $^{87}Sr/^{86}Sr$ ration requires a measurement precision of 0.01% or better and Sr isotope ration studies are therefore mostly done by high resolution mass spectrometry.

The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ration are commonly used as tracers to differentiate natural an anthropogenic lead. In Central Europe, the lead isotopic ratios, as

signatures of pollution sources, ranges from relatively high $^{206}Pb/^{207}Pb$ ratios (natural lead, fly ashes and coals, $^{206}Pb/^{207}Pb$ = 1.17-1.22) to low $^{206}Pb/^{207}Pb$ values (petrol combustion and gasoline, $^{206}Pb/^{207}Pb$ = 1.06-1.14) (Mihaljevič et al 2006; Avram et al 2014). The precision values are in the range of 0.0553% and 7.0446% for $^{206}Pb/^{207}Pb$ and 0.1816% and 6.6774% for $^{206}Pb/^{208}Pb$ isotopic rations.

The presence of lead in wine is due to two types of sources of contamination: one natural (soil related) and another one resulting from human activity. The latter is related with pesticides used in the vine, atmospheric precipitation, materials used to produce, transport and store the wine (Gulson et al 1992). The role of the different lead sources on the levels of the metal in the final product is unknown but a clarification of this issue deserves research in order to allow an efficient reduction of the lead levels from wine. Lead is composed by 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 the mentioned lead isotopes, originated from the rocks and ore deposits, which vary with geological ages and consequently with geographical areas (Augagneur et al 1996). Stable isotope ratio analysis can yield information about the origin of lead in wine sample. $^{206}Pb/^{204}Pb$ shows a variation depending on the years of production (Arvanitoyannis et al 1999). Isotope ration of lead and strontium in wine may explored in order to determine the origin of the beverage (Dehelean & Voica 2011).

In this work, the determination of the $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ isotope rations in wines from Dealu Bujorului vineyard (S-E) Romania, using quadrupole-based ICP-MS was studied. The purpose was to obtain a wine fingerprint for each wine and to establish whether the wines of the Dealu Bujorului vineyard could be classified according to area production using this information.

Material and Method

Sample. Dealu Bujorului vineyard is located in Galati, Romania. This area has a long tradition in culture of vine (especially vines for producing red wine), vineyard Dealu Bujorului was developed with the establishment of Research and Development Station for Viticulture and Enology Bujoru, from Targu Bujoru city. In Dealu Bujorului vineyard the predominant soil is levidated chernozem having a clayey sand texture with pH between values of 7.4 and 8.1, although moisture deficit, natural conditions offer viable ecosystem for the development of vineyard.

The wine samples used in this experiment were obtained from the wines produced from Muscat Ottonel, Aligoté, Băbească Gri, Fetească Albă, Fetească Regală, Sauvignon Blanc, Riesling Italian, Şarba, Fetească Neagră, Burgund Mare, Băbească Neagră, Merlot, and Cabernet Sauvignon from the wine production of the year 2014-2015 in the Dealul Bujorului Vineyard (Table 1). The wine samples resulted from micro-wine production. Vines were pruned according to the Guyot system and were grown on espaliers.

Microwine-making process. In order to evaluate the quality of white and red wines obtained in 2014-2015 crop from Dealu Bujorului vineyard, four microwine-making process was carried out for each treatment (Sampaio et al 2007). Grapes were harvested on September 2014-2015. Fifteen kilograms of grape were destemmed and crushed, then transferred to a microfermentor (10 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 20^0C and humidity 50-60%. Afterwards wine were clarified by means of bentonite (40 g/L 1:10 dilution) and combined with SO_2 up to 100 g/L. Then wines were allowed to cool for twenty days at -5 / -6^0C for cold stabilization, then stored at 4-6^0C until the polyphenols analyses. The wine samples were stored in glass bottles until analysis.

Table 1

Wine growing areas subjected to the present study

Wine	*Type of wine*	*Year production*	*Area cultivated*	*Hubs vines*	*Planting data*	*Distance between rows (m)*	*Distance between vine (m)*
Muscat Ottonel	White	2014 2015	2.00	8333	10.04.2008	2	1.2
Aligoté	White	2014 2015	1.60	6600	01.04.1980	2	1.2
Băbească Gri	White	2014 2015	1.27	5185	01.04.1980	2	1.2
Fetească Albă	White	2014 2015	0.72	3000	23.05.2012	2	1.2
Fetească Regală	White	2014 2015	1.18	4867	01.04.1980	2	1.2
Sauvignon Blanc	White	2014 2015	3.07	15350	24.04.2009	2	1
Italian Riesling	White	2014 2015	0.66	2667	01.04.1987	2	1.2
Sarba	White	2014 2015	0.48	1979	01.04.1980	2	1.2
Fetească Neagră	Red	2014 2015	0.58	2392	01.04.2000	2	1.2
Burgund Mare	Red Rosé	2014 2015	2.31	9336	01.04.1982	2	1.2
Băbească Neagră	Red Rosé	2014 2015	0.32	1306	01.04.1980	2	1.2
Merlot	Red	2014 2015	2.17	8589	01.04.1979	2	1.2
Cabernet Sauvignon	Red	2014 2015	0.36	1485	01.04.2000	2	1.2

Sampler preparation for determination of metals from wine using ICP-MS. For the determination of Pb and Sr in samples of wine were used an amount of 0.2 mL and placed into 8 mL (7 mL HNO_3 69% + 1 mL H_2O_2), after 15-30 minutes the mineralization was performed using a microwave system Milestone START D Microwave Digestion System set in three steps (Table 2). After mineralization, 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).

Table 2

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

			Wine		
Step	*Time*	*Ventilation*	*Temperature (^{0}C)*	*Pressure (Pa)*	*Power (W)*
I	00:10:00	-	200	-	1000
II	00:15:00	-	200	-	1000
III	00:60:00	+	38	-	0

Milestone START D Microwave Digestion System Device user manual.

ICP-MS analysis. The determination of tow mineral elements (Pb and Sr) 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 daily optimized 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 (0.83 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 (2.53±1.00°C). Accuracy was calculated for the elements taken into consideration (0.5-5.0%). The precision for isotopic determination of such an instrument is about 0.08%%

Chemical analysis. The calibration was performed using Certipur multielement standard XXI (10 mg/L [100 mL]) lead (Pb), and strontium (Sr). Stock standard solutions were prepared weekly or whenever an error is suspected due to these solutions. The intermediate solutions was stored in polyethylene bottles and glassware was cleaned by soaking in 10% v/v HNO_3 for 24 hours and rinsing at least three rimes with ultrapure water (Milli-Q Integral ultrapure water-Type 1). 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. Limit of detection (LoD) and Limit of quantification (LoQ) limits were calculated according to the next mathematical formulas: LoD = 3SD/s and LoQ = 10 SD/s (SD = estimation of the standard deviation of the regression line; s = slope of the calibration curve). The results obtained are shown in Table 3.

Table 3

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

Element	*Correlation coefficient*	*LoD (µg/L)**	*BEC (µg/L)***	*LoQ (µg/L)****
Pb	0.9999	0.1090	0.8400	0.3628
Sr	0.9999	0.2804	0.8720	0.9338

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

The 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 $p \leq 0.005$.

Results and Discussion. 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 the organic compounds of the lead are more important than the inorganic ones. The wine contains very small amounts of lead, a 60 µg/L average, with about 45-50% less than the must and 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 (Ţârdea 2007). The International Organization of Vine and Wine gives the admissible limits for the concentration of Pb in wine of 0.2 mg/L (OIV 2005).

Regarding the concentration of lead in the analyzed wine samples, we can see that lead varies within a wide range (46.59±0.57 µg/L and 9.78±0.58 µg/L). Based on the statistical analysis, the wine produced from Fetească Neagră (46.59±0.57 µg/L [2014], 38.68±0.87 µg/L [2015]) followed by the wine produced from Fetească Albă (31.57±0.39 µg/L [2014], 31.96±1.41 µg/L [2015]) have recorded the highest concentration of this heavy metal. In contrast, the lowest concentration was recorded in the wines made from the variety Băbească Neagră (9.78±0.58 µg/L [2014]) and the wines made from Cabernet Sauvignon (10.00±1.45 µg/L [2015]). The differences between the analyzed

variants were statistically displayed, as there is a very significant difference between them (F = 14.273, p≤0.000). This difference is the direct result of the influence of variety, year of culture on the vine crops, but also on the accumulation of lead. From the polyfactorial analysis we see that the factor Variety (F = 673.959; 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 = 46.930; p≤0.000) which also had a very significant influence; also the Year factor (F = 35.153; p≤0.000) had a significant influence on this character (Table 4).

Regarding the distribution of wines by color (white, red and rosé), it can be seen that the red wines have recorded the highest concentrations of lead, white wines have registered an average, whereas rosé wines have the lowest concentration of lead. A possible explanation is the technology used to obtain the white wines, red and rosé from the Dealu Bujorului vineyard, the eco-climatic and eco-pedological condition from this area, and not at least, the variety of vines studied. Reporting the results to national and international laws, we note that the concentrations of lead are below the maximum rate allowed by applicable law (0.2 mg/L, OIV 2005).

Strontium behaves similarly to calcium in many biological and geological processes, having the same valence and similar ionic radius, and can be used as a proxy for labile base cations in tracing the source and fluxes of soil nutrients in the soil–plant system (Bailey et al 1996; Capo et al 1998; Drouet et al 2005). Strontium in wines is associated with the vineyard soil composition and used for assessing wine authenticity (Taylor et al 2003; Díaz 2003; Almeida & Vasconcelos 2003). Regarding the concentration of strontium from the wine samples, based on the result, we can say that the concentration of this metal varies within a wide range (418.87±18.03 µg/L and 129.60±5.12 µg/L). The highest concentrations were recorded in the wine produced from Fetească Neagră (418.87±18.03 µg/L [2014] and 387.38±8.36 µg/L [2015]), followed by the Cabernet Sauvignon (323.35±10.22 µg/L [2014] and 360.95±15.94 µg/L [2015]). The differences were statistically displayed, with a significant difference between them (F = 106.651; p≤0.000). From the polyfactorial analysis we see that the factor Variety (F = 443.262; p≤0.000) had the greatest influence on the accumulation of strontium in wine, followed by the interaction between the two factors (Variety x Year) (F = 11.616; p≤0.000), while factor Year (F = 0.006; p = 0.640) had no influence on this character (Table 4).

The polyfactorial analysis also shows that the accumulation of strontium in wine was primarily influenced by the type of vine cultivated (varieties of grapevines for white, red or rosé wines) and by the interaction between type of the vine and year of culture.
Regarding the distribution of wines by color (white, red and rosé), it can be seen that red wines have recorded the highest concentrations of strontium (as in the case of lead), rosé wines recorded an average content, while white wines have the lowest concentration of strontium. In the case of strontium there is no maximum limit allowed by the applicable law to which we can relate. The obtained results are comparable with the research conducted by Avram et al (2014) (335.80 µg/L Sr [Sauvignon Blanc, Muntenia area]; (588.40 µg/L Sr [Fetească Albă, Moldova area]; (134.98 µg/L Sr [Italian Riesling, Oltenia area]) (33.30 µg/L Pb [Sauvignon Blanc, Muntenia area]; (48.30 µg/L Pb [Fetească Albă, Muntenia area]; 160.98 µg/ L Pb [Italian Riesling, Muntenia area]), and with research performed by Lara et al (2014) (60.00 µg/L Pb).

Table 4

The content of element in wine samples (µg/L) (Mean ± Standard deviation) (n = 3)

Variety	*Vineyard*	*Type*	*Year*	*Pb ± SD (RSD %)*	*Sr ± SD (RSD %)*
				M.P.L. (0.2 mg/L)***	*M.P.L. (-)*
Muscat Ottonel	Dealu Bujorului	White	2014	18.85 ± 0.54^{ghi} (2.85%)	275.73 ± 13.26^{efg} (4.81%)
			2015	20.43 ± 0.79^{efg} (3.87%)	279.20 ± 5.77^{efg} (2.07%)
Aligoté			2014	22.69 ± 0.49^{e} (2.16%)	231.52 ± 6.89^{i} (2.97%)
			2015	21.46 ± 0.44^{efg} (2.05%)	192.41 ± 6.13^{ijk} (3.19%)
Băbească Gri			2014	18.76 ± 0.91^{ghi} (4.83%)	296.73 ± 6.79^{e} (2.29%)
			2015	19.47 ± 0.35^{fgh} (1.82%)	285.02 ± 10.87^{ef} (3.81%)
Fetească Albă			2014	31.57 ± 0.39^{c} (1.23%)	189.71 ± 3.91^{ijk} (2.06%)
			2015	31.96 ± 1.41^{c} (4.40%)	202.59 ± 4.38^{j} (2.16%)
Fetească Regală			2014	10.28 ± 0.20^{j} (1.90%)	129.60 ± 5.12^{n} (3.95%)
			2015	13.85 ± 0.91^{î} (6.65%)	136.96 ± 7.20^{n} (5.26%)
Sauvignon Blanc			2014	16.31 ± 0.15^{iî} (0.92%)	157.75 ± 5.77^{mn} (3.66%)
			2015	18.62 ± 0.51^{ghi} (2.71%)	177.08 ± 7.29^{lm} (4.12%)
Italian Riesling			2014	17.94 ± 0.15^{ghi} (1.78%)	156.45 ± 5.47^{mn} (3.15%)
			2015	15.89 ± 1.15^{iî} (2.12%)	178.45 ± 3.45^{lm} (1.79%)
Șarba			2014	27.93 ± 0.50^{d} (1.79%)	260.63 ± 15.78^{fgh} (6.06%)
			2015	21.88 ± 0.43^{ef} (1.97%)	254.51 ± 1.86^{ghi} (0.73%)
Fetească Neagră		Red	2014	46.59 ± 0.57^{a} (1.21%)	418.87 ± 18.03^{a} (4.30%)
			2015	38.68 ± 0.87^{b} (2.26%)	387.38 ± 8.36^{b} (2.16%)
Burgund Mare			2014	27.83 ± 1.72^{d} (6.17%)	294.31 ± 7.04^{e} (2.39%)
			2015	23.34 ± 0.93^{fg} (4.00 %)	260.71 ± 16.20^{fgh} (6.21%)
Băbească Neagră			2014	9.78 ± 0.58^{j} (5.96%)	126.62 ± 5.15^{n} (4.14%)
			2015	15.57 ± 0.89^{iî} (5.72%)	132.61 ± 8.20^{mn} (6.18%)
Merlot			2014	22.03 ± 0.41^{ef} (1.86%)	142.17 ± 3.09^{mn} (2.18%)
			2015	21.26 ± 1.06^{efg} (5.00%)	179.56 ± 8.72^{jkl} (4.86%)
Cabernet Sauvignon			2014	17.08 ± 0.41^{hi} (2.43%)	323.35 ± 10.22^{d} (3.16%)
			2015	10.00 ± 1.45^{j} (14.45%)	360.95 ± 15.94^{c} (4.42%)
Băbească Neagră		Rosé	2015	12.35 ± 0.22^{î} (1.78%)	182.38 ± 6.30^{ijk} (3.45%)
Burgund Mare			2015	15.45 ± 0.59^{iî} (3.83%)	217.66 ± 5.19^{j} (2.39%)
	F.			13551.346	106.651
	Sig.			p≤0.000	p≤0.000
Variety		F.		673.959	443.262
		Sig.		p≤0.000	p≤0.000
Years		F.		35.153	0.006
		Sig.		p≤0.000	p=0.940
Variety x Year		F.		46.930	11.616
		Sig.		p≤0.000	p≤0.000

Romans represent the significance of the variety difference (p≤0.005). The difference between any two values, followed by a common letter is insignificant. *M.P.L = maximum permissible limit. ** OIV, 2005.

Lead and strontium isotopes ration. Lead isotopic analysis of wines from Bordeaux region France, showed that lead in the wines changed over time to reflect the dominant source of atmospheric lead pollution in southern of France (Médina et al 2000). Other European studies have found that lead isotopic compositions in wine may not always reflect those of leaded petrol, but reflect the isotopic signature of local, dominant metallurgical industries (Larcher et al 2003; Mihaljevič et al 2006). These researches confirm atmospheric deposition as being the dominant contributor to the lead content and isotopic composition from wine. Some studies have shown that contamination from tin-lead foil capsules in the presence of corrosion and cork disintegration can dominate the source of lead from wine (Gulson et al 1992). Other studies have attributed the lead in wine to machinery or additives used during the vinification process where environmental contamination is a minor source of lead (Almeida & Vasconcelos 2003; Stockley et al 2003).

Regarding $^{206}Pb/^{207}Pb$ isotopic ratios based on analyses we can say that Muscat Ottonel variety (1.1038±0.0175 [1.5886% 2014]) Băbească Gri variety (1.1079±0.0135 [0.2143% 2014]) and also Șarba variety (1.0417±0.0160 [1.5404% 2014]), the values of isotopic ratios of these varieties of vine traces of pollution comes from cars (automobile emissions) (if $^{206}Pb/^{207}Pb$ = 1.1000-1.1400 [automobile emissions]), and Sauvignon Blanc variety (1.1925±0.0246 [2.0623% 2014]); 1.1963±0.0174 [1.4560% 2015]), the values of isotopic ratios of $^{206}Pb/^{207}Pb$ traces of atmospheric pollution with lead on vine (if $^{206}Pb/^{207}Pb$=1.1700-1.1210 [atmospheric pollution]) (Table 5). The abundance of the lead isotopes ^{204}Pb (non-radiogenic), ^{206}Pb, ^{207}Pb and ^{208}Pb (radiogenic) originated from the genesis of the substrate varies with geological ages, the original composition of the rock upon its formation, and, consequently, with geographical areas (Shirahata et al 1980; Gulson et al 1981; Elbaz-Poulichet et al 1984). This property is useful in order to identify of the source of lead in a subjected wine sample provided that the measurements of the isotope ratios are precise and accurate.

The higher mean of $^{208}Pb/^{206}Pb$ isotopic ratios was obtained at the Burgund Mare variety 2.3510±0.1080 (4.5928% 2015), Cabernet Sauvignon variety 2.4099±0.0877 (3.4296% 2014) and Cabernet Sauvignon variety 2.3338±0.0267 (1.1423% 2015). In the wine from Aligoté variety we obtained a minimum mean of $^{208}Pb/^{206}Pb$ isotopic ratios of Aligoté 2.0500±0.0050 (0.2432% 2014), and also in wine from Șarba variety 2.0608±0.0557 (3.6730% 2015). Strontium isotopes allow recognizing false declarations because the vineyard soils from different wine producing regions almost always show different $^{87}Sr/^{86}Sr$ values. $^{87}Sr/^{86}Sr$ for most wines fall into the estimated ranges for country rocks and respective soils (Horn et al 1997). It is assumed that Sr isotopes abundances in wines could be directly to those in grapes and vineyard soil. In order to characterize a soil, vegetable system it is necessary to consider all possible natural and anthropogenic strontium sources. Almeida & Vasconcelos (2003) they also observed that the $^{87}Sr/^{86}Sr$ isotope ratio was statistically identical in wines and soil and, hence, can be used as tracer of wine origin. It can be observed that the average strontium isotope ration for the white wine samples from two different years have close values (Fetească Regală 1.1531±0.0727 [6.3090% 2014] and (Fetească Regală 1.1519±0.0344 [2.9899% 2015]).

Table 5

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

Variety	*Vineyard*	*Type*	*Year*	*$^{206}Pb/^{207}Pb$ ± SD (RSD %)*	*$^{208}Pb/^{206}Pb$ ± SD (RSD %)*	*$^{87}Sr/^{86}Sr$ ± SD (RSD %)*
Muscat Ottonel	Dealu Bujorului	White	2014	1.1038±0.0175 (1.5886%)	2.1342±0.0110 (0.5166%)	0.8957±0.0193 (2.1587%)
Aligoté				1.0996±0.0006 (0.0553%)	2.0500±0.0050 (0.2432%)	0.8420±0.0307 (3.6432%)
Băbească Gri				1.1079±0.0135 (0.2143%)	2.2579±0.1032 (4.5694%)	0.8302±0.0167 (2.0151%)
Fetească Albă				1.0992±0.0116 (1.0561%)	2.3181±0.1203 (5.1913%)	0.7638±0.0508 (6.6518%)
Fetească Regală				1.1531±0.0727 (6.3090%)	2.0760±0.0127 (0.6125%)	0.9345±0.0357 (3.8220%)
Sauvignon Blanc				1.1925±0.0246 (2.0623%)	2.2249±0.0962 (4.3229%)	0.8174±0.0261 (3.1915%)
Șarba				1.0417±0.0160 (1.5404%)	2.1645±0.0400 (1.8484%)	0.8044±0.0087 (1.0855%)
Riesling Italian				1.2233±0.0197 (1.6134%)	2.1187±0.0628 (2.9639%)	0.7174±0.0259 (3.6062%)
Muscat Ottonel	Dealu Bujorului	White	2015	1.2432±0.0521 (4.1884%)	2.1719±0.0549 (2.5255%)	0.8016±0.0127 (1.5787%)
Aligoté				1.2916±0.0479 (3.7052%)	2.2713±0.0384 (1.6920%)	0.8062±0.0144 (1.7904%)
Băbească Gri				1.0846±0.0258 (2.3806%)	2.2421±0.0843 (3.7617%)	0.8122±0.0128 (1.5712%)
Fetească Albă				1.0545±0.0819 (7.7655%)	2.0785±0.0588 (2.8272%)	0.8068±0.0097 (1.2059%)
Fetească Regală				1.1519±0.0344 (2.9899%)	2.0286±0.0147 (0.7230%)	0.8175±0.0168 (2.0609%)
Sauvignon Blanc				1.1963±0.0174 (1.4560%)	2.2859±0.0473 (2.0707%)	0.8092±0.0176 (2.1751%)
Șarba				1.0488±0.0386 (3.6793%)	2.0608±0.0557 (3.6730%)	0.8258±0.0110 (1.3280%)
Riesling Italian				1.1445±0.0094 (0.8256%)	2.2823±0.1044 (4.5758%)	0.8242±0.0120 (1.4573%)
Fetească Neagră	Dealu Bujorului	Red	2014	1.0339±0.0138 (1.3307%)	2.1503±0.0039 (0.1816%)	0.8430±0.0057 (0.6722%)
Burgund				1.2734±0.0664 (5.2140%)	2.2858±0.0518 (2.2674%)	0.8859±0.0062 (0.7009%)
Băbească Neagră				1.1571±0.0084 (0.7287%)	2.2901±0.1172 (5.1170%)	0.8781±0.0149 (1.6952%)
Merlot				1.2701±0.0484 (3.8141%)	2.3256±0.1553 (6.6774%)	0.8782±0.0283 (3.2180%)
Cabernet Sauvignon				1.4219±0.0322 (2.2640%)	2.4099±0.0877 (3.4296%)	0.8352±0.0261 (3.1254%)
Fetească Neagră	Dealu Bujorului	Red	2015	1.0562±0.0664 (6.2885%)	2.1431±0.0978 (4.5623%)	0.7625±0.0205 (2.6893%)
Burgund				1.2575±0.0565 (4.4952%)	2.3510±0.1080 (4.5928%)	0.8611±0.0146 (1.6906%)
Băbească Neagră				1.2075±0.0447 (3.7034%)	2.1013±0.0771 (3.6693%)	0.8071±0.0110 (1.3588%)
Merlot				1.3617±0.0517 (3.7979%)	2.0873±0.0693 (3.3201%)	0.9348±0.0192 (2.0538%)
Cabernet Sauvignon				1.0908±0.0768 (7.0446%)	2.3338±0.0267 (1.1423%)	0.8614±0.0141 (1.6353%)
Băbească Neagră	Dealu Bujorului	Rosé	2015	1.2781±0.0621 (4.8612%)	2.2669±0.0429 (1.8934%)	0.7845±0.0350 (4.4600%)
Burgund Mare				1.3378±0.0240 (1.7939%)	2.2030±0.1033 (4.6911%)	0.8054±0.0139 (1.7259%)

SD – standard deviation, RSD % – relative standard deviation.

The higher mean of $^{87}Sr/^{86}Sr$ isotopic ration was obtained at the Merlot variety 1.3617±0.0517 (3.7979% 2015) and Burgund Mare roze 1.3378±0.0240 (1.7939% 2015). A possible explanation for the higher mean of $^{87}Sr/^{86}Sr$ isotopic ration for wine can be the mineral consistency of the vineyard soil and its different eco-climatic conditions. In the wine from Riesling Italian variety we obtained a minimum mean of $^{87}Sr/^{86}Sr$ isotopic ration of 0.7174±0.0259 (3.6062% 2014). In general, strontium isotopic ration in order rocks such as granite are typically higher, while sedimentary carbonate rich rocks as limestone have lower isotopic ration (Barbaste et al 2002; Pillonel et al 2003). The strontium isotope ration in the bioavailable soil moisture is low for igneous rock (Avram et al 2014).

For predictions of the $^{87}Sr/^{86}Sr$ isotopic ration in wine, thorough knowledge of the geological and eco-pedological situation in the presumed regions is a prerequisite. Strontium concentration in wine not only depends on natural strontium from vineyard soil. An important source of strontium is anthropogenic in origin and enter the soil in the form of phosphate (fertilizers) which are deployed in viticulture. Regarding accumulation of strontium by aerosol uptake through leaves in vine and also in wine, does not necessarily possess the same isotopic signature as strontium from soil (Horn et al 1997). The $^{87}Sr/^{86}Sr$ isotopic ration may vary with the origin of the element, if anthropogenic contaminations does not occur during the wine-making process, that isotopic ration remain constant through the winemaking process (Almeida & Vasconcelos 2003). To confirm this hypothesis the $^{87}Sr/^{86}Sr$ isotopic ration should be determined also from vineyard soil. As wine processing changes country to country, from winery to winery and also from wine to win, more studies are required before one is able to generalize the suitability of the $^{87}Sr/^{86}Sr$ isotopic ration as tracer of wine origin.

Conclusions. Using inductively coupled plasma mass spectrometry (ICP-MS) technique, seven varieties of vines cultivated for obtain high quality of white wine (Muscat Ottonel, Aligoté, Băbească Gri, Fetească Albă, Fetească Regală, Sauvignon Blanc and Sarba), five varieties of vines cultivated for obtaining high quality red wine (Fetească Neagră, Burgund Mare, Băbească Neagră, Merlot, Cabernet) and two varieties of vines cultivated for obtained high quality of rosé wine (Băbească Neagră, Burgund Mare) from Dealu Bujorului vineyard were analyzed, in terms of 2014 and 2015 years of culture.

In all tested wine samples, the toxic metals contents (lead and strontium) were found in quantities below the limits imposed by legislation. 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 anthropogenic impact. Based on the results we can say that the accumulation of lead and strontium in wine was influenced by factor Variety, factor Years and also by the interaction of the two factors, (Variety x Years), except for the factor Years which had no influence on the accumulation of strontium in wine.

Regarding $^{206}Pb/^{207}Pb$ isotopic ratios, based on analyses we can say that Muscat Ottonel variety [2014]) Băbească Gri variety [2014]) and also Sarba variety [2014]), shows traces of pollution comes from cars (automobile emissions) (if $^{206}Pb/^{207}Pb$=1.1000-1.1400 [automobile emissions]) and Sauvignon Blanc variety (2014 and 2015), shows traces of atmospheric pollution with lead on vine (if $^{206}Pb/^{207}Pb$=1.1700-1.1210 [atmospheric pollution]). The higher mean $^{87}Sr/^{86}Sr$ isotopic ration was obtained by Merlot variety (2015) and Burgund Mare rosé (2015). A possible explanation for the higher mean of $^{87}Sr/^{86}Sr$ isotopic ration for wine can be mineral consistency of the vineyard soil and its different eco-climatic conditions. In the wine from Riesling Italian variety we obtained a minimum mean $^{87}Sr/^{86}Sr$ isotopic ration of 0.7174±0.0259 (3.6062% 2014).

As a conclusion, these results demonstrate that it is possible to distinguish between wines from different years of productions taking into account their strontium and lead isotopic ration composition, which indicate its usefulness for wine provenance determination. Nevertheless, it was not possible to differentiate all this wines through strontium isotope ration only, which suggested that it must be complemented whit other discriminating parameters.

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