



METAL AND LEAD-STRONTIUM ISOTOPE CHARACTERIZATION OF RED AND WHITE WINES FROM BUJORU, SMULTI AND OANCEA WINE CENTER, ROMANIA

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ABSTRACT

The goal of this research was to assess the potential of Sr and Pb composition and also isotopic signature of lead ($^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$), strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) of wines from Bujoru, Smulți and Oancea wine-growing centers from Dealu Bujorului vineyard. In this study 162 wine samples were investigated. The wine samples were obtained from micro-wine production under conditions of 2014-2016 from Dealu Bujorului vineyard. For all tested wine samples, the toxic metals contents were found in quantities below the limits established by legislation. The highest values were registered to wine obtained from Feteasca Neagra(2016) variety (0.74275 ± 0.00261) from Smulți wine-growing center, the lowest value of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio was recorded to wine obtained from Muscat Ottonel (2014) variety (0.70165 ± 0.00058) Oancea wine-growing center. A possible explanation for the higher mean of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ration for wine can be the mineral consistency of the vineyard soil and its different eco-climatic conditions. Regarding $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratios, we can say that the analyzed wine samples show traces of pollution comes from cars (automobile emissions) (if $^{206}\text{Pb}/^{207}\text{Pb}=1.1000-1.1400$ [automobile emissions]). The Pb isotope ratio from wines varies in range between 1.12305-1.18597 ($^{206}\text{Pb}/^{207}\text{Pb}$), 2.09404-2.14190 ($^{208}\text{Pb}/^{206}\text{Pb}$) and 17.21089-17.70857 ($^{206}\text{Pb}/^{204}\text{Pb}$) with average 1.15202 ($^{206}\text{Pb}/^{207}\text{Pb}$), 2.10878 ($^{208}\text{Pb}/^{206}\text{Pb}$) and 17.42240 ($^{206}\text{Pb}/^{204}\text{Pb}$). Heat map was discovered a separation of wine varieties for white of this red depending on elemental contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios.

1. Introduction

Among the different criteria adopted to protect and promote food quality, the European Union (UE) has introduced, with the use of quality schemes, the link between territory and food (Sighinolfi *et al.*, 2018). In this context, the protected designation of origin (PDO) represents the highest award that can be attributed to an aliment, and its implies that the entire food chain is within a delimited territory (Bora *et al.*, 2018). Although there are many

paper certifications for each food chain process that state for authenticity and quality arising from a particular geographical origin, none of these is based on objective criteria. In recent years, several attempts to develop tracking and tracing models for food processes have been made (Voerkelius *et al.*, 2010; Baroni *et al.*, 2011; Danezis *et al.*, 2016).

Geographical origin and authenticity are factors affecting the overall perception of wines in terms of their quality and price, hence, being

of great important to consumers and wine producers. We refer here to the origin certified products for which elevated prices are justified by the strict relationship which exist between the product quality and the areas of origin (Bora *et al.*, 2018).

Starting from the fact that de term origin has a considerable importance, which correlates to the quality of wines also wine classification in terms of geographical and varietal origins became an argument of significant interest both for consumer and producers. In this respect, various analytical and statistical tools have been proposed for identifying wine are of production, form largest (e.g., country) (Almeida *et al.*, 2016; Aoyama *et al.*, 2017) (e.g., ward, district, wine centers) (Larcher *et al.*, 2003; Avram *et al.*, 2014; Coetzee *et al.*, 2005; Bora *et al.*, 2018).

When dealing with traceability models, it is of utmost importance to determine the identify of geographical indicator that is used to monitor the food chain from the field to the final product. For geographical traceability issues, one of the indicators that can be used is the primary or direct type, such as metal concentration or isotope ratios as bio-elements ($^{13}\text{C}/^{12}\text{C}$, D/H, $^{18}\text{O}/^{16}\text{O}$, $^{15}\text{N}/^{14}\text{N}$, and $^{34}\text{S}/^{32}\text{S}$) or radiogenic heavy elements ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{145}\text{N}/^{143}\text{Nd}$, and $^{207}\text{Pb}/^{206}\text{Pb}$) (Horn *et al.*, 1993; Walker *et al.*, 1989; Price *et al.*, 2002; Fortunato *et al.*, 2004; Trinchnerini *et al.*, 2014; Marchionni *et al.*, 2016; Aoyama *et al.*, 2017).

Evaluation of natural abundance isotope ratios provides information on plant type or animal diet (carbon rations) and geographical origin (lead, strontium, deuterium and oxygen isotopic ratios) (Kelly *et al.*, 2005). However, the $^{13}\text{C}/^{12}\text{C}$ ratios of plants are affected not only by the botanical origin (C3 and C4 plants) but also by physiological and environmental factors that influence water used efficiently in the leaves. Stomatal conductance and intercellular and ambient CO_2 concentrations are influenced by humidity, precipitation, temperature, water stress plant age, and maturation. Strontium is found in nature as three abundant isotopes: ^{86}Sr (9.75-9.99%), ^{87}Sr (6.94-7.14%), ^{88}Sr (82.29-82.77%) and ^{84}Sr (0.55-0.58%) as less abundant

isotope (Berglund *et al.*, 2011). The ^{87}Sr is radiogenic and therefore the ^{87}Sr content increases with time due to radioactive decay of ^{87}Rb (Petrini *et al.*, 2015). Since the content of ^{87}Sr in soil varies with geological age and geographical location, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio can be used as a tracer for determining the geographical origin of wine (Vorster *et al.*, 2010). Lead is found in nature as four abundant isotopes: ^{206}Pb (20.84-27.48%), ^{207}Pb (17.62-23.65%), ^{208}Pb (51.28-56.21%) and ^{204}Pb (1.04-1.65%) as less abundant isotope (Rosman *et al.*, 1998). Their abundance extensively varies because of different decay pathways from ^{238}U , ^{235}U and ^{232}Th to ^{206}Pb , ^{207}Pb , ^{208}Pb respectively (Bora *et al.*, 2018). The Pb isotope of ore deposits and anthropogenic sources has their distinct isotopic ratios or signatures (Cheng *et al.*, 2010). The Pb isotope ratio did not change in industrial or environmental processing and retained its characteristic ratio from source ore (Ault *et al.*, 1970).

Each geologic substratum of vineyards is liable to heave its own Sr isotope composition, which can potentially represent a fingerprint to trace the wine production provenance (Marchionni *et al.*, 2016). The use of $^{87}\text{Sr}/^{86}\text{Sr}$ in tracking wine regional provenances was among the most pioneering application of isotope geology to other sciences (Barbaste *et al.*, 2002). In most of the cases, however, the analytical uncertainty observed in Sr isotopes analyses of wines from literature is larger than most of the soil/rock isotopic variability, giving strong difficulties in matching data of wines with those from geologic substrata of the vineyards. Recently, high precision analytical method for determining $^{87}\text{Sr}/^{86}\text{Sr}$ has been provide enabling then direct comparison between data on wines with those of the pedological and geological substrata (Durante *et al.*, 2015; Petrini *et al.*, 2015).

Long lived isotope ratios of heavy metals of geological interest, such as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, have in the last decades gained importance in tackling the issues of geographical food traceability as well as in solving issues related with archaeological,

environmental, medical and also forensic sciences (Hoogewerff *et al.*, 2001; Voerkelius *et al.*, 2010). This increasing consideration is mainly based on the fact that radiogenic isotopic ratios are extensively used either for tracking geological and environmental processes or dating Earth's materials and cosmological (Stewart *et al.*, 1998). In addition, radiogenic isotope ratios are fractionated by biogenic processes or by low-temperature, and then their abundance in geological materials (minerals and rocks) depends upon: i) the initial radiogenic isotopic abundance, ii) on the age of the mineral/rock and iii) on their parent/daughter isotope ration (Tommasini *et al.*, 2009).

The presence of lead in wine is associated with two major sources as follows: natural sources, which are due to the weathering of rocks, and human activity, which results from the use of fertilizers, pesticides and agricultural and food additives and environmental pollution (Larcher *et al.*, 2003).

The goal of this study is to determine the elemental composition (Pb and Sr) of wine from Bujoru, Smulți and Oancea wine-growing centers from Dealu Bujorului vineyard and to assess their ability to discriminate between geographical origin of wines. Also, the study enhances the knowledge of the large-scale distribution of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and lead ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) isotope ratios in wine from Dealu Bujorului vineyard. The wines from Smulți and Oancea wine-growing centers have not been analyzed yet regarding concentration of the elemental composition and distribution of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and lead ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) isotope ratio.

2. Materials and methods

2.1. Experimental section

2.1.1. Study area

For this study, a total of 162 wine samples (81 white wines and 3 red wines), samples originated from Bujoru, Smulți and Oancea wine-growing centers part of Dealu Bujorului vineyard (45°52'10" N, 27°55'8"E). The Dealu Bujorului vineyard is characterized by an

alternate landscape, from flat to hilly areas, with altitude between 100 and 230 m and the predominant soil is levigated chernozem having a clayey sand texture with pH between values 7.0 and 8.0. Although they have moisture deficit, natural conditions (ecoclimatic and ecopedological) offer viable ecosystem for the development of vineyard. The vineyard is crossed by the parallel 46° latitude north, intersected by the 28° longitude meridian. Dealu Bujorului vineyard belongs to Galati country. The specificity of the transition area is highlighted by the predominance of deposits of clays and sands. Versants were made from clay deposits and sandy sands.

The wines were selected from three consecutive vintages (2015, 2016 and 2017) were obtained by microvinification based on EC Regulation No. 2729/2000, consolidated with EC Regulation No. 2031/2006. Of these, 30 samples were from Bujoru wine-growing center, 56 from Smulți wine-growing center and 76 from Oancea wine-growing center. From the harvest of 2015, 2016 and 2017 were collected 54 wine samples.

2.1.2. Climatological data

The climate data used in this research was recorded through AgroExpert system at RSVE Bujoru and also from weather forecasting center. In experimental years the thermal balance values obtained are higher than multiannual average: global thermal balance ($\Sigma t^{\circ}\text{g}$) was 3560.9 °C (3484.0 °C multiannual average), active thermal balance ($\Sigma t^{\circ}\text{a}$) was 3526.6°C (3387.5 °C multiannual average) and beneficial thermal balance ($\Sigma t^{\circ}\text{u}$) was 1736.6°C (1700.1 °C multiannual average). The precipitation quantity was lower (405.4 mm) then average of the last ten years (505.7 mm). During the growing season, the recorded precipitations values were 257.6 mm, much lower than the multiannual average of 291.5 mm for Bujoru Wine Centre. The ecoclimatic conditions of Dealu Bujorului vineyard highlighted the exceptional viticultural characters of the Dealu Bujorului vineyard. These characters were found in the authenticity

and specificity of a wide assortment of wine obtained in the studied area.

2.1.3. Sample collection and microvinification process

The white cultivars consisted of Muscat Ottonel, Feteasca alba ad Feteasca regala, while red cultivars were Feteasca neagra, Merlot and Cabernet Sauvignon under the conditions of 2015, 2016 and 2017. The wine samples resulted from micro-wine production. Micro-wine production was done according to the methodology describe by Bora *et al.*, 2016; Bora *et al.*, 2018, Donici *et al.*, 2019. All wines were providing by the wineries as finished wines in 750 mL bottles with cork stoppers and were stored at 3-4°C before analysis. All vines were planted since 1979, and the vine plantation was organized with 2.2 x 1 m distance between rows and plants. Vines were pruned according to the Guyot system and were grown on speliers.

2.2. Material and methods used

2.2.1. Reagents and solution

2.2.1.1. Blanks

An appropriately diluted indium intern standard stock solution was prepared from 1000 mg/L In ICP-MS standard solution (Alpha Aeser).

The method blank for the 1:2 diluted wine samples was prepared to contain 7.6% ethanol in 1% nitric acid. The blank for the digested wine samples was prepared by subjecting the solution used for digestion (7 mL 65% nitric acid plus 1 mL H₂O₂) to the microwave digestion program and diluting to 50 mL with Milli-Q water.

2.2.1.2. Physical and chemical analysis

The physical and chemical analysis of young wine were performed in the Winemaking Laboratory of the RSDVV Bujoru and were applied in accordance to the methods of analysis described in the Compendium of international methods of analysis of wines and musts and to the Romanian STAS methods (Bora *et al.*, 2016; Bora *et al.*, 2018). During this analysis the following parameters were determined: alcohol (% vol.) – was determined using the

ebulliometric method, STAS 6182/6-70; total acidity (g/L C₄H₆O⁶) - titrimetric method, STAS 6182-1:2008; volatile acidity (g/L CH₃COOH) - according to STAS 6182-2:2008; residual sugar (mg/L) – according STAS 6182/17-81. The next parameters: acetic acid (g/L); amino nitrogen (mg/L); tartaric acid (g/L); L-lactic acid (g/L); D-malic acid (g L) were determinate using spectrophotometric method.

2.2.1.3. Standards

For analysis of the main quality of parameters of wine, all reagents used for calibration were of analytical grade (TDI - Tecnología Difusión Ibérica, S.L. Fr.).

Two elements (Pb and Sr) were determined in order to assess their ability to discriminate wines by geographical origin. The analysis was made using multielement analysis and ICP-MS technique, after an appropriate dilution, using external standard calibration method. The calibration was performed using XXICertiPUR multielement standard. The working standards and the control sample were prepared daily from the intermediate standards that were prepared from the stock solution. The intermediate solutions stored in polyethylene bottles and glassware was cleaned by soaking in 10% v/v nitric acid for 24 hours and rinsing at least ten times with ultrapure water (18.2 MΩ cm⁻¹ ultrapure water-Types 1). The accuracy of the methods was evaluated by replicate analyses of fortified samples (10 µL-10 mL concentrations) and the obtained values ranged between 0.8-13.1 percent, depending on the element. The global recovery for each element was estimated and the obtained values were between 84.6-100.9% (Bora *et al.*, 2016; Bora *et al.*, 2018).

Table 1. Instrumental conditions for the determination of each element (ICP-MS)

Element	Correlation coefficient	LoD* (µg/L)	LoQ*** (µg/L)	BEC** (µg/L)
Sr	0.9999	0.1434	0.4775	0.955
Pb	0.9999	0.0003	0.0010	0.002

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

For quality control purpose, blanks and triplicates samples ($n = 3$) were analyzed during the procedure. The variation coefficient was under 5% and detection limits (ppb) were determined by the calibration curve method. Limit of detection (LoD) and Limit of quantification (LoQ) limits were calculated according to the next mathematical formulas: $LoD = 3SD/s$ and $LoQ = 10 SD/s$ ($SD =$ estimation of the standard deviation of the regression line; $s =$ slope of the calibration curve) (Table 1).

For calibration and to verify the achieved accuracy and precision, ten NIST-SRM 987 and NIST-SRM 982 analysis results were pooled together with the calculated relative standard deviation presented in Table 2.

Table 2. Lead isotopic ration and Lead isotopic ration determination precision and accuracy based on the NIST SRM 982 (Lead) NIST SRM 987 (Strontium) ($n=10$)

$^{207}\text{Pb}/^{206}\text{Pb}$ (a)	$^{208}\text{Pb}/^{206}\text{Pb}$ (b)	$^{204}\text{Pb}/^{206}\text{Pb}$ (c)	$^{87}\text{Sr}/^{86}\text{Sr}$ (d)
0.46179	0.99736	0.02270	0.71117

^aCertified value = $^{207}\text{Pb}/^{206}\text{Pb}$ (0.46707 ± 0.00020);

^bCertified value = $^{208}\text{Pb}/^{206}\text{Pb}$ (1.00016 ± 0.00036);

^cCertified value = $^{204}\text{Pb}/^{206}\text{Pb}$ (0.027219 ± 0.00027);

^dCertified value = $^{87}\text{Sr}/^{86}\text{Sr}$ (0.71034 ± 0.00026).

Based on the obtained results, it was verified that, applying quadrupole ICP-MS, relative standard deviation and reproducibility of approximately 0.5% for $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are feasible. The results were in agreement with those reported by Avram *et al.*, 2014; Bora *et al.*, 2016; Bora *et al.*, 2018.

2.2.4. Sample preparation for determination of heavy metals and isotopic ration from wine using ICP-MS

For the determination of elements from wine samples were used an amount of 0.5 mL wine and adjust 8 mL (7 mL HNO_3 65%+1 mL H_2O_2) were placed in a clean Teflon digestion vessel, after 15-30 minutes the mineralization was performed using a microwave system Milestone START D Microwave Digestion System set in three steps: step I (time 10 min., temperature

200°C), step II (time 15 min., temperature 200°C) and step III (time 40 min., ventilation - temperature 32°C). After mineralization, samples were filtered through a 0.45 mm filter and brought to a volume of 50 mL. The Pb and Sr isotope ration in the analysed wine samples ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$.) were determined according to the methodology indicated by Bora *et al.*, 2016; Bora *et al.*, 2018.

Table 3. Standard additions for checking accuracy of the microwave digestion ICP-MS method ($n = 3$) (SRM 1643e)

Element	Certified Concentration (mg/L)	Measured Concentration (mg/L)
Sr	314.00±19.00	314.09±09.06
Pb	19.63±0.21	19.13±0.09

In order to confirm the best-chosen conditions for wine digestion standard additions for checking accuracy of the microwave digestion and recoveries were calculated (Table 3). The digestion seemed visually completed in all of the combinations, but the spiked recoveries showed significant differences for total elements content (p - Value = 0.005).

2.2.5. Instrumentation

In order to get a wider range of data about the quality of the tested wine and to determine the acetic acid, amino acid, tartaric acid, L-lactic acid, and M-malic acid the MIURA ONE I.S.E. S.r.l., Rome, Italy device was used.

All analyses were carried out with iCAP Q Thermo scientific model Coupled Plasma Mass Spectrometer (ICP-MS) equipped with nickel cones, a peristaltic sample delivery pump and a Cetac auto sampler. Instrumental conditions for the ICP-MS were optimized, after completing the mass calibration and detector cross-calibration, by following a manual tuning procedure using Thermo Tuning Solution A containing a manual tuning procedure using Ni, In, Ba, Ce, Pb, Bi and U at 10 $\mu\text{g/L}$, and As and Se at 100 $\mu\text{g/L}$. For data acquisition the ICP-MS was operated in peak pump mode, with a dwell time of 20 ms, 100 sweeps. Five replicate measurements were made. The isotopes ^{86}Sr ,

^{87}Sr , ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb . The elements selected are mostly metals and are considered to be useful as possible indicators of geographical origin, since they are not generally affected by vinification and are therefore in principle providing a link with the soil composition. Most of them have been tested in a number of previous studies (Almeida *et al.*, 2003; Coetzee *et al.*, 2005; Moreno *et al.*, 2008; van der Linde *et al.*, 2010).

The argon used was of 99.99% purity (Messer, Austria). The instrument was daily optimized to give maximum sensitivity for M^+ ions and the double ionization and oxides monitored by the means of the ratios between $\text{Ba}^{2+}/\text{Ba}^+$ and $\text{Ce}^{2+}/\text{CeO}^+$, respectively, these always being less than 2%. The experimental conditions were: argon flow on nebulizer (0.82 L/min.), auxiliary gas flow 0.80 L/min., argon flow in plasma 15 L/min., lens voltage 7.30 V; RF power in plasma 1100 W, spray chamber temperature ($2.42 \pm 1.00^\circ\text{C}$). Accuracy was calculated for the elements taken into consideration (0.5-5.0%).

To reduce molecular interferences, the data of ^{86}Sr , ^{87}Sr , ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb were collected using Collision Cell Technology (CCT). Tuning in CCT mode using 7% H/He gas was carried out using Autotune function and Thermo Tuning Solution A. To enhance the stability of the analyte signal, the sample uptake of the peristaltic pump was regularly replaced.

2.2.6. Statistical analysis

Data analysis was performed to test if significant differences can be highlighted between the geographical origin of wines samples by district. The statistical interpretation of the results was performed using the Duncan test, SPSS Version 24 (SPSS Inc., Chicago, IL., USA). The statistical processing of the results was primarily performed in order to calculate the following statistical parameters: average and standard deviation. The statistical analysis was performed by using the analysis of variance (ANOVA) followed by multiple comparisons tests in which the level of significance was set at $p \leq 0.05$. ANOVA determined, for each

parameter, the main effect of the region and of the year of harvest on the multiisotopic and multielement composition of samples. Secondly, the data were processed using the Linear Discriminant Analysis (LDA).

Multivariate chemometric method was used as a supervised learning technique for the differentiation of wines into groups on the basis of grape variety and year of production and finding markers which showed a significant discrimination value (variables with Wilk's lambda near zero, p value < 0.05). Stepwise linear discriminant analysis (LDA) was used to identify significant tracers for classification to the geographical discrimination of the wines samples. At each step, the variable with the best discriminating power, as described by an F-statistic and $p < 0.0001$, was entered into the model and then several discriminant functions were obtained. Stepwise Discriminant Analysis (LDA) was used to designate suitable variables for classification of the samples, eliminating the variables that do not contribute to discrimination of the wine. In order to validate the proposed statistic model, based on variables which showed higher significance in first LDA assessment, we performed a second Linear Discriminant Analysis (LDA) for the test set consisting of wines used to build statistical model (training set) together with data from other wine samples that are not included in the first LDA (control-set). Cross-validation was applied to determine the optimal number of variables required to obtain robust models. Linear discriminant analysis (LDA) was performed using Microsoft Excel 2016 and XLSTAT Addinsoft version 15.5.03.3707.

3. Results and discussions

3.1. Analysis of the main quality of parameters of wine

Based on the results regarding the qualitative assessment of the tested varieties, they have a very good suitability in the studied areas. In terms of quality rating, they display particular characters of the varieties, as well as the ecoclimatic conditions and ecopedological influence on the quality of wine (Table 4).

The physico-chemical analysis of wines showed that the highest alcohol content was recorded at the Merlot variety (15.40 % vol.), followed by Feteasca neagra (15.17 % vol.). The highest level of acidity was recorded at the Muscat Ottonel (6.37 g/L C₄H₆O₆) and the lowest acidity in the Feteasca regala (4.36 g/L C₄H₆O₆).

3.2. ²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁶Pb/²⁰⁴Pb, ⁸⁷Sr/⁸⁶Sr, isotope ratio in wine samples Bujoru, Smulți and Oancea Wine Center

Lead isotopic analysis of wines from France (Bordeaux) showed that lead in the wines changed over time and reflect the dominant source of atmospheric lead pollution in southern of France (Médina *et al.*, 2000). Other researchers 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 (Galani-Nikolakaki *et al.*, 2002). These studies confirm atmospheric deposition as being the dominant contributor to the lead total concentration and isotopic composition from wines. 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 wines (Gulson *et al.*, 1992). Other researchers have attributed the lead in wine to machinery or additives used during the vinification process where environmental contamination in this case is low (Almeida *et al.*, 2003). In Central Europe, the lead isotopic ratio, as signatures of pollution sources, ranges from relatively high ²⁰⁶Pb/²⁰⁷Pb ratios (natural Pb, coals, fly ashes, ²⁰⁶Pb/²⁰⁷Pb = 1.1700 - 1.2200) to low ²⁰⁶Pb/²⁰⁷Pb values (gasoline, petrol combustion, ²⁰⁶Pb/²⁰⁷Pb = 1.0600 - 1.1400) [30].

The original composition of soil samples retains its chemical composition from the geographical area it belongs to (Shirahata *et al.*, 1980; Gulson *et al.*, 1981; Elbaz-Poulichet *et al.*, 1984; Bora *et al.*, 2013). 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 ratio is precise and accurate.

The Pb isotope ratio from wines (Table 5) varies in range between 1.12305 - 1.18597 (²⁰⁶Pb/²⁰⁷Pb), 2.09404 - 2.14190 (²⁰⁸Pb/²⁰⁶Pb) and 17.21089 - 17.70857 (²⁰⁶Pb/²⁰⁴Pb) with average 1.15202 (²⁰⁶Pb/²⁰⁷Pb), 2.10878 (²⁰⁸Pb/²⁰⁶Pb) and 17.42240 (²⁰⁶Pb/²⁰⁴Pb). Regarding ²⁰⁶Pb/²⁰⁷Pb isotope ratios based on analyses it can be concluded that the wine obtained from vine varieties grown in the Bujoru wine-growing centers how's traces of pollution comes from cars (automobile emissions) (if ²⁰⁶Pb/²⁰⁷Pb = 1.1000 - 1.1400 [automobile emissions]).

The obtained isotope ratio values are comparable with Avram *et al.*, 2014 (1.1100 to 1.2000 Romania wines) and Almeida *et al.*, 2016 (1.1440 to 1.1820 Brazilian wines).

The highest values of ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁴Pb were registered to wine obtained from Muscat Ottonel (2015) variety from Bujoru wine-growing center (2.14190 ± 0.00743 ²⁰⁸Pb/²⁰⁶Pb) and Cabernet Sauvignon (2014) variety from Oancea wine-growing center (17.70857 ± 0.00394 [0.02238] ²⁰⁸Pb/²⁰⁶Pb) while Cabernet Sauvignon (2014) from Oancea wine-growing center (2.09205 ± 0.00576 ²⁰⁸Pb/²⁰⁶Pb) and Feteasca Regala (2014) from Oancea wine-growing center (17.21089 ± 0.00116 ²⁰⁶Pb/²⁰⁴Pb) recorded the lowest isotope ration. The results are comparable with Almeida *et al.*, 2016 (2.0700 to 2.1570 Brazilian wines ²⁰⁸Pb/²⁰⁶Pb; 16.6670 to 17.9960 Brazilian wines ²⁰⁴Pb/²⁰⁶Pb) and also with Barbaste *et al.*, 2002 (2.0990 to 2.1030 Italian wines ²⁰⁸Pb/²⁰⁶Pb; 17.544 to 18.3210 Italian wines ²⁰⁴Pb/²⁰⁶Pb).

The abundance of the lead isotopes ²⁰⁴Pb (non-radiogenic), ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb (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 (Gulson *et al.*, 1992), 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 ratio is precise and accurate.

Concerning $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio, the values are between the ranges from 0.70112 to 0.74275 with an average value of 0.71909. The highest values were registered to wine obtained from Fetească neagră (2016) variety (0.74275 ± 0.00261) from Smulți wine-growing center, the lowest value of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio was recorded to wine obtained from Muscat Ottonel (2014) variety (0.70165 ± 0.00058) Oancea wine-growing center.

The values of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio obtained are comparable with Geana *et al.*, 2017 (0.71015 to 0.72311 Romanian wines); Avram *et al.*, 2014 (0.7600 to 0.9300).

Variation of the $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, isotope ratio and heavy metals concentration from wines with different geographical origins confirm the link with geological substratum of the production territory, making the $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, isotope ratio and heavy metals concentration a robust instrument for tracing the geographical provenance of wines.

3.3. Combining multielement analysis and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, isotope ratio from wine samples for discrimination analysis

Multivariate techniques are methods of analysis generally recognized as very all know to study environmental problems (Tauler *et al.*, 1995). From this kind of methods, Linear

Discriminant Analysis (LDA) has been selected one of the most advantageous to have a close look of our system. LDA belongs to supervised pattern recognition methods (Vončina, 2009) and has the aim to assign object to several predetermined classes.

Linear Discriminant Analysis (LDA) was used as a supervised learning technique for the differentiation of wines into groups on the basis of grape variety and year of production and finding markers which showed a significant discrimination value (variables with Wilk's lambda near zero, p value < 0.05 and higher F coefficients). Stepwise linear discriminant analysis (LDA) was used to identify significant tracers for classification to the geographical discrimination of the wines samples. Stepwise Discriminant Analysis (LDA) was used to designate suitable variables for classification of the samples, eliminating the variables that do not contribute to discrimination of the wine. In order to validate the proposed statistic model, based on variables which showed higher significance in first LDA assessment, we performed a second Linear Discriminant Analysis (LDA) for the test set consisting of wines used to build statistical model (training set) together with data from other wine samples that are not included in the first LDA (control-set).

Cross-validation was applied to determine the optimal number of variables required to obtain robust models.

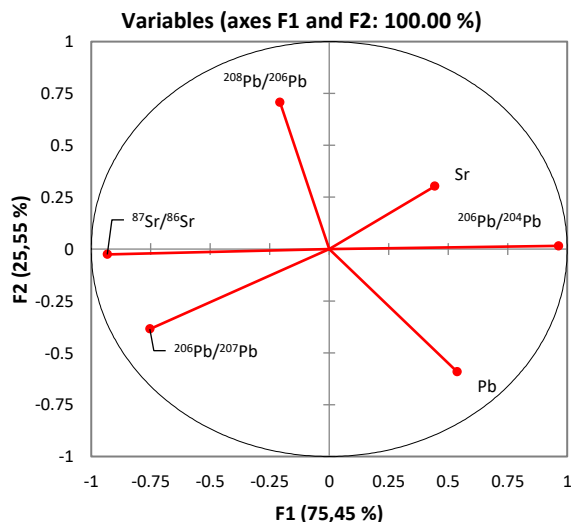


Figure 1. Correlation between analyzed parameters and the factors in discriminant analysis the origin of the wine

In this study, the content of certain wines shows high concentration of metals, but not exceeding the maximum recommended by International Organisation of Vine and Wine (O.I.V., 2015), and this mostly due to agricultural practices, fertilizers and technological winemaking processes.

Elements like Pb, Cu, Ni, Cd, U and Hg showed a high discriminatory power for geographic origin of Romanian wines, but additional new elements (Mn, Cr) and $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio have been investigate in order to identify new tracers for geographical traceability of Romanian wines (Geana *et al.*, 2017; Bora *et al.*, 2016; Bora *et al.*, 2018).

The wines obtained in the three wine-growing centers can be geographical fingerprints based on the concentration of Pb,

Cu, Ni, Cd, Hg, Mn, Cr, U and also based on the $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio (Bora *et al.*, 2016).

Based on the elemental contents and $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio, the cross-validation technique provided a 100 % percentage of predicted membership according to the origin of the wine (F1 = 75.45 % and F2 = 25.55 %). The linear correction revealed acceptable scores for the two defined discriminant factors (F1 and F2) (Figure 1).

A significant differentiation of wines according to wine-growing centers and year of wine production was carried out for wines samples, which demonstrates the importance of elemental profile for the geographical traceability of wines (Figure 2).

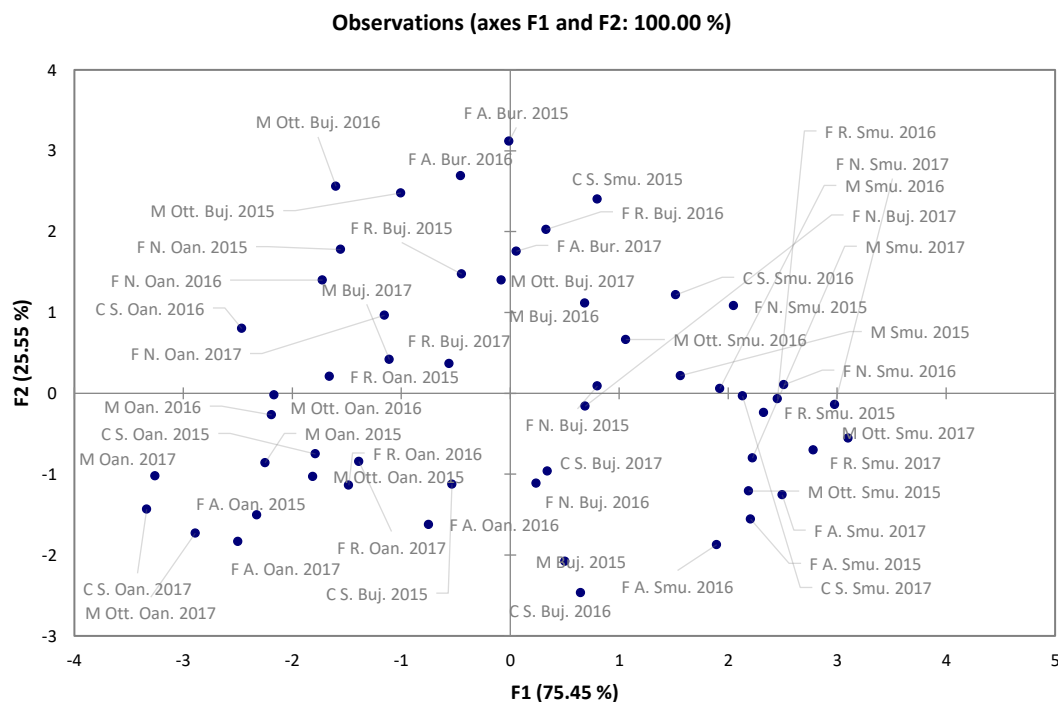


Figure 2. Differentiation of wines based on element contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios

Table 4. The analysis of the main quality parameters in wine samples from Dealu Bujorului Vineyard (Bujoru, Smulți and Oancea Wine Centre)

Wine Centre	Variety	Year	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₄ O ₆)	Volatility acidity (g/L CH ₃ COOH)	Residual Sugar (g/L)	Non reducing extract (g/L)	Acetic acid (g/L)	Amino acid (mg/L)	Tartaric acid (g/L)	L-Malic acid (g/L)	L-Lactic acid (g/L)
Bujoru Wine Center	M Ott.	2014	14.46 ± 0.12 abcde	4.68 ± 0.10 lmnop	0.32 ± 0.04 mnop	6.47 ± 0.25 ijklm	24.75 ± 0.53 cdefg	0.33 ± 0.01 ^{ab}	22.52 ± 0.95 ab	1.29 ± 0.05 jkl	1.12 ± 0.10 ⁱ	ULD
		2015	14.41 ± 0.45 abcdef	4.91 ± 0.06 ijkl	0.46 ± 0.03 cdefghijkl	4.59 ± 0.07 opqrst	21.88 ± 0.76 hijkl	0.34 ± 0.05 ^{ab}	17.37 ± 3.44 efghijklmnop	1.34 ± 0.12 jkl	1.23 ± 0.12 ⁱ	ULD
		2016	13.89 ± 0.59 cdefghii	4.70 ± 0.07 lmnop	0.50 ± 0.03 bcdefgh	11.19 ± 0.75 a	22.45 ± 1.00 fghijkl	0.31 ± 0.02 abc	23.03 ± 1.53 ^a	1.67 ± 0.19 efghijkl	2.07 ± 0.08 ^{abcd}	ULD
	F A.	2014	13.26 ± 0.34 fghijklmno	5.31 ± 0.31 efgh	0.46 ± 0.08 cdehijkl	3.63 ± 0.17 ^{stt}	21.81 ± 0.84 hijkl	0.34 ± 0.11 ^{ab}	22.10 ± 0.95 ^a	1.59 ± 0.63 ghijkl	1.18 ± 0.08 ⁱ	ULD
		2015	13.11 ± 0.59 hijklmno	5.25 ± 0.06 fghi	0.54 ± 0.03 abcd	3.85 ± 0.46 rsstt	22.86 ± 1.03 ghijkl	0.30 ± 0.02 abc	23.04 ± 1.53 ^a	1.19 ± 0.07 ^l	1.12 ± 0.10 ⁱ	ULD
		2016	14.39 ± 0.47 abcdefg	5.41 ± 0.42 defgh	0.46 ± 0.03 cdefghijkl	5.03 ± 0.43 nopqrs	20.11 ± 1.13 k	0.19 ± 0.05 efghijklmno	20.96 ± 1.57 abcdefg	2.14 ± 0.23 cdefghi	1.23 ± 0.01 ⁱ	ULD
	F R.	2014	13.59 ± 0.26 cdefghijkl	4.55 ± 0.02 mnop	0.60 ± 0.06 ^{ab}	5.51 ± 0.33 jklmnopq	22.56 ± 1.13 ghijkl	0.12 ± 0.02 mnopq	13.13 ± 1.58 ^{rs}	2.33 ± 0.01 bcdef	1.22 ± 0.11 ⁱ	ULD
		2015	14.03 ± 0.55 cdefghii	4.36 ± 0.15 ^p	0.61 ± 0.05 ^a	2.45 ± 0.19 ^t	20.96 ± 1.33 ijk	0.12 ± 0.03 nopq	19.77 ± 1.37 abcdefghiiij	1.77 ± 0.48 efghijkl	1.34 ± 0.12 ^{fghi}	ULD
		2016	12.76 ± 0.91 ijklmnop	4.48 ± 0.36 nop	0.52 ± 0.04 abcde	3.25 ± 0.04 ^{tt}	20.15 ± 1.18 k	0.19 ± 0.02 efghijklmno	20.84 ± 1.66 abcdefg	1.37 ± 0.07 ijkl	1.07 ± 0.04 ⁱ	ULD
	F N.	2014	14.55 ± 0.23 abcd	5.33 ± 0.02 efgh	0.43 ± 0.04 defghijklm	0.30 ± 0.06 ^u	26.22 ± 0.63 abcde	0.18 ± 0.05 ghijklmnop	22.26 ± 1.71 ab	1.62 ± 0.26 fghijkl	1.92 ± 0.23 ^{abcdefg}	ULD
		2015	15.17 ± 0.53 ^{ab}	5.43 ± 0.21 defgh	0.42 ± 0.06 defghijklmn	3.63 ± 0.62 ^{stt}	22.11 ± 1.16 ghijkl	0.36 ± 0.05 ^a	20.81 ± 0.80 abcdefg	1.37 ± 0.05 ijkl	1.30 ± 0.12 ^{fghi}	ULD
		2016	14.73 ± 1.00 abc	5.25 ± 0.06 fghi	0.48 ± 0.05 cdefghij	3.76 ± 0.33 sstt	21.68 ± 1.67 hijkl	0.21 ± 0.03 defghijkl	17.45 ± 3.38 efghijklmnop	2.04 ± 0.13 cdefghijk	1.28 ± 0.06 ^{fghi}	ULD
	M	2014	14.52 ± 0.27 abcde	4.83 ± 0.13 klmn	0.31 ± 0.03 ^{op}	3.59 ± 0.35 ^{stt}	27.19 ± 1.40 a	0.31 ± 0.09 abc	13.89 ± 3.78 pqrs	1.27 ± 0.06 ^l	1.21 ± 0.11 ⁱ	ULD
		2015	15.40 ± 0.63 ^a	5.31 ± 0.11 efgh	0.41 ± 0.03 efghijklmno	6.60 ± 1.08 ijkl	24.33 ± 1.12 defgh	0.16 ± 0.05 klmnopq	18.23 ± 2.70 cdefghijklmn	1.23 ± 0.12 ^l	1.29 ± 0.12 ^{fghi}	ULD
		2016	15.44 ± 0.48 ^a	4.66 ± 0.18 lmnop	0.52 ± 0.04 abcdef	6.65 ± 0.59 ^{ijk}	21.69 ± 0.67 hijkl	0.18 ± 0.02 fghijklmnop	17.08 ± 3.66 ghijklmnopq	1.78 ± 0.19 efghijkl	1.22 ± 0.01 ⁱ	ULD
	C S.	2014	13.47 ± 0.54 defghijklmn	5.29 ± 0.06 ^{fgh}	0.50 ± 0.06 bcdefgh	3.59 ± 1.33 ^{stt}	26.18 ± 1.46 abcde	0.16 ± 0.04 ijklmnopq	22.36 ± 1.88 ab	2.06 ± 0.16 cdefghii	1.23 ± 0.01 ⁱ	ULD
		2015	13.00 ± 0.46 gijklmnop	4.67 ± 0.12 lmnop	0.50 ± 0.04 bcdefghi	4.37 ± 1.67 pqrst	22.45 ± 0.95 fghijk	0.12 ± 0.01 nopq	21.40 ± 0.46 abcd	1.78 ± 0.19 efghijkl	1.29 ± 0.12 ^{fghi}	ULD
		2016	13.76 ± 0.85 cdefghij	5.32 ± 0.11 efgh	0.45 ± 0.03 cdefghijkl	5.67 ± 0.49 jklmnop	23.40 ± 1.79 fghij	0.31 ± 0.03 abc	21.52 ± 1.80 abcd	2.06 ± 0.15 cdefghii	1.92 ± 0.56 ^{abcdefg}	ULD

Wine Centre	Variety	Year	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₄ O ₆)	Volatile acidity (g/L CH ₃ COOH)	Residual Sugar (g/L)	Non reducing extract (g/L)	Acetic acid (g/L)	Amino acid (mg/L)	Tartaric acid (g/L)	L-Malic acid (g/L)	L-Lactic acid (g/L)
Smuți Wine Center	M Ott.	2014	13.52 ± 0.51 defghijkl	4.48 ± 0.12 nop	0.52 ± 0.03 abcdef	10.78 ± 0.51 ab	22.41 ± 1.05 fghijk	0.24 ± 0.07 cdefghi	9.61 ± 2.45 [§]	1.23 ± 0.12 ^l	1.29 ± 0.12 ^{ghi}	ULD
		2015	11.88 ± 0.90 opqrs	4.51 ± 0.18 nop	0.46 ± 0.03 cdefghijkl	7.37 ± 1.55 ghii	23.22 ± 1.52 fghij	0.20 ± 0.02 defghijklmn	12.96 ± 1.10 ^{rs}	1.34 ± 0.12 jkl	1.23 ± 0.01 ⁱ	ULD
		2016	13.36 ± 0.43 efghijklmno	5.08 ± 0.06 hijk	0.48 ± 0.03 cdefghij	8.87 ± 1.12 defg	22.78 ± 1.41 ghijk	0.09 ± 0.03 pq	16.21 ± 1.70 ijklmnopqr	2.19 ± 0.26 cdefgh	2.28 ± 0.10 ^{abc}	ULD
	F A.	2014	12.28 ± 0.74 mnopqr	4.73 ± 0.06 lmop	0.56 ± 0.15 abc	7.48 ± 0.79 ghii	26.60 ± 2.02 abcd	0.16 ± 0.04 ijklmnop	19.34 ± 1.71 abcdefghijk	1.70 ± 0.13 efghijkl	2.26 ± 0.12 ^{abcd}	ULD
		2015	12.33 ± 0.44 lmnopqr	4.64 ± 0.27 lmnop	0.49 ± 0.03 cdefghij	11.37 ± 0.96 a	27.88 ± 1.25 a	0.14 ± 0.03 lmnopq	18.11 ± 0.49 defghijklmno	1.44 ± 0.11 ijkl	2.07 ± 0.55 ^{abcd}	ULD
		2016	13.22 ± 0.43 ghijklmno	4.59 ± 0.23 lmnop	0.47 ± 0.04 cdefghijk	10.06 ± 0.14 abc	23.45 ± 1.11 fghij	0.17 ± 0.05 hijklmnop	22.99 ± 2.13 ^a	2.93 ± 0.22 ab	1.37 ± 0.17 ^{efghi}	ULD
	F R.	2014	11.52 ± 0.34 qrs	5.18 ± 0.11 ghij	0.45 ± 0.02 cdefghijkl	8.95 ± 0.95 cdef	21.20 ± 1.00 ijk	0.28 ± 0.05 abcd	13.40 ± 1.08 qrs	1.44 ± 0.47 ijkl	1.06 ± 0.14 ⁱ	ULD
		2015	11.07 ± 0.17 ^s	5.26 ± 0.05 fghi	0.36 ± 0.03 klmnop	5.36 ± 0.12 klmnopq	22.08 ± 1.59 ghijk	0.18 ± 0.05 ghijklmnop	19.56 ± 1.44 abcdefghij	1.88 ± 0.45 defghijkl	1.27 ± 0.06 ^{hi}	ULD
		2016	12.18 ± 0.37 nopqrs	5.15 ± 0.07 ghijk	0.42 ± 0.09 defghijklmn	10.01 ± 1.00 abcd	21.18 ± 1.98 hijk	0.24 ± 0.04 cdefghii	19.47 ± 1.99 abcdefghijk	1.48 ± 0.17 hijkl	2.12 ± 0.02 ^{abcd}	ULD
	F N.	2014	14.15 ± 0.78 bcdefgh	5.74 ± 0.07 bcd	0.50 ± 0.06 bcdefghi	11.04 ± 0.51 a	23.01 ± 2.08 fghij	0.15 ± 0.06 jklmnopq	17.17 ± 1.65 fghijklmnopq	2.65 ± 0.33 abc	2.52 ± 0.52 ^{ab}	ULD
		2015	12.96 ± 0.63 hijklmnop	5.29 ± 0.13 ^{fgh}	0.33 ± 0.04 lmnop	8.08 ± 1.32 fghi	28.76 ± 0.19 a	0.10 ± 0.01 ^q	17.40 ± 0.65 efghijklmnop	1.60 ± 0.25 ghijkl	2.00 ± 0.67 ^{abcd}	ULD
		2016	13.08 ± 0.58 hijklmno	5.17 ± 0.04 ghij	0.45 ± 0.07 cdefghijkl	6.26 ± 0.93 ijklmn	22.71 ± 1.51 ghijk	0.21 ± 0.02 defghijkl	21.10 ± 2.01 abcdef	2.12 ± 0.01 cdefghi	2.13 ± 0.03 ^{abcd}	ULD
	M	2014	13.10 ± 0.58 hijklmno	5.25 ± 0.06 fghi	0.37 ± 0.02 jklmnop	4.19 ± 0.29 qrsst	21.52 ± 1.80 hijk	0.26 ± 0.06 bcdefgh	21.08 ± 1.12 abcdef	1.33 ± 0.01 ^{kl}	1.29 ± 0.12 ^{ghi}	ULD
		2015	13.95 ± 0.52 cdefghii	4.88 ± 0.10 ijklm	0.38 ± 0.06 ijklmnop	6.85 ± 0.60 ^{ij}	22.49 ± 2.09 ghijk	0.28 ± 0.05 abcde	21.19 ± 1.23 abcde	2.49 ± 0.25 bcd	1.26 ± 0.06 ^{hi}	ULD
		2016	14.03 ± 0.43 cdefghi	4.48 ± 0.32 ^{op}	0.40 ± 0.06 ghijklmnop	8.29 ± 0.54 fgh	21.22 ± 0.23 hijk	0.21 ± 0.02 defghijkl	20.13 ± 1.41 abcdefghii	1.37 ± 0.16 ijkl	1.22 ± 0.01 ⁱ	ULD
	C S.	2014	11.74 ± 0.31 pqrs	5.38 ± 0.28 efgh	0.31 ± 0.03 ^{op}	3.74 ± 0.52 sstt	27.95 ± 1.00 a	0.20 ± 0.02 defghijklmn	19.92 ± 1.28 abcdefghii	1.85 ± 0.44 defghijkl	2.56 ± 0.58 ^a	ULD
		2015	13.07 ± 0.84 hijklmno	5.18 ± 0.06 ghij	0.34 ± 0.01 lmnop	5.22 ± 0.58 lmnopqr	27.63 ± 1.03 ab	0.21 ± 0.02 defghijkl	16.62 ± 2.00 hijklmnopqr	1.34 ± 0.11 jkl	1.29 ± 0.11 ^{ghi}	ULD
		2016	12.03 ± 0.34 ghii	5.22 ± 0.01 ghii	0.44 ± 0.01 defghijklm	6.51 ± 0.84 ijklm	21.34 ± 1.00 hijk	0.16 ± 0.03 ijklmnopq	14.32 ± 2.21 opqrs	2.37 ± 0.07 bcde	2.19 ± 0.13 ^{abcd}	ULD
Oancea Wine Center	M Ott.	2014	12.18 ± 0.64 nopqrs	6.37 ± 0.16 ^a	0.47 ± 0.02 cdefghijk	3.28 ± 0.36 ^{stt}	22.00 ± 2.11 ghijk	0.16 ± 0.07 ijklmnopq	2.66 ± 1.52 ^t	1.70 ± 0.56 efghijkl	1.34 ± 0.10 ^{fghi}	ULD
		2015	11.52 ± 0.34 qrs	5.44 ± 0.18 defgh	0.50 ± 0.06 bcdefgh	3.60 ± 0.17 ^{stt}	23.45 ± 2.21 fghij	0.20 ± 0.02 defghijklmn	10.81 ± 1.33 ^{ss}	1.71 ± 0.55 efghijkl	1.26 ± 0.07 ^{hi}	ULD

Wine Centre	Variety	Year	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₄ O ₆)	Volatile acidity (g/L CH ₃ COOH)	Residual Sugar (g/L)	Non reducing extract (g/L)	Acetic acid (g/L)	Amino acid (mg/L)	Tartaric acid (g/L)	L-Malic acid (g/L)	L-Lactic acid (g/L)
F A.	2016	13.08 ± 0.68 hijklmno	5.51 ± 0.15 cdefg	0.42 ± 0.08 defghijklmn	8.74 ± 0.17 defg	26.14 ± 1.44 abcde	0.26 ± 0.04 bcdefg	15.59 ± 3.01 klmnopqr	2.96 ± 0.23 ^a	1.66 ± 0.59 ^{cdefghi}	ULD	
		2014	12.25 ± 0.45 nopqrs	5.33 ± 0.01 efgh	0.39 ± 0.05 hijklmnop	5.12 ± 0.49 mnopqrs	25.10 ± 1.06 bcdef	0.21 ± 0.02 defghijk	15.14 ± 1.50 lmnopqr	1.67 ± 0.54 efghijkl	1.95 ± 0.55 ^{abcdef}	ULD
		2015	13.36 ± 0.34 efghijklmno	5.19 ± 0.19 ghij	0.39 ± 0.05 ijklmnop	5.52 ± 0.13 jklmnopq	23.01 ± 2.09 fghij	0.19 ± 0.02 efghijklmno	18.85 ± 3.03 bcdefghijkl	3.27 ± 0.16 ^a	1.06 ± 0.14 ⁱ	ULD
	F R.	2016	12.98 ± 0.55 hijklmnop	5.41 ± 0.17 defgh	0.43 ± 0.02 defghijklm	9.63 ± 0.52 bcde	23.36 ± 2.39 fghij	0.27 ± 0.06 abcdef	17.46 ± 0.53 efghijklmnop	1.70 ± 0.55 efghijkl	1.33 ± 0.10 ^{fghi}	ULD
		2014	11.88 ± 0.57 opqrs	5.25 ± 0.06 fghi	0.51 ± 0.06 abcdefg	10.48 ± 0.66 ab	21.40 ± 1.40 hijk	0.17 ± 0.05 hiijklmnop	17.37 ± 3.47 efghijklmnop	2.52 ± 0.88 bcd	2.51 ± 0.12 ^{ab}	ULD
		2015	11.29 ± 1.11 ^{rs}	4.37 ± 0.12 ^p	0.45 ± 0.07 cdefghijkl	5.74 ± 1.03 jklmnop	23.34 ± 1.13 fghij	0.17 ± 0.06 ijklmnopq	18.85 ± 3.02 bcdefghijkl	1.63 ± 0.61 fghijkl	1.63 ± 0.61 ^{cdefghi}	ULD
	F N.	2016	12.52 ± 0.33 klmnopq	4.99 ± 0.11 ijklm	0.52 ± 0.07 abcdefg	10.59 ± 0.55 ab	21.45 ± 0.95 ijk	0.19 ± 0.02 efghijklmno	19.28 ± 1.74 abcdefghijk	1.22 ± 0.18 ^l	1.93 ± 1.12 ^{abcdefg}	ULD
		2014	13.26 ± 0.72 fghijklmno	4.70 ± 0.49 lmnop	0.39 ± 0.06 ghijklmnop	4.70 ± 0.63 opqrss	22.73 ± 1.00 ghijk	0.27 ± 0.05 abcde	20.15 ± 1.96 abcdefghi	2.19 ± 0.13 cdefgh	1.23 ± 0.01 ⁱ	ULD
		2015	13.92 ± 0.53 cdefghij	5.10 ± 0.07 hijk	0.37 ± 0.06 jklmnop	8.52 ± 0.74 efgh	27.08 ± 0.44 abc	0.16 ± 0.04 ijklmnopq	19.55 ± 1.52 abcdefghij	2.03 ± 0.52 cdefghijk	1.38 ± 0.25 ^{efghi}	ULD
	M	2016	13.18 ± 0.29 hijklmo	5.24 ± 0.11 fghi	0.43 ± 0.03 defghijklm	5.81 ± 0.47 jklmno	22.44 ± 0.99 ghijk	0.19 ± 0.02 efghijklmno	14.63 ± 0.70 nopqrs	1.86 ± 0.42 defghijkl	1.26 ± 0.07 ^{hi}	ULD
		2014	13.52 ± 1.11 defghijkl	4.55 ± 0.01 mnop	0.30 ± 0.06 ^p	7.33 ± 0.55 ^{hii}	20.84 ± 0.90 jk	0.16 ± 0.06 ijklmnopq	15.95 ± 1.41 jklmnopqrs	1.60 ± 0.64 ghijkl	1.62 ± 0.01 ^{defghi}	ULD
		2015	12.37 ± 0.07 lmnopqrs	5.82 ± 0.40 ^{bc}	0.33 ± 0.05 lmnop	5.29 ± 0.56 klmnopq	23.77 ± 3.23 efghii	0.20 ± 0.02 defghijklmn	14.92 ± 3.01 mnopqrs	2.54 ± 1.15 bcd	1.90 ± 0.60 ^{bcdefgh}	ULD
C S.	2016	12.59 ± 1.28 jklmnopq	5.66 ± 0.29 cde	0.32 ± 0.03 mnop	7.41 ± 1.80 ghii	22.67 ± 1.52 ghijk	0.19 ± 0.07 efghijklmno	20.48 ± 1.38 abcdefgh	2.23 ± 0.19 cdefg	1.99 ± 0.47 ^{abcde}	ULD	
	2014	12.92 ± 0.74 ijklmno	6.04 ± 0.13 ^b	0.39 ± 0.05 ghijklmnop	2.45 ± 0.20 ^l	24.19 ± 2.21 defghi	0.21 ± 0.03 defghijkl	18.74 ± 0.39 bcdefghijklm	1.34 ± 0.01 jkl	1.26 ± 0.06 ^{hi}	ULD	
	2015	12.19 ± 0.26 nopqrs	5.32 ± 0.04 efgh	0.43 ± 0.11 defghijklmn	4.67 ± 0.57 opqrst	22.07 ± 0.44 ghijk	0.23 ± 0.06 cdefghijk	20.22 ± 0.77 abcdefghii	1.30 ± 0.07 ^{kl}	1.97 ± 0.64 ^{abcde}	ULD	
2016	11.63 ± 0.59 pqrs	5.59 ± 0.13 cdef	0.41 ± 0.03 efghijklmno	5.71 ± 0.55 jklmnop	21.67 ± 0.59 hijk	0.20 ± 0.02 defghijklmn	16.26 ± 1.67 ijklmnopqr	3.20 ± 0.05 ^a	2.20 ± 0.11 ^{abcd}	ULD		

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \leq 0.05$). The difference between any two values, followed by at least one common letter, is = insignificant; Ott. = Muscat Ottonel; F A. = Feteasca Alba; F R. = Feteasca Regala; F N. = Feteasca Neagra; M = Merlot; C S. = Cabernet Sauvignon. ULD = under the limit of detection.

Table 5. The ²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁶Pb/²⁰⁴Pb, ⁸⁷Sr/⁸⁶Sr, isotope ratios obtained from wine samples from Dealu Bujorului Vineyard (Bujoru, Smuți and Oancea Wine Centre)

Wine Centre	Variety	Year	²⁰⁶ Pb/ ²⁰⁷ Pb	SD	²⁰⁸ Pb/ ²⁰⁶ Pb	SD	RSD (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	RSD (%)	⁸⁷ Sr/ ⁸⁶ Sr	RSD (%)	Pb (µg/L) M.A.L.* 0.15 mg/L	Sr (µg/L) M.A.L.** -
Bujoru Wine Center	M Ott.	2014	1.13254 ^{ijk} βγδ	0.00036	2.12629 ^{cde} βγ	0.00053	0.09456	17.46918 ^d α	0.09456	0.71240 ^{klm} ε	0.01725	39.93±1.93 ^{lmno} αβγ	133.64±3.49 ^p ι
		2015	1.12757 ^{klm} γδε	0.00452	2.14190 ^a α	0.00743	0.34696	17.43110 ^{de} αβγ	0.12536	0.71572 ^{ijk} δε	0.44613	41.95±1.60 ^{klm} α	152.57±4.74 ^{m0}
		2016	1.12391 ^m ε	0.00133	2.12926 ^{bcd} βγ	0.00799	0.37512	17.41786 ^{de} βγ	0.03015	0.72304 ^{gh} αβ	0.41614	26.22±1.16 ^{vw} ζ	326.81±2.05 ^b α
	F A.	2014	1.14202 ^{efg} α	0.00822	2.12488 ^{cde} βγ	0.00288	0.13531	17.43660 ^{de} αβγ	0.07738	0.72135 ^{ghi} αβ	0.04199	36.29±1.63 ^{opr} βγδ	273.79±5.29 ^d γ
		2015	1.13349 ^{ijk} βγ	0.00188	2.12629 ^{cde} βγ	0.00539	0.25334	17.39880 ^e βγ	0.20089	0.71227 ^{klm} ε	0.03451	41.73±3.38 ^{klm} α	214.67±2.41 ^{hi} ζ
	F R.	2016	1.12772 ^{klm} γδε	0.00423	2.12378 ^{cde} γ	0.00190	0.08933	17.31524 ^f δ	0.03479	0.71810 ^{hij} γδ	0.83133	40.50±2.08 ^{lmn} αβ	109.39±1.32 ^u κ
		2014	1.13487 ^{ijh} βγ	0.00233	2.12289 ^{de} γ	0.00058	0.02748	17.39163 ^e γ	0.41595	0.71844 ^{hij} βγδ	0.69694	26.90±2.41 ^{xy} ζ	214.94±0.87 ^{hi} ζ
		2015	1.13349 ^{ijk} βγ	0.00188	2.12228 ^e γ	0.00081	0.03830	17.42611 ^{de} αβγ	0.12511	0.72156 ^{gh} αβ	0.01270	33.20±2.56 ^{rst} δε	217.20±1.79 ^{hi} ζ
	F N.	2016	1.12776 ^{klm} γδε	0.00422	2.12258 ^e γ	0.00234	0.11034	17.43908 ^{de} αβγ	0.13200	0.72208 ^{gh} αβ	0.15312	35.78±3.33 ^{prs} γδ	181.55±3.05 ^η
		2014	1.13469 ^{hij} βγ	0.00219	2.12569 ^{cde} βγ	0.00040	0.01862	17.42780 ^{de} αβγ	0.11945	0.72602 ^{defg} α	0.57532	30.29±0.78 ^{utvx} εζ	234.15±5.53 ^ε
		2015	1.13547 ^{ghij} αβ	0.00083	2.12975 ^b βγ	0.00448	0.21026	17.42310 ^{de} αβγ	0.05384	0.72529 ^f εα	0.05395	26.18±3.10 ^w ζ	325.16±4.00 ^b α
	M	2016	1.12776 ^{klm} γδε	0.00339	2.12600 ^{cde} βγ	0.00640	0.30112	17.42147 ^{de} βγ	0.00080	0.72568 ^{efg} α	0.11648	32.79±2.67 ^{rst} δε	300.14±1.96 ^β
		2014	1.12938 ^{ijklm} βγδε	0.00559	2.12790 ^{cde} βγ	0.00379	0.17816	17.40896 ^e βγ	0.03385	0.72298 ^{gh} αβ	0.34219	33.43±1.03 ^{rst} δε	107.49±2.08 ^κ
		2015	1.12305 ^m ε	0.00266	2.13343 ^b β	0.00150	0.07040	17.41815 ^{de} βγ	0.03441	0.72523 ^f εα	0.07722	35.89±2.42 ^{prs} γδ	261.40±6.37 ^δ
	C S.	2016	1.12773 ^{klm} γδε	0.00333	2.12418 ^{cde} γ	0.00093	0.04382	17.39969 ^e βγ	0.17041	0.71430 ^{ijkl} δε	0.21700	41.20±1.81 ^{klmn} α	276.10±2.00 ^γ
		2014	1.13161 ^{ijkl} βγδ	0.00560	2.13011 ^{bc} βγ	0.00619	0.29060	17.42141 ^{de} βγ	0.02771	0.72339 ^{gh} αβ	0.28125	41.78±2.24 ^{klm} α	130.23±1.62 ^p ι
		2015	1.12391 ^m ε	0.00133	2.12701 ^{cde} βγ	0.00652	0.30661	17.41199 ^{de} βγ	0.06782	0.72254 ^{gh} αβ	0.23652	42.06±3.12 ^{kl} α	109.72±0.83 ^u κ
			2016	1.13320 ^{ijk} βγ	0.00203	2.12657 ^{cde} βγ	0.00431	0.20260	17.44611 ^{de} αβ	0.12788	0.72137 ^{ghi} αβ	0.03197	40.99±3.71 ^{klmn} α
Smuți Wine Center	M Ott.	2014	1.18229 ^{abc} αβγ	0.00028	2.10364 ^{fg} αβ	0.00108	0.05110	17.21643 ^e γδ	0.02526	0.73086 ^{bcdef} βγ	0.15148	22.80±1.75 ^{wz} ζη	116.56±2.75 ^s λ
		2015	1.18415 ^{ab} αβγ	0.00210	2.10266 ^{fgh} αβ	0.00041	0.01973	17.21351 ^e γδ	0.01071	0.73455 ^b β	0.51894	37.79±1.10 ^{nop} δ	245.14±4.02 ^f β
		2016	1.18523 ^a αβ	0.00107	2.10723 ^{fg} αβ	0.00501	0.23773	17.22768 ^e α	0.03155	0.73304 ^{bc} βγ	0.41046	32.89±2.03 ^{rst} ε	258.09±1.29 ^e α
	F A.	2014	1.18502 ^a αβ	0.00235	2.10382 ^{fg} αβ	0.00206	0.09777	17.21852 ^e βγδ	0.03237	0.73127 ^{bcde} βγ ^f	0.14192	28.13±3.16 ^{vxy} η	127.65±1.80 ^f κ
		2015	1.17677 ^{cd} γδ	0.00741	2.10191 ^{hijk} αβ	0.00040	0.01895	17.21930 ^e βγ	0.03086	0.73224 ^{bc} βγ	0.11604	30.78±1.63 ^{utv} εζη	106.62±1.35 ^u ξ
	F R.	2016	1.17765 ^{bcd} βγδ	0.00741	2.10192 ^{hijk} αβ	0.00054	0.02553	17.21549 ^e γδ	0.03216	0.73144 ^{bcde} βγ	0.02684	32.30±0.82 ^{stu} εζ	114.33±2.15 st λ
		2014	1.18504 ^a αβ	0.00207	2.10868 ^f α	0.00592	0.28051	17.21089 ^e δ	0.00677	0.73177 ^{bcde} βγ	0.10621	53.16±1.00 ^{cd} α	199.66±2.60 ^{ij} ε
		2015	1.18312 ^{abc} αβγ	0.00146	2.10741 ^{fg} αβ	0.00457	0.21674	17.21584 ^e γδ	0.02606	0.73265 ^{bc} βγ	0.22273	51.62±0.55 ^{de} α	176.73±1.47 ^{lm} η
	F N.	2016	1.18452 ^a αβ	0.00196	2.10153 ^{hijk} β	0.00053	0.02529	17.21536 ^e γδ	0.03313	0.73195 ^{bc} βγ	0.16894	50.29±0.67 ^{defg} α	218.82±2.67 ^h γ
		2014	1.17462 ^d δ	0.00216	2.10756 ^{fg} αβ	0.00471	0.22341	17.21444 ^e γδ	0.00703	0.73258 ^{bc} βγ	0.91340	43.40±2.65 ^{ijkl} βγ	124.29±7.59 ^f κ
		2015	1.18532 ^a αβ	0.00109	2.10225 ^{ghij} αβ	0.00010	0.00467	17.21707 ^e γδ	0.02226	0.73076 ^{bcde} βγ ^f	0.69139	44.73±3.32 ^{ijk} β	129.00±3.76 ^p κ
	M	2016	1.17784 ^{bcd} βγδ	0.00336	2.10473 ^{fg} αβ	0.00672	0.31908	17.21688 ^e γδ	0.02298	0.74275 ^a α	0.35191	37.59±1.60 ^{nop} δ	106.86±2.34 ^u ξ
		2014	1.18597 ^a α	0.00059	2.10190 ^{hijk} αβ	0.00058	0.02736	17.21491 ^e γδ	0.03356	0.73152 ^{bcde} βγ	0.00832	28.88±5.32 ^{vxy} ζη	140.97±1.56 ^p ι
		2015	1.18303 ^{abc} αβγ	0.00268	2.10130 ^{hijk} β	0.00013	0.00639	17.23090 ^e α	0.00410	0.73077 ^{bcdef} βγ	0.68614	22.49±1.20 ^z θ	179.19±0.88 ^{lm} η
	C S.	2016	1.18098 ^{abcd} αβγδ	0.00839	2.10242 ^{ifgh} αβ	0.00187	0.08896	17.22479 ^e αβ	0.02298	0.73402 ^b β	0.20095	27.29±1.16 ^{vxy} η	153.22±6.73 ⁿ θ
		2014	1.18515 ^a αβ	0.00020	2.10206 ^{hijk} αβ	0.00055	0.02615	17.21491 ^e γδ	0.03356	0.72750 ^{bcde} βγ	0.57915	43.44±2.33 ^{ijkl} βγ	216.46±1.81 ^h γ
		2015	1.18396 ^{ab} αβγ	0.00130	2.10483 ^{fg} αβ	0.00623	0.29610	17.21343 ^e γδ	0.01220	0.73239 ^{bc} βγ	0.25200	40.47±0.80 ^{lmn} γδ	209.50±1.54 ^δ
			2016	1.17964 ^{abcd} αβγδ	0.00654	2.10397 ^{fg} αβ	0.00546	0.25930	17.21474 ^e γδ	0.00203	0.73120 ^{bcdef} βγ	0.02999	39.47±1.10 ^{lmnop} δ

Wine Centre	Variety	Year	²⁰⁶ Pb/ ²⁰⁷ Pb	SD	²⁰⁸ Pb/ ²⁰⁶ Pb	SD	RSD (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	RSD (%)	⁸⁷ Sr/ ⁸⁶ Sr	RSD (%)	Pb (µg/L) M.A.L.* 0.15 mg/L	Sr (µg/L) M.A.L.** -
M Ott.		2014	1.14230 ^{ef} αβγ	0.00187	2.09557 ^{ijkl} α	0.00015	0.00729	17.61229 ^c βγ	0.05492	0.70165 ^p βγ	0.08200	55.78±0.81 ^{bc} β	174.80±5.33 ^m θ
		2015	1.14184 ^{efg} αβγ	0.00286	2.09531 ^{kl} α	0.00026	0.01218	17.61543 ^c βγ	0.02934	0.70788 ^{mno} αβγ	1.35361	57.36±1.38 ^b β	192.81±3.20 ^k η
		2016	1.14537 ^e αβ	0.00268	2.09557 ^{ijkl} α	0.00010	0.00482	17.61396 ^c βγ	0.08560	0.70326 ^{op} βγ	0.10740	48.46±0.85 ^{efg} δε	187.54±2.93 ^k η
F A.		2014	1.14212 ^{efg} αβγ	0.00166	2.09541 ^{kl} α	0.00001	0.00028	17.70222 ^{ab} αβ	0.15455	0.70221 ^{op} βγ	0.01809	57.28±0.81 ^b β	193.09±3.07 ^k η
		2015	1.14018 ^{efgh} γ	0.00003	2.09404 ^l αβ	0.00230	0.10978	17.64307 ^c αβγ	0.24352	0.70247 ^{op} βγ	0.08219	27.32±1.52 ^{vy} η	273.46±4.00 ^d γ
		2016	1.14605 ^e α	0.00169	2.09651 ^{ijkl} α	0.00168	0.02529	17.64396 ^c βγ	0.08560	0.70175 ^{op} βγ	0.04854	42.63±1.05 ^{kl} ζ	216.14±2.66 ^h ζ
F R.		2014	1.14121 ^{efgh} βγ	0.00173	2.09412 ^l αβ	0.00171	0.22341	17.61823 ^c βγ	0.06862	0.70171 ^p βγ	0.11789	47.57±2.25 ^{fgh} ε	260.66±3.04 ^e δ
		2015	1.14435 ^e αβγ	0.00390	2.09528 ^{kl} α	0.00028	0.01323	17.61146 ^c βγ	0.06004	0.70288 ^{op} βγ	0.20128	51.54±2.90 ^{de} γ	244.49±3.51 ^f ε
		2016	1.14629 ^e α	0.00142	2.09411 ^l αβ	0.00105	0.04990	17.6127 ^c βγ	0.05553	0.70542 ^{nop} βγ	0.97519	51.20±1.44 ^{def} γ	215.68±0.78 ^h ζ
F N.		2014	1.14114 ^{efgh} βγ	0.00163	2.09576 ^{ijkl} α	0.00076	0.03433	17.62720 ^c αβγ	0.11928	0.70560 ^{nop} βγ	0.68843	50.18±2.18 ^{defg} γδ	326.16±2.66 ^b β
		2015	1.14435 ^e αβγ	0.00390	2.09528 ^{kl} α	0.00028	0.01323	17.63062 ^c αβγ	0.11989	0.71448 ^{ijkl} α	0.25095	51.66±1.87 ^e γ	249.15±4.62 ^f ε
		2016	1.14500 ^e αβ	0.00317	2.09577 ^{ijkl} α	0.00074	0.03537	17.60973 ^c γ	0.04787	0.70916 ^{lmn} αβ	1.03156	61.33±1.21 ^a α	270.16±1.00 ^d γ
M		2014	1.14121 ^{efgh} βγ	0.00177	2.09612 ^{ijkl} α	0.00149	0.07126	17.70857 ^a βγ	0.94776	0.70112 ^p γ	0.10738	36.59±1.13 ^{opr} η	249.43±2.40 ^f ε
		2015	1.14287 ^{ef} αβγ	0.00435	2.09556 ^{ijkl} α	0.00010	0.00468	17.63746 ^c αβγ	0.06768	0.70412 ^{nop} βγ	0.35258	40.93±1.81 ^{klmn} ζ	362.15±2.90 ^a α
		2016	1.14550 ^e αβ	0.00034	2.09532 ^{kl} α	0.00028	0.01338	17.61914 ^c βγ	0.02278	0.70317 ^{op} βγ	0.29783	42.13±0.55 ^{kl} ζ	118.42±1.12 ^s λ
C S.		2014	1.14184 ^{efg} αβγ	0.00286	2.09205 ^l β	0.00576	0.27513	17.70857 ^a α	0.02238	0.70203 ^{op} βγ	0.13326	55.60±0.89 ^{bc} β	148.54±3.16 ⁿ τκ
		2015	1.14200 ^{efg} αβγ	0.00313	2.09565 ^{ijkl} α	0.00003	0.00146	17.63840 ^c αβγ	0.25064	0.70573 ^{nop} βγ	0.69427	38.10±0.79 ^{mno} η	114.09±4.41 ^s λ
		2016	1.14407 ^e αβγ	0.00224	2.09592 ^{ijkl} α	0.00052	0.02479	17.65393 ^{bc} αβγ	0.30105	0.70120 ^p γ	0.03128	46.66±0.78 ^{ghi} ε	212.78±3.86 ^{hi} ζ
Average			1.15202	0.00279	2.10878	0.00238	0.11248	17.42240	0.09244	0.71909	0.31542	40.64±1.85	187.36±3.15
Minimum Values			1.12305	0.00003	2.09404	0.00001	0.00467	17.21089	0.00080	0.70112	0.00832	22.49±1.20	107.49±2.08
Maximum Values			1.18597	0.00839	2.14190	0.00799	0.37512	17.70857	0.94776	0.74275	1.35361	61.33±1.21	326.81±2.05
Almeida <i>et al.</i> , 2016			1.14400		2.15700		1.00000					76.00±13.00	
Avram <i>et al.</i> , 2014			1.14000	0.10000	2.10000	0.15000	7.10000			0.76000	1.30000	35.90	171.40
Mihaljevnić <i>et al.</i> , 2006			1.74000	0.00300	2.09200	0.00700						11.11±5.28	
Barbaste <i>et al.</i> , 2002			1.14200	0.00200	2.12500	0.00300	0.16000	17.60000	1.70000			42.90±0.05	
Geana <i>et al.</i> , 2017													905.00

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \leq 0.05$). The difference between any two values, followed by at least one common letter, is insignificant; Ott. = Muscat Ottonel; F A. = Feteasca Alba; F R. = Feteasca Regala; F N. = Feteasca Neagra; M = Merlot; C S. = Cabernet Sauvignon.

**M.A.L. for Sr = -.

The cluster heat map is a rectangular tiling of a data matrix cluster trees appended to its margins. Within a relatively compact display area, it facilitates inspection of row, column, and joint cluster structure. Moderately large data matrices (several thousand rows/columns) can be displayed effectively on a high-resolution color monitor and even larger matrices can be handled in print or in megapixel displays.

Heat map was used to discover sample groups, discover groups and also to discover related sample/feature groups. In of elemental contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from wine (horizontal dendrogram) the dendrogram clearly show two cluster, first cluster is formed from the Sr and second cluster was formatted from Pb, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$, and $^{87}\text{Sr}/^{86}\text{Sr}$.

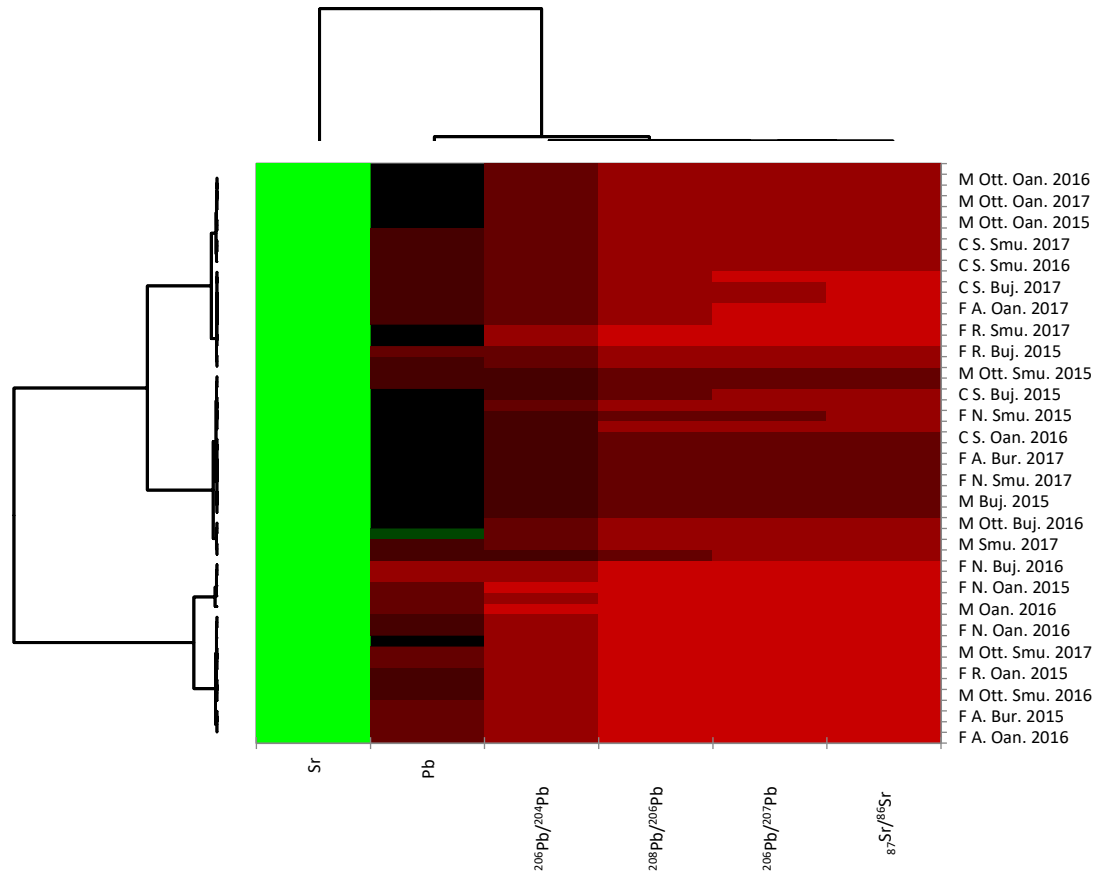


Figure 3. Heat map obtained by cluster analysis of the element contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios

Based on this distribution in can be seen that the Sr recorded the highest values

followed by Pb. The vertical dendrogram show also two cluster, the first M Smu. 2015, C S. Buj. 2015, F R. Buj. 2015, M Buj. 2017, M Oan.

2016, M Oan. 2015, F R. Smu. 2015, F R. Buj. 2017, C S. Smu. 2017, F A. Bur. 2017, F A. Bur. 2015, C S. Buj. 2017, C S. Smu. 2016, F N. Oan. 2016, F N. Oan. 2015 and second cluster was formed from F A. Smu. 2017, M Ott. Smu. 2017, M Ott. Smu. 2016, F R. Oan. 2015, M Ott. Oan. 2017, F R. Oan. 2016, M Buj. 2015, F A. Oan.

2016, F R. Smu. 2017, C S. Oan. 2016, F A. Smu. 2016, M Ott. Buj. 2017. Based on this distribution in can be seen that there is a separation of wine varieties for white of these red depending on elemental contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, except for a few varieties that do not fit into this rule (F R. Buj. 2015, F R. Smu. 2016, F R. Buj. 2017, F A. Buj. 2017, F A. Buj. 2015 (which have been introduced in red wine cluster)) and M Buj. 2015, C S. Oan. 2016, 2015 (which have been introduced in white wine cluster)) (Figure 3).

4. Conclusions

In this work the Sr and Pb composition and $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of white wines (Muscat Ottonel, Feteasca Alba, Feteasca Regala) and red wines (Feteasca Neagra, Merlot, Cabernet Sauvignon) production years 2014-2016 from Bujoru, Smulți and Oancea wine-growing centers was studied in order to highlight geographical traceability of elemental composition and isotope ratio for fingerprints of the wines.

Concentration of Pb in analysed wine samples were under Maximum Limit Allowed (M.L.A.), respectively as published by the Organization of Vine and Wine. The content of potentially toxic elements such as Pb are lower than the recommended values found in literature, highlighting the safety and quality of the analysed Romanian wines.

From discrimination analysis of wine samples, was found additional new elements Mn and Cr to tracers for geographical traceability of Romanian wines. Our results confirm that the $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio can be used to track the origin of wine, discriminate between the wine produced in different years, and be used to characterize wine terroirs for forensic purpose. The wines obtained in the three wine-growing centers can be geographical fingerprints based on the concentration of Sr, Pb and also based on the $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio. The proposed methodology allowed 100 % successful

classification of wines according to the region of provenance and also the years of wine obtaining.

Heat map was discovering a separation of wine varieties for white of this red depending on elemental contents and $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios.

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