Optimization and validation of a microwave digestion method for multi-element characterization of Romanian wines

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Abstract. An analytical method for determination of multi-element composition of Romanian wines using microwave digestion for sample preparation and ICP-MS (inductively coupled plasma mass spectrometry) was optimized and validated. Best recoveries, ranging from 85.63 % to 119.08 were analyzed elements, using a volume of 0.5 mL wine, 7 mL HNO_3 and 1 mL H_2O_2. In total 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V and Zn) were determined in the wine samples. A total of 156 wine samples (96 white wines, 54 red wines and 6 rose wines) were analyzed in this work. All wines used in this study were form the 2011 vintage and were collected directly from the Romanian wineries in 750 mL glass bottles. The calibration curves of all elements were linear with correlation coefficients (R^2) ranging from 0.9991 for Cd to 0.9999 Al, As, Ba, Be, Ca, Co, Fe, Ga, Li, Mg, Mo, Na, P, ^{208}Pb, Sb, Se, Sn, Te, Ti and Zn. The accuracy of the method was checked with a standard addition method showing good repeatability and reproducibility (relative standard deviation, RSD<10%). In this study the characterization of Romanian wines according to their elemental composition was performed. Potassium, magnesium and calcium were the most abundant elements in all investigated wine samples. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analyzed wine samples were under the maximum permissible limits (MPL).

Key Words: multi-element concentration, ICP-MS, inductively coupled plasma mass spectrometry, enology, viticulture.

Introduction. Around the world wine is a beverage of great economic and social significance. It has a very complex matrix, which, besides alcohol, sugar and water, contains a great variety of inorganic as well as organic components (Sperkova & Suchanek 2005; Fabani et al 2010; Zinicovscaia et al 2017). The following compounds are present in small quantities and are considered important for wine quality: polyphenols (anthocyanins, flavan-3-ols, flavonols, phenolic acids and stilbenes), carbohydrates, proteins, organic acids, amino acids, vitamins as well as minerals. Therefore, sample pre-treatments are necessary for its multielement analysis In fact, it is necessary to dilute or decompose the wine because of the possible matrix interferences. Elements Al, Cu, Cd, Fe, Pb, Ni and Zn could be determined without dilution, while elements Mg, Ca, K, Na are analyzed after dilution of wine sample with water (Frias et al 2001; Frias et al 2003; Diaz et al 2003). Decomposition could be performed by wet digestion on a hot place or in a microwave oven using concentrated HNO_3, $HClO_4$ and H_2SO_4 or mixtures of these acids (Frias et al 2001; Frias et al 2003; Castiñeira Gómez et al 2004; Álvarez et al 2007; Ivanova-Petropulos et al 2015).

The knowledge of mineral composition and content in wine is an important factor influencing its quality and nutritional values. In fact, the determination of the elemental composition of wines is very important not only from the toxicological point of view since it could contain harmful elements, such as As, Pb and Cd but also from the nutritional point of view, since wine contains essential elements for the human organism, such as Se, Ca, Cr, Co, K and Zn (Grindlay et al 2011).

The presence of metals (Pb, Fe, Al, Zn and Cu) in wine is important for efficient alcoholic fermentation and for its sensorial characteristics (freshness, flavor, aroma), and therefore, their concentrations in wine must be monitored. A great number of anthropogenic and natural factors such as type of grape, soil characteristics, area of production, fertilizers, environmental conditions, inorganic pesticides, application of additives, winemaking practices, transport and storage could significantly influence the concentration of major as well as trace elements in wine (Gonzálvez et al 2009; Fabani et al 2010; Sperkova & Suchanek 2005; Geana et al 2013; Grindlay et al 2011; Moreno et al 2007; Zinicovscaia et al 2017). The concentration of macro-, and microelements characteristic and comprises the largest part of the total element concentration in wine. It is connected with the climatic conditions during their growth, maturity of the grapes, the type of soil in the vineyard, their variety. The contribution of metals of a secondary origin is associated with external impurities that reach wine during growth of grapes or at different stages in winemaking (from harvesting to bottling and cellaring). During the growth of grapes in a vineyard, contaminations can be classified as geogenic (originating in the soil), from protection and growing practices, or from environmental pollution (Dugo et al 2005).

Accordingly, wines from vineyards in the vicinity of ocean or sea result in a higher Na content compared to wines from other regions (Frias et al 2001). Differences in Ca, Na and Cu concentration can be due to fertilizers used for cultivation (Diaz et al 2003). Application of fungicides, pesticides and fertilizers containing Cu, Cd, Pb, Mn and Zn compounds during the growing season of vines season of vines leads to increases in the amounts of these metals in wine (Galani-Nikolakaki et al 2002; Álvarez et al 2007). Wines from vineyards located close to road traffic or situated in industrial areas contain higher levels of Pb and Cd because of vehicle exhaust fumes or other emissions to air, soil and water (Galani-Nikolakaki et al 2002; Álvarez et al 2007). Finally, there is a winemaking (enological) sources of metals, as contamination may occur at different steps of wine production. The reason for this is the long contact of wine with materials (stainless steel, aluminium, brass, glass and wood) from which winemaking machinery and pipes, casks and barrels used for handling and storing wine are made. This is the usual sources of Al, Cr, Cu, Cd, Cu and Fe (Núñez et al 2000; Lara et al 2005). Contaminations with Al, Ca, or Na can be associated with fining and clarifying substances (flocculants such as bentonites) added to wine to remove suspended solids after fermentation and to reduce turbidity (Núñez et al 2000; Galani-Nikolakaki et al 2002; Diaz et al 2003; Lara et al 2005; Álvarez et al 2007). Ca concentration can also be affected by adding $CaCO_3$ or $CaSO_4$ for de-acidification of must and wine or enhancement or acidity of grape juices, respectively (Galani-Nikolakaki et al 2002; Diaz et al 2003; Lara et al 2005; Álvarez et al 2007).

Wines typically contain major elements such as Ca, Na, Mg and K, whose concentration is greater than 10 mg/L; trace elements such as Pb, Al, Mn, Fe and Zn whose concentration overpass 10 µg/L and ultra-trace elements such as Cr, Ni, As, or Cd, whose concentration is lower than micrograms per liter (Geana et al 2013; Zinicovscaia et al 2017). Although the list of elements commonly found in wines was more numerous, we had restrained to those elements which are either major components of soil or was more or less related with the human activity. For this reason, the determination of the elements content of wines was well intensively investigated. Moreover, the content of the same elements was used to test the wine region or provenance of origin (Perez-Jordan et al 1998; Castiñeira et al 2001; Taylor et al 2003; Coetzee et al 2005; Sperkova & Suchanek 2005; Fabani et al 2010; Geana et al 2013; Šelih et al 2014).

During the technological process of winemaking, composition of elements is changing mainly due to the precipitation of Ca and K tartrates as well precipitation of Cr, Cu, Al, Fe, Mn, Ni, Pb and Zn (Rodriguez Mozaz et al 1999). In addition, the concentration of elements in wine could be modified by presence of living or non-living *Saccharomyces cerevisiae* yeast lowering significantly the final content of some metals. Yeast consumes of Zn, Ca, Cu, Fe, K and Mg causing decrease of their content during the fermentation process (Volesky & May-Phillips 1995; Blackwell et al 1995; Rodriguez Mozaz et al 1999; Nicolini & Larcher 2003).

Daily consumption of wine in moderate quantities contributes significantly to the requirements of the human organism for essential elements, such as Co, Ca, Cr, K, Se, and Zn, however, above optimal level, elements such Al, Fe, Cu, K, Mn and Zn may have detrimental effects on the stability of wine and its commercial acceptability, while As, Pb, Cd and Br are known to be potentially toxic (Galani-Nikolakaki et al 2002).

Different methods of rare metal analysis were employed in these studies the majority being atomic absorption and atomic emission. The following method was reported for studies in relation to atomic absorption techniques: FAAS (flame Atomic Absorption Spectrometry) (Sauvage et al 2002; Bakircioglu et al 2003; Monasterio & Wuilloud 2009; Paneque et al 2010; Fabani et al 2010; Trujillo et al 2011; Calin et al 2012; Bora et al 2015), HGAAS (Hydride Generated Atomic Absorption Spectrometry) (Elçi et al 2009; Klarić et al 2011), ETAAS (Electrothermal Atomic Absorption Spectrometry) (Freschi et al 2001; Nikolakaki et al 2002; Lara et al 2005). On the other hand studies dealing with the following methods in relation to atomic emission techniques have also been reported in literature; ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) (Kallithraka et al 2001; Kment et al 2005; Catarino et al 2006; Moreno et al 2007; Chopin et al 2008; Cozzolino et al 2008; Serepinas et al 2008; Capron et al 2007; Fabani et al 2010; Ferrerira et al 2008; Gonzálvez et al 2009; Grindlay et al 2009; Provenzano et al 2010; Santos et al 2010; Vrcek et al 2011; Fiket et al 2011; Rodrigues et al 2011; Geana et al 2013; Bora et al 2016a; Bora et al 2016b; Bora et al 2017a; Bora et al 2017b; Bora et al 2018a; Bora et al 2018b).

Research on accumulation of heavy metals in food, especially oil, dry tea, canned tuna, mushrooms and peanuts have been seen in the literature since the early 1970s (Reilly 2002; Eschnauer 1986). However the number of analysis in alcoholic beverages is considered limited even today. Only a few studies dealing with heavy metal concentration of high alcoholic drinks has been reported in literature. Among the reported studies wine samples are not rare. Determination of elemental concentration from wines is a very useful tool to differentiate wines from different geographic origins, to detect adulterations and falsification of wines and also to indicate the Certified Brands of Origin (CBO) (Lara et al 2005).

In this study, we decided to use digestion microwave method for wine preparation in order to (i) eliminate the plasma disorders and molecular interferences caused by organic content of the wine samples, (ii) to avoid the presence of the particulates and colloidal suspensions on the nebulization system, and (iii) to equalize matrix influences.

Material and Method

Reagents and solutions. For all analytical procedures, ultrapure water was used (0.065 μS/cm), obtained from water purification system TKA Microlab, ASTM II water (Thermo Electron LED GmbH, Germany). Nitric acid (69.0% w/w, trace select, Sigma Aldrich, Munich, Germany) was used for wine digestion and for the conservation of standard solutions for construction of calibration curves. Multi-element certificate standard solution (Periodic table Mix 1 for ICP, 10 mg/L, sigma Aldrich, Munich, Germany) contained 33 elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Pb, Se, Si, Ag, Na, Sr, S, Te, Tl, V and Zn). Single element standards were used for the construction of the calibration curves for Tl, Ge, Sb, Sn, and Mo (10 ppm in 10% HNO_3 trace select, Sigma Aldrich, Munich, Germany). Tuning solution (ICP-MS Tuning Solution, contains 10 mg/L each of Ba, Bi, Ce, Co, In, Li, U in a matrix of 2% HNO_3, Analytika) was used for optimization of the ICP-MS instrument. Rhodium standard solution (1 mg/L Sigma Aldrich, Munich, Germany) was used as an internal standard for correction of the drift for external calibration curves.

Grapes from *Vitis vinifera* L. cultivated in Dealu Bujorului, Târnave, Murfatlar, Iași and Ștefănești-Argeș, were harvested in September 2011, at optimal technological maturity (20.0 ^{0}brix). All vines were planted since 1979, and the vine plantation was organized with 2.2 x 1 m distance between rows and plants. Grapes were manually harvested early in the morning and placed in crates.

Study area and wine samples. A total of 156 wine samples (96 white wines, 54 red wines and 6 rose wines) were analyzed in this work. All wines used in this study were form the 2011 vintage and were collected directly from the Romanian wineries in 750 mL glass bottles. Wines were located in four different vineyard areas: Dealu Bujorului, Târnave, Murfatlar, Iași and Ștefănești-Argeș. The wine varieties under this study and production areas are presented in Table 1. Micro-wine production it was done according to the methodology described by Bora et al (2016b). Samples were kept in a cooling room at 4^{o}C before analysis. All samples were taken in triplicates (n = 3) from the defined experimental plot.

Table 1

Wine varieties and production area

No	*Type*	*Variety*	*Area of production*	*Abbreviation of wines with wine area*
1	White	Feteasca Albă	Dealu Bujorului	F.A.$_{DB}$
2	White	Feteasca Regală	Dealu Bujorului	F.R.$_{DB}$
3	White	Muscat Ottonel	Dealu Bujorului	M.O.$_{DB}$
4	White	Băbească Gri	Dealu Bujorului	B.G.$_{DB}$
5	White	Șarba	Dealu Bujorului	Ș.$_{DB}$
6	White	Italian Riesling	Dealu Bujorului	I.R.$_{DB}$
7	White	Sauvignon Blanc	Dealu Bujorului	S.B.$_{DB}$
8	White	Aligoté	Dealu Bujorului	A.$_{DB}$
9	Red	Feteasca Neagră	Dealu Bujorului	F.N.$_{DB}$
10	Red	Merlot	Dealu Bujorului	M.$_{DB}$
11	Red	Băbească Neagră	Dealu Bujorului	B.N.$_{DB}$
12	Red	Cabernet Sauvignon	Dealu Bujorului	C.S.$_{DB}$
13	Rosé	Burgund Mare	Dealu Bujorului	B.M.$_{DB}$
14	Rosé	Băbească Neagră	Dealu Bujorului	B.N.$_{DB}$
15	White	Feteasca Albă	Târnava	F.A.$_{T}$
16	White	Feteasca Regală	Târnava	F.R.$_{T}$
17	White	Italian Riesling	Târnava	I.R.$_{T}$
18	White	Neuburger	Târnava	N.$_{T}$
19	White	Pinot Gris	Târnava	P.G.$_{T}$
20	White	Muscat Ottonel	Târnava	M.O.$_{T}$
21	White	Traminer	Târnava	T.$_{T}$
22	White	Pinot Gris	Murfatlar	P.N.$_{M}$
23	White	Chardonnay	Murfatlar	C.$_{M}$
24	White	Italian Riesling	Murfatlar	I.R.$_{M}$
25	White	Muscat Ottonel	Murfatlar	F.R.$_{M}$
26	White	Sauvignon Blanc	Murfatlar	S.B.$_{M}$
27	Red	Cabernet Sauvignon	Murfatlar	C.S.$_{M}$
28	Red	Pinot Noir	Murfatlar	P.N.$_{M}$
29	Red	Merlot	Murfatlar	M.$_{M}$
30	Red	Fetească Neagră	Murfatlar	F.N.$_{M}$
31	White	Feteasca Albă	Iași	F.R.$_{I}$
32	White	Aligoté	Iași	A.$_{I}$
33	White	Italian Riesling	Iași	I.R.$_{I}$
34	White	Pinot Gris	Iași	P.G.$_{I}$
35	White	Sauvignon Blanc	Iași	S.B.$_{I}$
36	White	Muscat Ottonel	Iași	M.O.$_{I}$
37	Red	Feteasca Neagră	Iași	F.N.$_{I}$
38	Red	Băbească Neagră	Iași	B.N.$_{I}$
39	Red	Pinot Noir	Iași	P.N.$_{I}$
40	Red	Cabernet Sauvignon	Iași	C.S.$_{I}$
41	Red	Merlot	Iași	M. $_{I}$
42	Red	Burgund Mare	Iași	B.M.$_{I}$

No	*Type*	*Variety*	*Area of production*	*Abbreviation of wines with wine area*
43	White	Feteasca Albă	Ștefănești-Argeș	F.A.$_{\text{Ş-A}}$
44	White	Aligoté	Ștefănești-Argeș	A.$_{\text{Ş-A}}$
45	White	Feteasca Regală	Ștefănești-Argeș	F.R.$_{\text{Ş-A}}$
46	White	Italian Riesling	Ștefănești-Argeș	I.R.$_{\text{Ş-A}}$
47	White	Sauvignon Blanc	Ștefănești-Argeș	S.B.$_{\text{Ş-A}}$
48	White	Pinot Gris	Ștefănești-Argeș	P.G.$_{\text{Ş-A}}$
49	White	Muscat Ottonel	Ștefănești-Argeș	M.O.$_{\text{Ş-A}}$
50	White	Pinot Gris	Ștefănești-Argeș	P.G.$_{\text{Ş-A}}$
51	White	Băbească Gri	Ștefănești-Argeș	B.G. $_{\text{Ş-A}}$
52	White	Chardonnay	Ștefănești-Argeș	C.$_{\text{Ş-A}}$
53	Red	Cabernet Sauvignon	Ștefănești-Argeș	C.S.$_{\text{Ş-A}}$
54	Red	Merlot	Ștefănești-Argeș	M.$_{\text{Ş-A}}$
55	Red	Feteasca Neagră	Ștefănești-Argeș	F.N.$_{\text{Ş-A}}$
56	Red	Burgund Mare	Ștefănești-Argeș	B.M.$_{\text{Ş-A}}$
57	Red	Pinot Noir	Ștefănești-Argeș	P.N. $_{\text{Ş-A}}$
58	Red	Băbească Neagră	Ștefănești-Argeș	B.N. $_{\text{Ş-A}}$

Sample preparation. To remove the appreciable amounts and colloidal suspensions present, the wine samples were filtered (cellulose acetate membrane, 0.45 µm pore size) and then acid digested in a microwave oven Milestone START D Microwave Digestion System. For the determination of metals 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). The operation conditions for applied microwave digestion system are given in Table 2.

Table 2

Microwave digestion operating programme

Step	*Initial temperature (^{0}C)*	*Final temperature (^{0}C)*	*Ranging time (min.)*	*Time hold (min.)*	*Power (W)*
1	25	100	15	10	800 (75 %)
2	100	150	10	5	800 (100 %)
3	150	200	10	10	1600 (85 %)

ICP-MS analysis. The quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS) was used for all isotopic measurements (Thermo scientific model). The instrument was tuned for standard robust plasma conditions, equipment with PFA micro flow concentric nebulizer. The argon and helium used was daily optimized to give maximum sensitivity for M^+ ions and the double ionization and oxides monitored by the means of the ration between Ba^{2+}/Ba^+ and Ce^{2+}/CeO^+, respectively these always being less than 2%. Tuning was performed by optimizing the signal measured counts per ratio (CPS) for ^{7}Li, ^{89}Y, and ^{205}Tl, form aqueous standard solution (Tune solution) that contained 10 ng/mL of Li, Y, Co, Ce, and Tl. For the ICP-MS analysis, the following 39 isotopes were recorded: ^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{28}Si, ^{31}P, ^{34}S, ^{43}Ca, ^{48}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{56}Fe/^{57}Fe, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{75}As, ^{77}Se, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{107}Ag, ^{114}Cd, ^{115}In, ^{120}Sn, ^{121}Sb, ^{125}Te, ^{137}Ba, ^{205}Tl, ^{205}Pb/^{207}Pb/^{208}Pb, and ^{209}Bi. All relevant instrument conditions are given in Table 3.

Instrument drifts where corrected using rhodium as an internal standard, at concentration level of 10 µg/L, added to both calibration standards and wine samples, to normalize the instrument response. Rhodium was selected as an internal standard due to the very low background signal found for these elements, and because it was not present in the wine samples. Additions of the internal standard to the samples were performed by a peristaltic pump.

Table 3

ICP-MS operating conditions

Instrument	*Q-ICP-MS*
Sampler cone	Ni (standard)
Skimmer cone	Ni (standard)
Nebulizer	MicroMist (standard)
Plasma torch	Quartz, 2.5 mm (standard)
Integration time	
Si, Sb, Ga, B	0.5 s x 1 point
Li, Be, As, Be, Cd	0.3 s x 1 point
All other	0.1 s x 1 point
Replicates	3
RF power	1500 W
Sample depth	7.6 mm
Carrier gas Ag	1.00 L/min.
Makeup gas	0.25 L/min.
Extract 1	+ 6 V
Extract 2	-145 V
Energy discrimination	3 V
Reaction gas He	5.5 mL/min.
CeO/Ce	0.65%
Ce^{++}/Ce	2.08%

A synthetic wine sample (12% ethanol, 4 g/L tartaric acid, and pH 3.4) was prepared containing 5% HNO_3 and 10 µg/L of the multi-element certificate standard solution to give rise to multiple interferences across a range of common analytes and test the ability of He collision mode to remove all overlapping polyatomic species. Two sets of spectra were acquired to show the ability of the He collision mode to remove multiple interferences: one He added and the second ”no gas” mode added to the collision cell. Data correction or background subtraction was applied in He mode for the elements As, Bi, Ca, Co, Cs, Cu, Fe, Ga, Ge, Mg, Ni, P, Pd, S, Se, Si, Ti, T, and Zn (Ivanova-Petropulos et al 2016).

Validation of the method*. *Limit of quantification (LoQ). Ten blank samples were run to determine the instrument limits of detection (ILD) and limit of quantitation (LoQ), as suggested by the International Union of Pure and Applied Chemistry (IUPAC) (Hopfer et al 2013; Ivanova-Petropulos et al 2016). Background equivalent concentration (BEC) was calculated as an indicator for the calibration offset expressed as a concentration, due to the elemental concentration of the blank. The analysis of the blank solution for all target elements for 10 times with three repetitions at each measurement was conducted (Ivanova-Petropulos et al 2016).

Recovery. Due to the lack of a sufficient wine certified reference material, the accuracy of the procedure was checked using synthetic wine (10% ethanol, 4 g/L tartaric acid, and pH 3.4), and red and white wine, spiked with two different standard additions: 10 µg/L (for trace elements) and 1 mg/L (for macro elements) (Ivanova-Petropulos et al 2016).

Repeatability and reproducibility. The intra-day repeatability and inter-day reproducibility have been also studied. One wine sample containing known amounts of the added elements was digested five subsequent times (in 1 day) applying the procedure describe above, and the obtained solutions were analyzed by ICP-MS in order to study the intra-day repeatability. Furthermore, the wine samples were digested three times during three consecutive days, in order to study the inter-day reproducibility (Ivanova-Petropulos et al 2016).

Calibration curves. For quantitative analysis of the elements in digested wine samples, external calibration curves were built at different concentration levels: 0.5, 1, 3, 5, 10, 30, 50 µg/L for the trace elements (Li, Be, Al, Ti, V, Cr, Co, Ni, Ga, Ge, As, Se, Mo, Pb, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Tl, Pb, and Bi); 100, 300, and 500 µg/L for the elements Cu, Zn, Rb, Mn, and Fe; and 1, 3, 5, and 10 mg/L for macro elements Na, P, S, Ca, Mg, K and Si.

Statistical analysis. Statistical treatments, including mean, relative standard deviation, standard deviation, t test, and one-way ANOVA were performed using the SPSS Version 24 (SPSS Inc., Chicago, IL., USA), and XLSTAT Software, Version 2012.6.09, Copyright Addinsoft 15.5.03.3707, applied to the multi-element data set in order to extract de important information and to represent the pattern of similarity or differences between the studies wines in order to make a conclusion about the possible wine classification.

Results and Discussion

Optimization of the method. The ICP-MS system was optimized under typical tuning conditions for variable and high sample matrices (plasma conditions optimized for 0.65% CeO/Ce) using multi-element standard solution. No attempt was made to optimize any parameter for the targeted removal of any specific interference. A flow of 5.5 mL/min. He gas was added to the cell for collision mode measurements (Ivanova-Petropulos et al 2016). Normal background components of the argon plasma gas and aqueous sample solution (H, O, Ar), together with the additional components of the synthetic sample matrix (ethanol and HNO_3) lead to formation of several high-intensity background peaks $^{40}Ar^{16}O$, $^{40}Ar^{38}Ar$, $^{40}Ar^{18}O$, and $^{40}Ar_2$, from plasma. Also, $^{40}Ar^{18}OH$, $^{40}Ar^{12}C$, $^{36}Ar^{16}OH$, $^{40}Ar^{12}CH$, $^{40}Ar^{12}C$, $^{40}Ar^{13}C$, $^{38}Ar^{12}C^{14}N$, and $^{40}Ar^{14}N$, were qualitatively determined as polyatomic interferences from the matrix (Ivanova-Petropulos et al 2016).

Their higher-intensity background peaks show why several interfered elements (^{52}Cr, ^{53}Cr, ^{53}Fe, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{77}Se, ^{78}Se, and ^{80}Se) were traditionally measured in to the cell for collision mode. Despite the optional helium gas for the polyatomic interferences removal, for some of the isotopes, very low sensitivity (spike recoveries <80%) was obtained to ^{52}Cr, ^{58}Ni, ^{78}Se, and ^{80}Se (Ivanova-Petropulos et al 2016). For total microwave digestion of the wine samples, different temperatures were tested, 150, 180 and 220^{0}C, observing best digestion at 220^{0}C. Finally, the applied power effect (400, 800 and 1600 W) was also examined in each digestion step.

In order to confirm the best chosen conditions for wine digestion, synthetic sample, white and red wine were digested and recoveries were calculated (Table 4). The digestion seems visually completed, but the spiked recoveries showed significant differences for total element concentration ($p<0.05$). The best recoveries (R >90%, on average for total elements) were obtained when volume of 0.5 mL samples (synthetic, white and red wine) was digested with 7 mL HNO^3 + 1 mL H_2O_2. The recoveries for the individual isotopes of 36 analyzed elements determined with three repetitions for each element is presented in Table 4. Values ranged from 87.56 % for Se to 118.19 % for Ti in synthetic wine, 87.19 % for S to 119.08 % for Ba in red wine, and 83.56 % for Ca to 117.49 % for Sn in the white wine sample.

Table 4

Standard additions for checking the accuracy of the microwave digestion and ICP-MS method (n = 3)

Element	*Recovery ± RSD (%)*		
	White wine	*Red wine*	*Synthetic wine*
Ag	85.63±4.78	89.56±1.14	93.15±2.87
Al	89.05±3.48	93.87±6.89	87.06±3.89
As	112.47±0.35	99.58±7.89	93.67±5.68
B	97.08±5.09	98.94±0.36	98.56±4.89
Ba	110.45±4.76	119.08±8.56	109.36±2.18
Be	92.56±8.56	110.25±4.58	87.96±6.78
Bi	96.23±1.02	89.26±5.46	87.56±5.06
Ca	83.56±1.78	92.01±7.74	87.52±5.63
Cd	85.65±9.26	98.06±1.06	99.78±4.26
Co	117.56±4.06	118.16±5.16	111.26±2.36
Cr	110.78±0.26	110.21±9.63	96.36±7.45
Cu	93.26±6.23	98.16±4.16	109.23±2.26
Fe	85.81±1.29	88.09±3.26	91.56±2.89
Ga	89.73±8.59	91.03±1.98	94.56±2.58
Ge	89.56±4.29	96.08±5.19	87.94±4.98
In	98.03±4.09	98.56±1.45	97.86±1.56
Li	112.36±1.58	108.56±7.46	110.23±2.91
Mg	108.06±8.49	115.87±1.89	109.28±7.23
Mn	97.58±6.73	109.09±6.49	93.58±7.48
Mo	89.47±5.58	99.06±8.94	86.28±8.56
Na	91.45±3.26	98.56±1.25	92.58±8.14
Ni	112.78±6.21	103.28±2.19	91.48±3.48
P	89.56±2.56	87.12±6.45	87.59±1.52
Pb	91.26±1.92	89.59±2.29	91.56±4.59
Rb	94.78±4.19	91.29±8.49	114.59±2.57
S	89.56±8.94	87.19±2.41	115.13±5.06
Sb	114.59±2.98	109.56±7.98	98.79±1.26
Se	89.79±5.47	94.58±7.45	87.56±1.59
Si	87.12±8.94	86.54±7.16	85.56±7.51
Sn	117.49±5.46	117.46±9.36	95.28±4.98
Sr	113.26±7.19	109.56±7.16	94.59±7.56
Te	89.56±4.26	94.93±3.19	109.06±3.29
Ti	89.26±2.09	88.19±8.65	118.19±3.26
Tl	98.26±7.11	96.58±1.29	94.58±6.19
V	88.19±9.26	94.58±4.16	90.48±5.13
Zn	97.91±2.39	109.26±8.49	98.56±3.26

RSD - relative standard deviation.

Optimization of the method. The linearity data, external calibration linear range, including correlation coefficient, are present in Table 5. As it can see from the table, the linearity is satisfactory in all cases with correlation coefficients (R^2>0.99) ranging from 0.9991 for Cd to 0.9999 Al, As, Ba, Be, Ca, Co, Fe, Ga, Li, Mg, Mo, Na, P, ^{208}Pb, Sb, Se, Sn, Te, Ti and Zn. The estimated instrument detection limit based on calibration linearity (external calibration), limit of detection (LoD) and limit of quantification (LoQ), as well as the background estimated concentration (BEC), was calculated for all elements in three consecutive days. Results are presented in Table 5. The lowest instrument detection limit (0.19 ng/L) was obtained with satisfactory sensitivity for ^{59}Co in helium mode (R^2 = 0.9999).

Table 5

Linear regression data

Element	Isotope	Unit	Mode	External calibration linear range	R^2	LoD	LoQ	BEC
Ag	107	µg/L	Ar	0.5-5	0.9998	0.021	0.077	0.036
Al	27	µg/L	Ar	10-100	0.0999	0.350	1.187	5.354
As	75	µg/L	He	0.5-10	0.9999	0.0015	0.0049	0.068
B	11	µg/L	Ar	0.1-1	0.9998	0.05	0.17	0.49
Ba	137	µg/L	Ar	10-100	0.9999	0.23	0.7351	0.24
Be	9	µg/L	Ar	0.5-5	0.9999	0.019	0.069	0.015
Bi	209	µg/L	He	0.5-10	0.9998	0.08	0.202	0.06
Ca	42	µg/L	He	1-10	0.9999	0.09	0.217	0.05
Cd	114	µg/L	Ar	0.5-10	0.9991	0.0056	0.018	0.088
Co	59	µg/L	He	0.5-5	0.9999	0.00019	0.0006	0.00038
Cr	53	µg/L	He	0.5-10	0.9998	0.0059	0.018	0.0053
Cu	63	µg/L	He	5-50	0.9998	0.026	0.084	0.051
Fe	56	µg/L	He	50-500	0.9996	0.2987	0.981	2.26
Fe	57	µg/L	He	50-500	0.9999	1.24	4.094	1.58
Ga	69	µg/L	He	0.5-5	0.9999	0.0098	0.036	0.018
Ge	72	µg/L	He	0.5-5	0.9998	0.0019	0.0058	0.026
In	115	µg/L	Ar	10-100	0.9998	0.08	0.21	0.14
Li	7	µg/L	Ar	0.0594	0.9999	0.0208	0.018	0.054
Mg	24	mg/L	He	1-10	0.9999	0.0518	0.168	0.587
Mn	55	µg/L	Ar	0.1-1	0.9998	0.0036	0.0109	0.0058
Mo	95	µg/L	Ar	0.5-5	0.9999	0.0018	0.0047	0.0026
Na	23	µg/L	Ar	1-10	0.9999	0.0068	0.026	0.0059
Ni	60	µg/L	He	0.5-10	0.9998	0.0016	0.0039	0.0031
P	31	µg/L	He	1-10	0.9999	0.058	0.18	0.0069
Pb	206	µg/L	Ar	0.5-10	0.9998	0.013	0.028	0.019
Pb	207	µg/L	Ar	0.5-10	0.9997	0.029	0.089	0.041
Pb	208	µg/L	Ar	0.5-10	0.9999	0.036	0.109	0.069
Rb	85	µg/L	Ar	50-500	0.9998	0.45	1.74	1.59
S	34	µg/L	He	1-10	0.9998	0.026	0.084	0.036
Sb	121	µg/L	Ar	0.5-5	0.9999	0.19	0.569	3.16
Se	77	µg/L	He	0.5-5	0.9999	0.00057	0.0023	0.00058
Si	28	µg/L	He	0.5-5	0.9998	0.069	0.198	0.963
Sn	120	µg/L	Ar	0.5-5	0.9999	0.0029	0.0098	0.0036
Sr	88	µg/L	Ar	0.1-1	0.9998	0.00087	0.0036	0.0016
Te	125	µg/L	He	0.5-5	0.9999	0.036	0.16	0.047
Ti	48	µg/L	He	0.5-5	0.9999	0.029	0.087	0.036
Tl	205	µg/L	He	0.5-5	0.9997	0.00036	0.0019	0.00039
V	51	µg/L	He	0.5-10	0.9998	0.00040	0.0018	0.039
Zn	66	µg/L	He	10-100	0.9999	0.0019	0.0052	0.0018

LoQ - limit of quantification; LoD - limit of detection; BEC - background estimated correction.

The accuracy of the procedure was checked using the standard addition method. One Dealu Bujorului wine sample was spiked with appropriate volumes of the multi-element standard solution: standard addition 1 with concentration of 10 µg/L, for the trace elements, and standard addition 2 with concentration of 1,000 µg/L for the macro elements. The satisfactory for the recovery ranged between 87 and 120 (%) and confirmed that the method is accurate and convenient for quantitative analysis of elements in red and white wines. Precision of the method was defined as a relative standard deviation (RSD) calculated as a percentage using the standard deviation divided by the mean of replicated samples (Table 6). The values for the RSD ranged from 84.70 and 125.70 (Table 6) and confirmed that the method is accurate and convenient for quantitative analysis of elements in red and white wines. Precision of the method was defined as a RSD calculated as a percentage using the standard deviation divided by the mean of replicated samples (Table 6).

Table 6

Standard additions for checking the accuracy of the digestion procedure and the ICP-MS method for determination of multi element composition of wine sample (n = 3)

El.	*Unit*	*C*	*R (%)*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*Mean*	*SD*	*RSD (%)*
Ag	µg/L	0.24	84.70	8.69	8.68	8.45	8.66	8.74	8.45	8.66	8.78	8.58	8.66	8.63	0.12	1.34
Al	mg/L	0.23	87.50	1.06	1.15	1.16	1.11	1.05	1.08	1.06	1.11	1.14	1.11	1.10	0.04	3.58
As	µg/L	1.22	106.10	11.44	11.57	11.71	11.17	11.63	11.64	12.13	12.58	12.64	12.43	11.89	0.51	4.32
B	mg/L	3.41	125.70	4.56	4.36	5.12	4.89	4.78	4.66	4.89	4.55	4.89	4.68	4.74	0.22	4.65
Ba	mg/L	0.37	117.50	1.46	1.58	1.66	1.79	1.48	1.58	1.55	1.69	1.84	1.65	1.63	0.12	7.59
Be	µg/L	0.16	118.30	11.70	11.43	11.86	11.91	12.38	12.27	12.14	11.78	12.06	11.89	11.94	0.28	2.35
Bi	µg/L	< LoD	107.40	9.73	10.12	9.89	9.99	10.21	10.63	9.98	9.99	10.12	10.11	10.07	0.26	2.54
Ca	mg/L	81.60	121.30	83.62	84.78	83.26	84.16	83.27	85.96	83.63	83.36	82.69	83.25	83.80	0.95	1.13
Cd	µg/L	0.26	105.21	10.94	11.23	10.56	10.78	10.26	10.84	10.33	10.56	10.48	10.65	10.66	0.29	2.75
Co	µg/L	2.20	117.89	14.56	13.98	14.21	14.56	14.02	14.23	14.12	14.36	14.25	13.65	14.19	0.27	1.93
Cr	µg/L	0.018	106.12	9.36	9.56	9.63	9.65	8.98	9.45	9.49	9.66	9.24	9.63	9.47	0.22	2.32
Cu	µg/L	0.024	112.39	11.26	11.36	11.48	11.29	11.45	11.32	11.25	11.24	11.32	11.28	11.33	0.08	0.73
Fe	µg/L	0.58	97.31	11.23	10.21	11.24	11.15	11.28	11.21	11.45	11.31	11.32	11.02	11.14	0.35	3.11
Ga	µg/L	11.56	121.36	23.69	23.18	23.45	23.15	23.15	23.15	23.18	23.69	23.14	23.15	23.29	0.23	0.98
Ge	µg/L	0.06	103.33	9.16	9.18	9.26	9.13	9.18	9.25	9.36	9.15	9.15	9.12	9.19	0.07	0.81
In	µg/L	< LoD	117.21	11.26	11.36	12.04	12.06	11.62	11.34	11.45	11.26	12.01	11.25	11.57	0.34	2.97
Li	µg/L	3.79	89.25	12.56	12.47	12.36	12.15	12.14	12.14	12.54	12.16	12.32	12.14	12.30	0.18	1.43
Mg	mg/L	95.81	108.56	97.56	96.32	97.89	98.56	98.56	98.48	98.45	98.45	98.45	98.16	98.09	0.70	0.72
Mn	mg/L	0.94	117.26	2.15	2.18	2.16	2.17	2.14	2.17	2.25	2.26	2.26	2.14	2.19	0.05	2.25
Mo	µg/L	1.73	89.63	10.89	10.79	10.58	10.58	10.54	10.58	10.46	10.48	10.26	10.56	10.57	0.17	1.63
Na	mg/L	5.89	86.54	86.09	86.19	86.58	86.15	86.19	87.45	86.16	86.32	87.00	86.89	86.50	0.46	0.54
Ni	µg/L	20.16	123.09	31.26	32.16	31.45	32.16	32.16	31.26	32.00	32.26	32.15	32.18	31.90	0.41	1.28
P	mg/L	136.23	114.36	135.26	135.89	136.29	136.18	136.59	134.56	136.00	136.8	138.19	136.19	136.20	0.96	0.71
Pb	µg/L	4.19	116.23	15.36	16.23	16.28	15.78	16.18	15.69	16.68	16.56	16.58	16.78	16.21	0.47	2.90
Rb	mg/L	3.86	90.16	4.89	4.76	4.69	4.98	4.99	4.84	4.55	4.29	4.56	4.48	4.70	0.23	4.91
S	mg/L	78.90	121.36	78.98	80.56	80.29	79.89	79.86	80.16	80.45	80.16	80.45	80.16	80.10	0.45	0.57
Sb	µg/L	0.30	87.96	8.69	8.59	8.66	8.89	8.56	8.98	8.78	8.55	8.55	8.45	8.67	0.16	1.93
Se	µg/L	1.97	108.87	13.26	12.58	12.98	12.54	12.26	12.48	12.45	12.41	12.62	12.48	12.61	0.30	2.35
Si	mg/L	15.26	120.58	121.03	120.59	120.45	121.09	121.58	121.09	120.03	120.54	120.36	120.45	120.72	0.46	0.38
Sn	µg/L	1.03	94.63	10.98	10.26	10.28	10.56	11.06	10.89	10.98	11.62	11.00	10.65	10.83	0.41	3.75
Sr	µg/L	0.61	91.26	9.56	9.00	9.65	9.24	9.36	9.28	9.39	9.57	9.21	9.64	9.39	0.21	2.28
Te	µg/L	0.19	86.98	8.36	8.44	8.51	8.56	8.78	8.56	8.78	8.45	8.65	8.77	8.59	0.15	1.78
Ti	µg/L	3.54	85.16	12.69	12.45	12.65	12.89	12.16	12.89	12.78	12.16	12.00	12.06	12.47	0.35	2.82
Tl	µg/L	0.96	87.65	9.56	9.78	9.48	9.98	9.56	9.78	9.87	8.49	8.49	8.55	9.35	0.60	6.44
V	µg/L	0.46	87.56	9.16	9.26	9.36	9.25	9.48	9.56	9.26	9.56	9.65	9.45	9.40	0.16	1.75
Zn	µg/L	0.08	103.69	10.87	10.56	10.87	10.56	10.98	10.56	10.48	10.46	10.36	10.58	10.63	0.21	1.93

El. – element; LoQ for Bi: 0.202 µg/L; LoQ for In: 0.21 µg/L; C - element concentration in not spiked wine determined with three repetitions; R (%) - recoveries for the spiked addition in wine, calculated from the 10 measurements of spiked wine (three repetitions for one measurement); 1-10 ten repetitions from one digested spiked wine sample in 1 day; SD - standard deviation; RSD - relative standard deviation.

Additionally, to confirm the accuracy of the method and to check the repeatability, five replicated measurements on an actual red and white wine samples were performed within 1 day. Every digested sample was injected three times into the ICP-MS system. The RSD of the five replicate samples for each element are present in Table 7. Satisfactory values for the RSD ranging from 1.04 % for Na to 10.9 % were found in red wine and RSD values for white wine were 1.16 % for Li to 11.8 % for Ni (Table 7).

Table 7

Results for repeatability data for each element in red and white wine (5 measurements per day with 3 injections per measurement)

Element	*Unit*	*White wine*		*Red wine*	
		Mean concentration	*RSD (%)*	*Mean concentration*	*RSD (%)*
Ag	μg/L	26.89	5.19	2.48	1.91
Al	mg/L	1.45	2.08	0.87	0.63
As	mg/L	86.78	2.36	21.06	1.36
B	mg/L	2.39	0.78	2.56	1.79
Ba	μg/L	87.49	2.78	169.48	4.54
Be	μg/L	6.08	3.78	0.54	0.16
Bi	μg/L	39.56	2.78	45.19	2.78
Ca	mg/L	42.69	4.06	37.98	8.63
Cd	μg/L	8.36	2.16	0.0098	2.18
Co	μg/L	4.95	2.51	3.45	1.62
Cr	mg/L	1.84	1.26	1.16	6.75
Cu	μg/L	29.46	3.78	26.19	1.35
Fe	mg/L	1.26	1.47	1.78	3.29
Ga	μg/L	46.78	6.35	15.26	6.75
Ge	μg/L	0.079	3.16	0.0078	2.35
In	μg/L	248.45	1.39	7.78	4.28
Li	μg/L	5.36	1.87	4.59	1.53
Mg	mg/L	62.78	6.41	69.54	3.56
Mn	mg/L	0.94	3.05	0.89	3.48
Mo	μg/L	4.78	6.78	3.45	2.94
Na	mg/L	26.78	7.06	10.26	3.77
Ni	μg/L	36.45	12.78	18.26	6.34
P	mg/L	115.84	2.39	116.78	10.78
Pb	μg/L	26.78	9.48	13.48	1.98
Rb	mg/L	1.26	3.46	1.16	4.59
S	mg/L	96.45	3.86	76.85	6.36
Sb	μg/L	2.36	5.78	0.56	7.93
Se	μg/L	56.36	2.46	13.49	2.79
Si	mg/L	25.78	1.98	35.44	3.38
Sn	μg/L	4.59	3.58	6.55	2.84
Sr	μg/L	554.74	2.43	657.11	6.19
Te	μg/L	103.56	1.59	0.86	5.59
Ti	μg/L	28.03	5.62	22.45	3.08
Tl	μg/L	4.59	1.89	2.29	1.45
V	μg/L	57.48	5.47	12.55	4.09
Zn	μg/L	55.16	7.09	47.15	6.38

Results are average values of five repetitions in five consecutive days; RSD - relative standard deviation.

Reproducibility was also checked with replicate samples analyzed in three different days (3 replicates x injections x 3 days), and the RSD for each element was calculated (Table 8) (Ivanova-Petropulos et al 2016).

Table 8

Reproducibility for the analyzed elements in white and red wines (3 replicates x 3 injections x 3 days)

El.	*Conc.*	*White wine*						*Red wine*					
		Day 1	*RSD (%)*	*Day 2*	*RSD (%)*	*Day 3*	*RSD (%)*	*Day 1*	*RSD (%)*	*Day 2*	*RSD (%)*	*Day 3*	*RSD (%)*
Ag	µg/L	2.36	1.25	2.69	6.12	2.48	0.58	2.36	1.36	2.48	4.05	2.78	0.39
Al	mg/L	1.21	2.37	1.24	0.85	1.28	2.47	0.69	2.57	0.68	1.25	1.36	0.25
As	µg/L	78.32	0.96	83.76	7.29	84.66	4.89	24.89	4.86	22.65	6.32	23.84	4.06
B	mg/L	2.39	4.36	2.58	1.55	2.78	1.59	2.65	3.25	2.47	0.94	2.74	0.77
Ba	µg/L	87.56	3.74	91.48	5.29	86.74	1.29	150.65	3.58	158.66	5.62	149.68	4.59
Be	µg/L	5.86	3.16	6.32	4.29	6.48	3.29	0.45	6.28	0.59	3.26	0.38	2.89
Bi	µg/L	34.81	4.26	34.55	2.56	36.47	2.19	47.58	2.59	47.16	47.15	47.59	4.59
Ca	mg/L	42.18	3.15	41.69	3.84	41.29	2.47	38.59	1.48	37.89	3.86	41.28	1.19
Cd	µg/L	7.26	4.18	7.15	1.06	7.09	1.25	0.0096	2.78	0.0095	3.56	0.0096	7.26
Co	µg/L	5.26	1.26	5.48	0.98	4.59	2.69	1.56	5.29	1.52	4.06	1.59	1.58
Cr	mg/L	0.52	1.23	0.46	0.59	0.52	1.48	0.59	1.06	0.32	1.48	0.48	2.43
Cu	µg/L	28.29	2.89	27.89	0.96	27.88	3.58	29.06	1.79	28.89	3.98	27.19	4.55
Fe	mg/L	1.52	7.21	1.53	6.35	1.59	3.70	1.36	2.98	1.35	1.95	1.36	4.06
Ga	µg/L	46.73	3.76	47.36	3.69	43.89	4.63	12.75	2.09	13.26	5.73	13.22	2.96
Ge	µg/L	0.079	1.59	0.079	3.58	0.079	1.63	0.0063	0.89	0.0059	8.56	0.0065	4.36
In	µg/L	236.19	1.26	235.79	4.70	239.16	4.59	6.28	2.56	6.02	4.36	5.35	2.56
Li	µg/L	4.56	1.28	4.86	1.39	4.38	3.87	4.89	2.56	4.96	3.25	5.18	3.28
Mg	mg/L	62.35	2.58	63.78	4.88	62.45	3.96	63.25	4.58	63.22	2.06	66.56	3.54
Mn	mg/L	0.95	5.26	0.89	4.22	0.89	2.21	0.79	0.56	0.81	1.39	0.78	5.23
Mo	µg/L	3.45	1.48	3.69	1.56	3.59	2.65	2.89	4.79	2.56	3.89	2.56	0.92
Na	mg/L	21.48	2.56	20.97	3.89	22.98	3.52	9.79	3.16	9.69	4.88	9.31	2.84
Ni	µg/L	30.56	0.54	32.14	1.78	31.55	0.89	19.66	2.48	16.23	1.86	20.97	1.23
P	mg/L	109.89	4.79	108.88	2.65	112.79	3.25	114.22	4.70	115.79	2.23	114.56	3.25
Pb	µg/L	25.23	2.36	25.45	1.79	24.36	1.36	12.56	2.48	12.56	3.26	12.95	2.56
Rb	mg/L	0.96	2.49	0.96	4.26	0.99	2.79	1.34	0.99	1.56	2.22	2.62	1.79
S	mg/L	92.26	5.26	91.66	2.07	91.89	1.25	72.03	5.81	75.62	4.58	72.18	4.47
Sb	µg/L	2.56	2.14	2.69	1.17	2.66	1.79	0.57	1.29	0.55	2.96	0.56	1.03
Se	µg/L	52.66	3.06	51.48	2.98	52.77	1.01	14.79	1.25	14.98	0.26	14.99	1.06
Si	mg/L	24.16	2.96	24.65	1.65	24.59	0.96	32.96	2.98	33.98	0.98	32.55	3.47
Sn	µg/L	6.23	1.79	6.78	2.06	6.55	0.66	4.32	3.25	5.79	2.95	5.65	2.20
Sr	µg/L	509.56	4.32	51.69	1.25	52.16	3.06	653.22	4.78	655.50	5.63	651.99	5.78
Te	µg/L	94.01	5.89	94.63	5.03	96.91	4.56	0.63	2.56	0.89	1.32	0.69	5.44
Ti	µg/L	23.05	1.09	24.82	2.18	24.06	1.26	22.63	1.26	23.08	5.21	23.36	4.19
Tl	µg/L	4.12	4.99	4.09	3.78	4.23	2.79	1.29	1.48	0.41	2.79	2.41	1.50
V	µg/L	54.89	2.86	55.93	2.56	55.87	4.03	21.79	3.89	22.09	4.06	22.96	3.45
Zn	µg/L	56.56	2.36	54.92	2.56	57.19	3.06	57.49	3.06	55.89	4.06	53.98	3.06
		Day 1/Day 2		Day 1/Day 2		Day 1/Day 2		Day 1/Day 2		Day 1/Day 2		Day 1/Day 2	
t		-1.26		-1.36		-1.27		-1.09		-1.06		0.89	
p		0.36		0.23		0.24		0.28		0.31		0.45	

El. – element; Conc. – concentration; *t* test for dependent samples: differences are not significantly different at p>0.05

Elemental characterization and method applications. Table 9-14 shows the content of 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V and Zn) determined in Romanian wines. For all wines, the total content of elements ranged from 359.28 to 632.91 mg/L (mean 513.70 mg/L). Elements B, Ca, Mg, Na, P, S and also Si were dominant in all wines. In fact, the group of major elements (Ca, Mg, Na, B, P, Si) represented the highest proportion in all wines ranging from 1.25 to 278.39 mg/L, followed by the minor elements (Al, Ba, Cu, Fe, Mn, Rb, Sr, and Zn) present in a range of 0.01 to 3.28 mg/L and trace elements (Ag, As, Be, Bi, Cd, Co, Cr, Cs, Ga, Ge, In, Li, Mo, Ni, Pb, Pd, Sb) ranging between 0.01 to 61.57 μg/L, comparable to those reported in the literature (Pohl 2007). Boron is an essential element for plants is easily mobilized from soil into the plant. Similar P, is an essential plant element, which is often added to the soil with fertilizers, while Si, Mg, and Mn are mainly influenced the soil mineral content (Hopfer et al 2013).

These results agree with values reported in the literature (Iglesias et al (2007) average values of 819.61 mg/L, Álvarez et al (2012) average values of 865.30 mg/L). The values obtained for the Ca and Mg contents in our selected wines were in good agreement with the result for Macedonian (Ivanova-Petropulos et al 2013 - average values of 83.5 mg/L ca and 98.20 mg/L Mg), Serbian (Ražić & Onjia 2010 - average values of 37 mg/L Ca and 95.73 mg/L Mg), Croatian (Vrček et al 2011 - average value of 65.90 mg/L Ca and 68.70 mg/L Mg) and Czech wines (Kment et al 2005 - average value of 108.00 mg/L Ca and 75.40 mg/L Mg). On the other hand, our Ca and Mg contents were significantly higher than published data for wines from Argentina (Lara et al 2005 - average value of 12.50 mg/L Ca) and Belgium (Coetzee & van Jaarsveld 2014 - average values of 6.73 mg/L and 12.05 mg/L Mg). In case of Na concentration, the results are in agree with Ražić & Onjia (2010) where they obtained the similar concentration of Na in wine from north Serbia (33.00±11.00 mg/L). The Na concentration in our study are similar with the results published on Serbian (Ražić & Onjia 2010 - average values of 29.65 mg/L Na), Czech (Kment et al 2005 - average value of 14.70 mg/L Na) and Spanish (Iglesias et al 2007 - average values of 37.19 mg/L Na) wines.

All wines presented high values of P ranging from 62.30 to 278.39 mg/L confirming the high nutritional values of Romanian wines. Moreover, results for all determined elements are in accordance to previous data about multi-element composition of Romanian wines (Avram et al 2014; Geana et al 2016). In addition, analyzed wines presented higher content of Mg and Ca, but lower amount of Na compared to Vranec wines (Ivanova-Petropulos et al 2016) and other red wines produced in Serbia (Mitic et al 2014).

Considerable amounts of S were found in all Romanian wines (63.16 to 374.19 mg/L). In fact, S is mainly present due to the SO_2 which is usually an added agent into grape must to protect the non-enzymatic and enzymatic oxidation of phenolics, amino acids and sugars that could cause browning of the wine. The addition of SO_2 is traditionally considered as an efficient method to protect and preserve the wine at different stages of its elaboration.

Regarding the harmful elements, the content of Cd, As, Cu, Fe, Pb and Zn was below the maximal allowed concentration in all wines. Thus, As ranged from 0.15 to 0.86 μg/L, Cd from 0.14 to 1.36 μg/L, Cu was present in range of 0.010 to 0.263 μg/L, concentration of Fe ranged from 0.35 to 1.62 mg/L and levels for Pb and Zn ranged between 4.19 to 19.63 μg/L and 0.05 to 0.79 mg/L respectively. Maximal acceptable limits for these toxic elements are as follows: As 0.2 mg/L, Cd 10 μg/L, Cu 1 mg/L, Pb 0.15 mg/L and Zn 5 mg/L.

Li, Cu, Fe, Mn, Co and V are also present in concentration similar to previously published results (Pohl 2007; Fabani et al 2010; Di Paola-Naranjo et al 2011; Ivanova-Petropulos et al 2013; Avram et al 2014; Catarino et al 2014; Geana et al 2016). The results indicated that Romanian wines are moderately rich in vanadium and the results obtained are similar with Macedonian (Ivanova-Petropulos et al 2013), Spanish (Iglesias et al 2007) and Czech (Kment et al 2005) wines and have more vanadium than Belgian (Coetzee & van Jaarsveld 2014) ones.

Table 9

Concentration of elements in Romanian wine samples

El.	*Unit*	*F.A.*$_{DB}$	*F.R.*$_{DB}$	*M.O.*$_{DB}$	*B.G.*$_{DB}$	*Ș.*$_{DB}$	*I.R.*$_{DB}$	*S.B.*$_{DB}$	*A.*$_{DB}$	*F.N.*$_{DB}$	*M.*$_{DB}$
Ag	µg/L	0.16±0.007	0.26±0.008	0.19±0.005	0.28±0.012	0.15±0.006	0.20±0.009	0.22±0.0015	0.19±0.007	0.21±0.009	0.31±0.002
Al	mg/L	0.21±0.01	0.18±0.001	0.24±0.06	0.14±0.005	0.23±0.007	0.12±0.01	0.15±0.03	0.17±0.13	0.24±0.003	0.15±0.02
As	µg/L	0.53±0.04	0.39±0.11	0.41±0.02	0.61±0.20	0.49±0.02	0.51±0.06	0.47±0.03	0.36±0.02	0.41±0.09	0.15±0.001
B	mg/L	4.56±0.17	5.21±1.25	4.78±0.08	3.28±0.16	2.31±0.84	3.47±0.57	4.85±0.18	5.87±0.24	4.06±0.16	3.54±0.54
Ba	mg/L	0.25±0.05	0.39±0.17	0.09±0.04	0.14±0.09	0.27±0.16	0.09±0.06	0.24±0.04	0.19±0.01	0.26±0.01	0.32±0.04
Be	µg/L	0.12±0.01	0.23±0.005	0.16±0.01	0.26±0.01	0.19±0.01	0.22±0.01	0.18±0.01	0.17±0.01	0.26±0.001	0.29±0.02
Bi	µg/L	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	4.16±1.12	2.15±0.12	1.26±0.16	3.15±1.12
Ca	mg/L	87.36±3.28	69.25±2.71	95.47±2.36	72.06±4.70	64.18±4.71	55.79±2.69	91.06±2.57	87.00±4.79	82.57±2.76	46.09±4.09
Cd	µg/L	0.36±0.015	0.28±0.019	0.22±0.003	0.19±0.002	0.39±0.018	0.20±0.01	0.26±0.018	0.35±0.006	0.24±0.01	0.29±0.04
Co	µg/L	2.15±0.051	1.45±0.04	2.78±0.15	0.89±0.02	3.54±0.035	2.89±0.03	1.39±0.45	2.55±0.032	0.81±0.006	1.79±0.03
Cr	mg/L	0.012±0.003	0.01±0.001	0.011±0.004	0.018±0.002	0.025±0.001	0.011±0.001	0.011±0.009	0.012±0.003	0.011±0.006	0.015±0.003
Cu	mg/L	0.045±0.009	0.129±0.006	0.039±0.007	0.029±0.003	0.018±0.007	0.015±0.06	0.019±0.001	0.148±0.004	0.130±0.005	0.049±0.016
Fe	mg/L	0.59±0.015	0.71±0.12	1.42±0.57	0.98±0.05	0.86±0.06	0.76±0.012	0.55±0.008	0.60±0.05	0.76±0.008	1.21±0.008
Ga	µg/L	14.79±0.24	5.26±0.19	3.68±0.007	1.53±0.002	12.89±0.38	10.11±0.01	7.35±0.04	4.12±0.01	3.15±0.008	1.78±0.004
Ge	µg/L	0.24±0.01	0.12±0.04	0.19±0.04	0.26± 0.01	0.14±0.004	0.09±0.04	0.24±0.04	0.36±0.07	0.24±0.009	0.39±0.14
In	µg/L	7.78±0.07	5.12±0.19	0.71±0.01	0.45±0.01	0.98±0.006	< LoQ	< LoQ	< LoQ	0.96±0.008	5.23±0.007
Li	µg/L	41.15±2.15	47.98±0.08	7.12±0.009	36.58±0.47	52.04±0.007	53.16±1.24	21.78±0.01	0.32±0.07	0.41±0.009	9.18±0.14
Mg	mg/L	157.15±4.63	183.56±7.15	214.30±6.98	81.56±2.58	78.56±0.16	126.32±5.87	147.18±2.59	156.18±2.89	98.58±0.16	118.15±3.69
Mn	mg/L	2.31±0.35	0.89±0.12	0.53±0.06	0.49±0.006	1.14±0.007	0.66±0.015	1.23±0.008	2.15±0.004	0.36±0.008	0.91±0.007
Mo	µg/L	1.14±0.002	0.69±0.008	0.53±0.007	6.53±0.21	3.15±0.009	2.14±0.007	1.12±0.08	0.25±0.006	1.45±0.009	2.57±0.009
Na	mg/L	42.16±12.89	10.96±4.69	6.22±1.89	8.26±3.98	5.85±3.16	1.26±0.79	2.55±0.96	1.89±0.009	32.56±0.86	2.56±0.09
Ni	mg/L	0.018±0.003	0.025±0.008	0.010±0.006	0.027±0.007	0.065±0.004	0.018±0.005	0.063±0.005	0.078±0.005	0.021±0.006	0.032±0.001
P	mg/L	123.25±3.78	119.58±4.36	109.56±3.57	86.31±4.03	89.14±0.06	278.39±5.98	258.16±12.78	147.15±0.36	69.56±5.18	66.32±4.78
Pb	µg/L	6.32±1.28	12.56±1.98	8.63±2.58	6.32±3.14	14.79±2.65	10.45±3.26	9.14±3.65	7.35±2.17	6.98±3.17	5.56±0.32
Rb	mg/L	2.14±0.002	1.29±0.007	1.10±0.003	2.09±0.001	1.89±0.002	2.56±0.001	1.45±0.002	2.32±0.009	1.47±0.007	1.32±0.052
S	mg/L	128.13±6.98	139.36±0.06	96.16±5.49	163.18±6.98	165.96±3.48	318.16±4.96	258.16±9.17	93.16±4.79	98.17±9.26	247.91±2.36
Sb	µg/L	0.26±0.14	0.18±0.05	0.32±0.04	0.19±0.02	0.23±0.01	0.31±0.09	0.38±0.18	0.22±0.02	0.24±0.02	0.29±0.03
Se	µg/L	2.13±0.05	1.02±0.06	1.39±0.02	2.29±0.21	2.14±0.01	2.19±0.01	1.26±0.01	1.48±0.01	1.98±0.12	1.26±0.05
Si	mg/L	15.63±0.089	13.01±0.002	9.18±0.008	19.96±0.04	23.38±0.59	14.02±0.06	19.26±0.01	22.63±1.07	18.93±0.04	17.09±0.08
Sn	µg/L	1.58±0.025	25.06±0.001	2.08±0.009	18.11±2.89	14.17±0.02	11.14±0.03	1.89±0.008	2.31±1.04	3.25±0.008	4.65±0.001
Sr	mg/L	1.23±4.89	0.63±0.01	0.29±0.002	0.98±0.06	0.59±0.01	0.58±0.01	0.52±0.02	0.18±0.003	0.98±0.06	1.14±0.01
Te	µg/L	0.62±0.021	0.19±0.013	0.54±0.007	0.23±0.001	0.24±0.02	0.39±0.01	0.28±0.01	0.14±0.01	0.21±0.01	0.19±0.01
Ti	µg/L	4.15±1.06	2.89±0.147	4.66±0.18	3.14±0.78	5.06±0.01	2.18±0.005	1.49±0.007	2.63±0.001	1.48±0.06	2.63±0.47
Tl	µg/L	0.91±0.14	0.63±0.18	0.56±0.023	0.96±0.005	0.54±0.001	0.82±0.018	0.99±0.004	0.41±0.009	0.63±0.001	0.51±0.001
V	µg/L	0.78±0.001	0.59±0.017	0.69±0.018	0.62±0.003	0.78±0.008	0.63±0.002	0.45±0.01	0.39±0.01	0.84±0.001	0.63±0.017
Zn	mg/L	0.38±0.0019	0.44±0.01	0.05±0.002	0.32±0.01	0.49±0.01	0.53±0.01	0.06±0.02	0.09±0.001	0.14±0.02	0.16±0.01

El. – element.

Table 10

Concentration of elements in Romanian wine samples

El.	*Unit*	*M.*$_{DB}$	*B.N.*$_{DB}$	*C.S.*$_{DB}$	*B.M.*$_{DB}$	*B.N.*$_{DB}$	*F.A.*$_{T}$	*F.R.*$_{T}$	*I.R.*$_{T}$	*N.*$_{T}$	*P.G.*$_{T}$
Ag	µg/L	0.32±0.009	0.19±0.005	0.35±0.012	0.15±0.007	0.19±0.003	0.24±0.025	0.41±0.006	0.35±0.003	0.22±0.008	0.31±0.006
Al	mg/L	0.21±0.08	0.23±0.004	0.14±0.02	0.16±0.07	0.24±0.04	0.23±0.07	0.21±0.02	0.18±0.09	0.14±0.03	0.10±0.02
As	µg/L	0.64±0.01	0.59±0.03	0.45±0.12	0.38±0.01	0.23±0.05	0.19±0.02	0.56±0.06	0.48±0.01	0.36±0.01	0.16±0.009
B	mg/L	2.39±0.06	1.39±0.58	3.31±0.02	4.78±0.59	3.68±0.84	4.12±0.18	3.19±0.25	4.21±0.13	2.34±0.16	3.57±0.17
Ba	mg/L	0.16±0.07	0.18±0.02	0.11±0.04	0.25±0.04	0.11±0.01	0.35±0.04	0.27±0.01	0.12±0.05	0.23±0.04	0.18±0.01
Be	µg/L	0.15±0.01	0.19±0.03	0.12±0.01	0.13±0.02	0.16±0.03	0.14±0.01	0.13±0.02	0.15±0.01	0.19±0.03	0.14±0.03
Bi	µg/L	1.26±0.16	< LoQ	< LoQ	2.58±1.16	2.89±0.14	< LoQ	< LoQ	1.45±0.15	2.16±0.78	2.12±0.15
Ca	mg/L	78.36±0.63	43.15±6.87	46.78±9.15	71.16±6.41	32.39±2.06	28.47±1.99	94.16±1.47	51.09±10.95	47.12±7.89	42.26±9.15
Cd	µg/L	0.29±0.04	0.32±0.04	0.22±0.016	0.14±0.01	0.16±0.04	0.35±0.01	0.39±0.01	0.41±0.002	0.32±0.023	0.35±0.023
Co	µg/L	2.58±0.04	1.79±0.003	2.06±0.56	3.54±0.41	0.98±0.02	2.34±0.02	2.98±0.12	0.96±0.023	0.86±0.003	162±0.08
Cr	mg/L	0.019±0.006	0.01±0.003	0.010±0.002	0.014±0.05	0.010±0.006	0.015±0.002	0.010±0.0003	0.018±0.006	0.022±0.002	0.026±0.009
Cu	mg/L	0.153±0.003	0.263±0.07	0.058±0.09	0.183±0.02	0.028±0.003	0.018±0.06	0.063±0.001	0.279±0.001	0.241±0.006	0.042±0.012
Fe	mg/L	0.52±0.14	0.54±0.08	1.03±0.15	0.98±0.005	0.38±0.04	0.49±0.06	1.24±0.08	0.87±0.05	0.96±0.01	1.15±0.06
Ga	µg/L	3.12±0.001	2.89±0.02	17.49±0.03	16.06±0.04	14.26±0.14	13.00±1.12	17.11±0.005	5.89±0.01	4.81±0.02	4.18±0.56
Ge	µg/L	0.17±0.04	0.48±0.007	0.45±0.07	0.25±0.14	0.06±0.07	0.015±0.004	0.28±0.04	0.39±0.07	0.58±0.15	0.36±0.41
In	µg/L	0.59±0.008	3.56±0.004	< LoQ	< LoQ	4.20±0.017	2.10±0.52	0.49±0.004	0.37±0.005	0.68±0.004	< LoQ
Li	µg/L	30.17±0.07	24.17±0.07	21.78±0.01	14.70±0.012	9.56±0.008	48.17±0.008	52.29±0.004	52.14±0.006	21.17±2.37	6.32±1.25
Mg	mg/L	256.98±7.89	136.15±2.56	48.89±3.56	53.69±2.59	114.78±0.16	258.26±3.69	98.16±8.06	236.17±8.79	103.14±2.25	127.26±6.29
Mn	mg/L	1.05±0.001	0.24±0.008	0.39±0.007	0.85±0.001	1.83±0.24	0.58±0.06	0.47±0.006	0.69±0.02	0.89±0.006	0.17±0.002
Mo	µg/L	7.14±2.48	5.89±1.45	0.69±0.005	0.73±0.004	1.28±0.58	2.56±1.25	3.29±1.14	4.78±1.26	0.79±0.006	0.43±0.006
Na	mg/L	25.88±18.06	11.26±3.79	5.89±1.26	4.66±1.68	4.79±3.69	8.56±1.65	3.36±2.59	4.76±1.12	3.69±0.56	1.49±0.63
Ni	mg/L	0.023±0.002	0.039±0.004	0.017±0.001	0.040±0.025	0.016±0.006	0.047±0.009	0.018±0.006	0.054±0.009	0.079±0.037	0.031±0.001
P	mg/L	187.14±4.29	240.01±0.09	140.65±8.81	132.06±4.18	147.06±9.63	235.01±8.06	162.32±9.56	140.23±8.63	132.05±2.14	87.13±5.89
Pb	µg/L	6.39±1.49	5.98±9.16	14.78± 9.36	10.45±1.26	7.89±4.16	8.63±0.25	11.27±1.38	12.06±1.96	10.36±0.36	15.18±4.63
Rb	mg/L	3.12 ±0.08	2.92±0.001	2.34±0.004	3.09±0.001	2.47±0.001	2.14±0.004	1.45±0.004	2.59±0.009	3.17±0.001	2.01±0.004
S	mg/L	63.16±9.17	79.18±6.18	351.79±21.65	214.10±6.35	96.18±9.17	123.36±8.47	369.10±9.14	374.19±8.39	96.08±6.18	97.16±9.31
Sb	µg/L	0.16±0.08	0.23±0.04	0.38±0.08	0.42±0.01	0.23±0.04	0.36±0.04	0.29±0.04	0.33±0.01	0.48±0.01	0.52±0.001
Se	µg/L	1.25±0.01	2.89±1.15	1.39±0.05	2.36±0.01	1.16±0.01	2.56±0.01	2.61±0.09	1.13±0.13	1.29±0.06	1.05±0.01
Si	mg/L	11.08±0.025	18.37±0.005	16.11±0.058	15.92±0.004	14.42±0.01	9.63±1.05	11.48±0.06	15.07±0.009	18.18±0.018	9.36±0.02
Sn	µg/L	8.37±2.58	4.15±1.18	6.89±1.21	5.12±2.11	1.47±2.36	1.14±0.12	17.05±0.005	1.10±0.001	16.14±0.002	2.48±2.31
Sr	mg/L	0.28±0.021	0.86±0.02	0.36±0.005	1.47±0.26	0.96±0.11	0.62±0.02	0.17±0.01	0.87±0.06	0.79±0.08	1.02±0.21
Te	µg/L	0.78±0.39	0.52±0.01	0.58±0.01	0.89±0.02	0.63±0.009	0.28±0.001	0.26±0.001	0.29±0.07	0.41±0.15	0.65±0.009
Ti	µg/L	4.19±0.26	4.69±0.13	2.81±0.027	3.84±0.01	2.18±0.01	3.59±0.03	3.25±0.09	3.51±0.08	3.32±0.01	3.58±0.01
Tl	µg/L	0.56±0.017	0.50±0.01	0.91±0.02	0.81±0.006	0.47±0.003	0.79±0.01	0.63±0.01	0.48±0.06	0.94±0.04	0.98±0.023
V	µg/L	0.63±0.01	0.59±0.02	0.96±0.14	0.47±0.13	0.74±0.21	0.42±0.008	0.46±0.021	0.63±0.01	0.79±0.02	0.58±0.11
Zn	mg/L	0.46±0.01	0.19±0.03	0.25±0.06	0.49±0.003	0.51±0.01	0.31±0.06	0.22±0.003	0.48±0.028	0.52±0.003	0.61±0.006

El. – element.

Table 11

Concentration of elements in Romanian wine samples

El.	*Unit*	$M.O._{T}$	$T._{T}$	$P.N._{M}$	$C._{M}$	$I.R._{M}$	$F.R._{M}$	$S.B._{M}$	$C.S._{M}$	$P.N._{T}$	$M._{T}$
Ag	µg/L	0.36±0.008	0.39±0.014	0.24±0.008	0.30±0.003	0.17±0.006	0.19±0.005	0.27±0.009	0.35±0.005	0.13±0.001	0.12±0.009
Al	mg/L	0.19±0.02	0.22±0.02	0.11±0.02	0.22±0.07	0.16±0.03	0.21±0.04	0.18±0.03	0.19±0.08	0.22±0.05	0.17±0.03
As	µg/L	0.68±0.06	0.57±0.03	0.46±0.03	0.59±0.02	0.50±0.013	0.45±0.12	0.61±0.16	0.28±0.01	0.21±0.01	0.26±0.02
B	mg/L	4.18±0.39	3.27±0.18	5.28±0.98	3.25±0.17	2. 58±0.55	3.28±0.57	4.12±0.78	3.26±0.25	4.18±0.24	4.18±0.21
Ba	mg/L	0.16±0.05	0.26±0.04	0.16±0.09	0.29±0.08	0.31±0.05	0.11±0.03	0.29±0.01	0.14±0.01	0.17±0.03	0.14±0.06
Be	µg/L	0.068±0.007	0.12±0.02	0.15±0.01	0.06±0.01	0.13±0.02	0.16±0.02	0.057±0.009	0.16±0.007	0.21±0.03	0.18±0.01
Bi	µg/L	1.25±0.11	1.98±0.45	< LoQ	< LoQ	4.15±0.56	2.16±0.15	1.25±0.45	3.98±0.47	< LoQ	1.45±0.12
Ca	mg/L	56.78±3.98	61.89±4.70	41.66±4.05	59.18±5.36	61.83±1.76	26.36±4.03	39.42±3.96	75.36±2.15	78.44±2.96	54.41±3.65
Cd	µg/L	0.32±0.005	0.45±0.002	0.41±0.02	0.24±0.01	0.35±0.06	0.32±0.005	0.23±0.007	1.27±0.02	0.48±0.09	0.58±0.02
Co	µg/L	2.56±0.009	1.38±0.04	2.89±0.02	3.25±0.03	2.15±0.08	1.96±0.58	3.58±1.25	2.03±0.35	2.59±0.26	3.14±0.09
Cr	mg/L	0.010±0.005	0.019±0.003	0.028±0.005	0.010±0.003	0.015±0.009	0.011±0.002	0.010±0.006	0.011±0.001	0.019±0.009	0.029±0.006
Cu	mg/L	0.139±0.01	0.17±0.09	0.026±0.08	0.016±0.004	0.010±0.001	0.029±0.005	0.105±0.001	0.049±0.004	0.98±0.09	0.026±0.005
Fe	mg/L	0.99±0.08	1.16±0.05	0.66±0.08	0.45±0.08	0.93±0.011	1.27±0.045	0.98±0.04	0.63±0.12	0.54±0.08	0.35±0.001
Ga	µg/L	17.02±0.05	14.79±0.14	12.20±0.04	4.06±0.12	2.50±2.14	2.05±0.14	3.06±0.04	4.79±0.04	2.50±1.26	4.78±0.01
Ge	µg/L	0.18±0.15	0.48±0.025	0.34±0.01	0.28±0.11	0.57±0.05	0.14±0.01	0.36±0.01	0.48±0.05	0.56±0.001	0.69±0.005
In	µg/L	7.12±0.04	0.65±0.001	< LoQ	0.35±0.001	0.29±0.004	0.92±0.0008	1.25±0.007	3.15±0.003	0.89±0.004	1.01±0.058
Li	µg/L	14.18±3.59	10.58±0.078	6.35±0.007	29.17±0.004	47.03±0.014	28.89±2.45	31.18±0.004	24.78±0.04	21.14±0.006	23.23±2.09
Mg	mg/L	168.78±5.63	247.16±2.50	103.06±5.89	86.78±2.59	36.59±0.25	121.26±4.79	123.26±5.87	88.91±4.06	52.15±0.26	53.16±2.78
Mn	mg/L	2.45±1.24	0.40±0.001	0.83±0.004	0.55±0.06	0.67±0.002	0.39±0.07	0.73±0.004	0.61±0.004	1.09±0.35	0.33±0.007
Mo	µg/L	8.16±3.46	2.19±0.009	0.98±0.006	1.25±0.004	2.36±0.009	2.57±0.006	1.24±0.08	2.36±0.079	3.56±1.29	6.98±2.49
Na	mg/L	4.16±1.63	5.63±2.89	36.89±16.03	12.15±0.89	11.75±0.009	4.17±0.015	1.16±0.06	3.58±0.009	26.32±11.23	47.96±14.63
Ni	mg/L	0.045±0.009	0.018±0.003	0.036±0.004	0.045±0.006	0.087±0.007	0.054±0.003	0.023±0.004	0.039±0.002	0.062±0.019	0.096±0.032
P	mg/L	187.15±9.66	140.23±9.63	68.15±9.14	136.25±4.89	166.00±7.09	143.63±9.16	87.92±8.16	71.26±4.79	62.30±8.14	79.26±8.15
Pb	µg/L	6.98±1.15	12.36±1.06	18.06±1.26	7.81±1.09	8.14±0.02	7.96±0.06	12.69±0.03	13.25±0.63	18.21±0.21	19.63±2.14
Rb	mg/L	1.98±0.004	2.39±0.003	1.04±0.01	2.80±0.14	1.99±0.004	2.61±0.007	2.48±0.005	1.14±0.001	1.00±0.21	3.28±0.001
S	mg/L	147.06±9.16	98.26±9.32	114.78±5.18	294.18±4.97	196.39±2.79	91.68±4.98	69.63±8.19	126.09±5.89	147.06±0.37	154.39±9.36
Sb	µg/L	0.09±0.01	0.16±0.01	0.25±0.04	0.36±0.01	0.49±0.06	0.32±0.01	0.36±0.004	0.41±0.09	0.32±0.01	0.39±0.02
Se	µg/L	1.46±0.16	1.03±0.01	1.96±0.76	1.06±0.06	2.06±0.06	2.03±0.18	1.22±0.31	1.09±0.02	1.96±0.08	1.29±0.03
Si	mg/L	21.01±3.08	9.58±1.16	9.63±1.02	8.14±0.01	15.86±0.09	12.17±1.24	17.18±0.06	13.25±0.09	14.00±5.78	11.96±2.58
Sn	µg/L	4.08±1.23	1.14±0.01	1.08±0.03	1.14±0.07	2.14±0.005	3.65 ± 1.14	1.55±0.014	1.03±0.007	4.09±0.001	1.21±0.004
Sr	mg/L	0.52±0.002	1.36±0.098	0.99±0.001	0.29±0.01	0.96±0.001	0.58±0.03	0.49±0.002	0.94±0.001	0.32±0.01	0.41±0.001
Te	µg/L	0.36±0.02	0.26±0.001	0.59±0.002	0.58±0.002	0.71±0.21	0.69±0.012	0.21±0.007	0.93±0.11	0.78±0.001	0.23±0.001
Ti	µg/L	2.39±0.19	5.02±1.94	2.03±0.89	4.91±0.01	4.45±0.28	2.14±0.15	3.69±0.01	2.58±1.06	4.91±2.06	4.09±0.23
Tl	µg/L	0.47±0.014	0.89±0.010	0.94±0.011	0.43±0.040	0.80±0.01	0.64±0.01	0.55±0.09	0.59±0.01	0.99±0.54	0.63±0.01
V	µg/L	0.47±0.12	0.91±0.12	0.62±0.02	0.45±0.02	0.58±0.09	0.94±0.21	0.74±0.01	0.46±0.039	0.59±0.023	0.63±0.02
Zn	mg/L	0.51±0.03	0.14±0.01	0.38±0.002	0.69±0.03	0.16±0.066	0.09±0.001	0.39±0.01	0.69±0.001	0.14±0.0015	0.63±0.008

El. – element.

Table 12

Concentration of elements in Romanian wine samples

El.	*Unit*	*F.N.*$_{M}$	*F.R.*$_{I}$	*A.*$_{I}$	*C.*$_{M}$	*I.R.*$_{I}$	*P.G.*$_{I}$	*S.B.*$_{I}$	*M.O.*$_{I}$	*F.N.*$_{I}$	*B.N.*$_{I}$
Ag	µg/L	0.18±0.002	0.23±0.007	0.34±0.003	0.15±0.002	0.27±0.004	0.17±0.006	0.40±0.014	0.34±0.003	0.24±0.008	0.17±0.009
Al	mg/L	0.12±0.03	0.14±0.03	0.15±0.03	0.16±0.02	0.14±0.02	0.16±0.02	0.14±0.2	0.15±0.16	0.16±0.02	0.21±0.03
As	µg/L	0.58±0.01	0.63±0.02	0.47±0.11	0.61±0.14	0.25±0.15	0.36±0.06	0.58±0.16	0.45±0.02	0.36±0.02	0.41±0.14
B	mg/L	3.87±0.87	5.12±0.14	4.78±0.14	3.28±0.97	2.17±0.47	3.57±0.99	4.15±1.02	3.09±0.14	4.15±0.14	3.78±0.09
Ba	mg/L	0.26±0.15	0.32±0.09	0.10±0.05	0.02±0.01	0.12±0.01	0.21±0.01	0.08±0.001	0.14±0.01	0.16±0.07	0.31±0.01
Be	µg/L	0.15±0.01	0.18±0.06	0.36±0.016	0.48±0.05	0.14±0.06	0.16±0.01	0.15±0.002	0.19±0.009	0.26±0.02	0.15±0.01
Bi	µg/L	2.12±2.16	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ
Ca	mg/L	63.15±4.15	68.22±4.06	96.10±4.78	49.14±5.26	51.26±4.09	55.92±4.91	63.36±0.89	65.12±2.18	66.89±1.18	67.49±2.58
Cd	µg/L	0.25±0.02	0.48±0.06	0.23±0.006	1.36±0.05	0.36±0.006	0.29±0.016	0.36±0.45	0.45±0.02	0.26±0.01	0.39±0.04
Co	µg/L	2.99±0.005	1.06±0.51	2.37±0.02	2.89±0.06	3.01±0.13	2.89±0.01	0.85±0.009	0.89±0.56	1.63±0.089	0.56±0.02
Cr	mg/L	0.016±0.006	0.031±0.001	0.025±0.006	0.014±0.006	0.014±0.003	0.016±0.002	0.012±0.002	0.010±0.006	0.017±0.003	0.20±0.006
Cu	mg/L	0.206±0.12	0.132±0.20	0.59±0.21	0.019±0.015	0.029±0.012	0.43±0.15	0.117±0.011	0.89±0.25	0.74±0.06	0.55±0.17
Fe	mg/L	1.05±0.005	0.56±0.04	0.68±0.014	0.76±0.002	1.17±0.05	0.98±0.014	0.54±0.012	0.55±0.01	0.46±0.012	0.59±0.01
Ga	µg/L	17.06±0.04	12.45±0.09	10.12±0.01	4.75±0.01	3.56±0.04	4.78±0.09	2.55±0.01	3.01±0.01	4.45±0.05	11.15±0.07
Ge	µg/L	0.36±0.005	0.48±0.014	0.36±0.074	0.48±0.05	0.63±0.04	0.69±0.07	0.39±0.01	0.09±0.008	0.35±0.07	0.56±0.09
In	µg/L	< LoQ	< LoQ	0.63±0.04	0.78±0.007	0.52±0.007	0.31±0.001	< LoQ	< LoQ	< LoQ	< LoQ
Li	µg/L	4.56±0.54	3.26±0.006	41.56±3.98	21.05±2.54	12.69±2.36	8.98±0.01	14.78±0.005	31.18±7.45	24.48±0.23	21.22±0.91
Mg	mg/L	87.16±4.79	59.06±7.89	63.19±5.28	61.48±6.32	118.16±4.79	75.16±6.89	214.06±12.16	116.16±5.89	84.63±4.79	98.79±8.68
Mn	mg/L	0.61±0.004	0.94±0.36	1.16±0.21	0.89±0.04	0.68±0.06	0.52±0.001	0.37±0.004	0.23±0.002	0.83±0.008	0.67±0.008
Mo	µg/L	0.69±0.006	1.46±0.56	3.89±0.009	2.36±1.25	0.98±0.08	0.43±0.004	0.59±0.006	0.68±0.005	0.79±0.006	0.93±0.007
Na	mg/L	10.66±2.56	4.89±3.26	1.25±0.009	28.06±14.78	6.36±3.16	4.16±0.02	5.89±1.16	6.89±0.063	14.79±6.36	10.56±0.026
Ni	mg/L	0.025±0.03	0.056±0.02	0.025±0.09	0.048±0.06	0.032±0.005	0.018±0.003	0.051±0.012	0.036±0.021	0.048±0.023	0.051±0.001
P	mg/L	123.65±7.16	107.06±4.79	98.56±9.91	63.28±4.79	217.28±15.63	189.36±4.89	162.91±8.15	96.32±4.89	38.99±4.10	113.06±14.79
Pb	µg/L	4.19±0.09	5.18±0.06	9.63±1.14	8.91±0.15	13.63±0.06	18.14±0.09	9.63±0.14	6.61±0.06	14.98±2.68	12.05±0.09
Rb	mg/L	2.88±0.002	1.48±0.02	1.26±0.004	2.79±0.005	2.32±0.04	1.50±0.63	1.24±0.21	2.58±0.001	1.14±0.001	1.23±0.001
S	mg/L	203.69±13.28	148.06±1.96	86.32±6.08	96.02±1.18	259.16±0.18	145.03±1.26	326.77±2.09	231.15±1.98	140.23±9.36	112.06±1.06
Sb	µg/L	0.13±0.03	0.16±0.04	0.29±0.01	0.32±0.01	0.25±0.01	0.19±0.01	0.29±0.02	0.31±0.02	0.21±0.01	0.36±0.05
Se	µg/L	1.98±0.52	2.39±0.04	1.09±0.007	1.33±0.29	1.99±0.69	2.38±0.01	1.53±0.14	1.25±0.03	1.65±0.01	1.98±0.98
Si	mg/L	16.23±4.79	19.91±0.66	12.78±0.40	11.48±0.25	14.78±2.56	11.89±0.23	12.45±0.09	14.17±0.05	9.52±0.067	18.83±0.059
Sn	µg/L	2.14±0.063	1.84±0.001	3.05±0.48	1.14±0.007	2.58±0.001	1.01±0.007	1.14±0.001	17.12±0.89	12.14±0.18	1.10±0.001
Sr	mg/L	0.15±0.009	0.25±0.001	0.98±0.15	1.28±0.51	0.69±0.03	0.54±0.001	0.68±0.001	0.25±0.01	0.63±0.006	1.17±0.59
Te	µg/L	0.63±0.17	0.36±0.01	0.81±0.19	0.53±0.01	0.41±0.02	0.48±0.02	0.27±0.17	0.26±0.12	0.96±0.012	0.01±0.03
Ti	µg/L	3.68±1.02	4.96±0.18	2.49±2.14	3.69±0.01	5.49±0.01	3.21±0.036	2.87±0.07	3.31±0.19	4.91±0.061	3.50±0.24
Tl	µg/L	0.81±0.47	0.52±0.001	0.70±0.03	0.60±0.009	0.81±0.15	0.43±0.001	0.91±0.02	0.68±0.02	0.74±0.001	0.62±0.003
V	µg/L	0.63±0.008	0.59±0.001	0.75±0.021	0.96±0.01	0.63±0.006	0.74±0.002	0.69±0.03	0.83±0.05	0.63±0.04	0.49±0.051
Zn	mg/L	0.26±0.12	0.45±0.005	0.61±0.01	0.59±0.006	0.31±0.01	0.40±0.03	0.65±0.23	0.59±0.03	0.79±0.003	0.18±0.002

El. – element.

Table 13

Concentration of elements in Romanian wine samples

El.	*Unit*	*P.N.*$_{I}$	*C.S.*$_{I}$	*M.*$_{I}$	*B.M.*$_{I}$	*F.A.*$_{S\text{-}A}$	*A.*$_{S\text{-}A}$	*F.R.*$_{S\text{-}A}$	*I.R.*$_{S\text{-}A}$	*S.B.*$_{S\text{-}A}$	*P.G.*$_{S\text{-}A}$
Ag	µg/L	0.25±0.008	0.43±0.004	0.14±0.004	0.27±0.006	0.38±0.005	0.24±0.009	0.31±0.002	0.15±0.005	0.24±0.006	0.21±0.004
Al	mg/L	0.16±0.04	0.22±0.11	0.15±0.2	0.13±0.001	0.15±0.001	0.23±0.001	0.14±0.003	0.12±0.1	0.13±0.01	0.14±0.03
As	µg/L	0.75±0.16	0.64±0.21	0.55±0.11	0.48±0.01	0.26±0.03	0.47±0.04	0.49±0.01	0.53±0.01	0.55±0.09	0.23±0.01
B	mg/L	4.11±0.12	3.78±0.08	4.15±0.47	4.19±0.45	3.14±0.17	2.32±0.14	3.99±1.25	4.18±0.47	3.02±1.089	2.59±0.98
Ba	mg/L	0.15±0.01	0.06±0.01	0.23±0.07	0.31±0.09	0.14±0.03	0.04±0.001	0.14±0.006	0.25±0.04	0.26±0.06	0.13±0.06
Be	µg/L	0.13±0.02	0.16±0.09	0.56±0.16	0.13±0.01	0.16±0.06	0.32±0.06	0.28±0.01	0.39±0.06	0.19±0.06	0.24±0.08
Bi	µg/L	< LoQ	1.25±0.15	2.48±0.16	1.14±0.48	< LoQ	1.12±0.45	< LoQ	1.25±0.14	2.89±0.14	3.12±0.09
Ca	mg/L	45.12±6.39	46.87±2.19	75.16±3.31	42.19±3.78	45.12±9.96	35.16±4.79	32.56±4.78	66.78±4.78	67.79±2.56	45.66±2.89
Cd	µg/L	0.35±0.01	0.28±0.05	0.36±0.01	0.48±0.01	0.59±0.03	0.23±0.01	0.25±0.01	0.36±0.08	0.45±0.01	0.63±0.012
Co	µg/L	2.59±0.06	3.15±0.02	0.96±0.023	1.48±0.61	2.89±0.02	3.80±1.25	2.45±0.02	3.15±0.89	0.36±0.003	0.59±0.05
Cr	mg/L	0.25±0.001	0.28±0.009	0.18±0.01	0.21±0.05	0.31±0.02	0.012±0.002	0.29±0.006	0.31±0.001	0.18±0.002	0.12±0.009
Cu	mg/L	0.065±0.002	0.32±0.15	0.016±0.002	0.032±0.06	0.48±0.96	0.32±0.01	0.25±0.06	0.015±0.03	0.016±0.006	0.20±0.001
Fe	mg/L	0.48±0.005	1.47±0.009	0.56±0.01	0.79±0.04	0.55±0.09	0.68±0.05	0.76±0.01	0.86±0.01	0.79±0.009	0.86±0.008
Ga	µg/L	6.13±0.12	7.48±0.09	12.14±0.04	19.87±0.005	14.00±1.54	5.89±0.04	3.14±0.04	2.11±0.014	3.25±0.04	2.89±0.04
Ge	µg/L	0.56±0.008	0.21±0.01	0.32±0.04	0.45±0.07	0.24±0.04	0.32±0.03	0.18±0.01	0.23±0.04	0.48±0.01	0.53±0.01
In	µg/L	0.56±0.07	0.80±0.01	0.69±0.005	0.74±0.008	1.25±0.07	< LoQ	0.36±0.001	0.49±0.007	0.51±0.09	0.55±0.007
Li	µg/L	21.56±2.47	19.87±0.05	23.56±2.56	21.48±0.79	19.18±2.68	39.21±4.79	21.25±3.68	18.56±0.04	21.55±2.39	21.48±3.01
Mg	mg/L	63.18±4.79	117.06±8.44	235.87±9.58	102.36±4.48	47.15±0.58	30.11±7.18	41.56±6.62	51.79±8.19	47.16±8.18	55.16±2.35
Mn	mg/L	0.30±0.0001	0.49±0.007	1.39±0.32	2.02±0.63	1.58±0.48	0.79±0.006	0.54±0.007	0.36±0.008	1.24±0.008	1.31±2.39
Mo	µg/L	1.26±0.009	0.96±0.008	1.49±0.006	0.38±0.09	0.96±0.005	1.39±0.078	4.56±2.89	2.09±1.39	3.58±1.18	2.19±0.009
Na	mg/L	27.36±2.59	36.69±12.36	13.97±5.58	4.16±0.18	6.25±1.89	6.63±1.47	4.79±0.06	18.16±0.06	19.26±2.36	29.03±3.36
Ni	mg/L	0.029±0.006	0.036±0.008	0.023±0.004	0.024±0.002	0.063±0.006	0.079±0.005	0.082±0.009	0.057±0.023	0.049±0.001	0.059±0.003
P	mg/L	147.03±4.96	119.36±9.36	158.16±7.49	162.30±9.63	132.63±8.16	94.26±9.81	76.03±9.14	95.16±9.76	113.05±8.16	118.06±9.64
Pb	µg/L	17.63±0.05	12.18±0.007	5.01±0.004	9.68±1.04	8.79±0.005	9.01±0.02	8.69±2.36	10.25±0.006	18.05±2.36	9.63±0.09
Rb	mg/L	2.13±0.14	1.49±0.004	2.18±0.01	1.79±0.04	1.23±0.001	2.22±0.09	1.41±0.002	2.13±0.009	1.14±0.18	1.53±0.96
S	mg/L	102.26±9.26	136.06±1.30	328.00±4.15	177.29±4.15	149.03±1.59	248.06±9.16	98.26±6.23	118.16±4.19	123.16±9.14	125.06±6.32
Sb	µg/L	0.18±0.003	0.26±0.01	0.23±0.01	0.29±0.01	0.26±0.08	0.41±0.03	0.26±0.02	0.36±0.01	0.42±0.03	0.45±0.06
Se	µg/L	2.36±1.06	1.25±0.03	1.18±0.12	1.78±0.23	1.24±0.31	1.06±0.05	2.36±0.58	2.14±0.21	1.48±0.51	1.23±0.12
Si	mg/L	21.48±2.58	14.18±2.36	13.25±2.25	10.96±1.38	17.52±0.23	14.05±1.00	14.40±0.25	17.18±1.29	21.46±3.69	25.17±1.89
Sn	µg/L	4.15±1.13	4.98±0.006	1.18±0.001	18.66±4.17	21.11±0.007	9.55±4.47	6.21±2.14	7.14±0.006	2.17±0.008	25.02±0.003
Sr	mg/L	0.52±0.01	0.96±0.01	1.24±0.06	0.96±0.001	1.38±0.04	0.64±0.002	0.14±0.004	1.26±0.001	0.21±0.001	0.79±0.001
Te	µg/L	0.28±0.006	0.39±0.005	0.84±0.01	0.26±0.003	0.48±0.011	0.48±0.99	0.26±0.004	0.84±0.002	0.28±0.001	0.56±0.003
Ti	µg/L	4.63±1.87	2.08±1.02	5.14±0.003	3.28±1.94	4.16±0.87	3.36±1.47	2.59±0.12	3.25±1.98	1.03±0.06	3.98±0.07
Tl	µg/L	0.40±0.12	0.63±0.02	0.87±0.14	0.49±0.03	0.75±0.06	0.63±0.009	0.41±0.001	0.78±0.18	0.61±0.19	0.74±0.001
V	µg/L	0.75±0.36	0.45±0.02	0.64±0.029	0.56±0.02	0.59±0.036	0.63±0.14	0.58±0.002	0.64±0.009	0.58±0.006	0.74±0.01
Zn	mg/L	0.56±0.003	0.36±0.0019	0.49±0.001	0.26±0.10	0.31±0.01	0.43±0.016	0.59±0.01	0.48±0.01	0.62±0.03	0.56±0.09

El. – element.

Table 14

Concentration of elements in Romanian wine samples

El.	*Unit*	*M.O.*$_{S-A}$	*P.G.*$_{S-A}$	*B.G.*$_{S-A}$	*C.*$_{S-A}$	*C.S.*$_{S-A}$	*M.*$_{S-A}$	*F.N.*$_{S-A}$	*B.M.*$_{S-A}$	*P.N.*$_{S-A}$	*B.N.*$_{S-A}$
Ag	µg/L	0.23±0.012	0.20±0.004	0.31±0.009	0.43±0.021	0.18±0.012	0.14±0.009	0.25±0.004	0.38±0.021	0.24±0.008	0.15±0.002
Al	mg/L	0.18±0.01	0.19±0.06	0.12±0.03	0.11±0.03	0.13±0.008	0.16±0.06	0.14±0.01	0.21±0.02	0.18±0.03	0.19±0.02
As	µg/L	0.86±0.19	0.79±0.14	0.65±0.12	0.47±0.16	0.55±0.08	0.63±0.21	0.59±0.16	0.39±0.14	0.56±0.02	0.63±0.04
B	mg/L	6.25±2.17	3.55±0.94	4.55±0.39	6.03±0.26	4.16±0.58	2.79±0.29	3.15±0.47	4.19±0.78	4.65±0.18	3.16±0.87
Ba	mg/L	0.12±0.01	0.10±0.01	0.19±0.01	0.27±0.06	0.03±0.001	0.09±0.01	0.15±0.12	0.19±0.01	0.27±0.06	0.31±0.01
Be	µg/L	0.16±0.003	0.25±0.06	0.42±0.09	0.39±0.01	0.58±0.06	0.69±0.01	0.26±0.18	0.38±0.01	0.42±0.01	0.59±0.06
Bi	µg/L	6.12±1.26	3.89±1.14	2.78±0.89	2.02±0.56	< LoQ	1.45±0.45	1.89±0.78	3.25±0.14	2.89±1.14	1.48±0.59
Ca	mg/L	92.65±2.89	96.54±2.79	66.71±4.72	36.09±4.00	49.58±4.06	58.99±6.69	52.36±2.79	69.58±2.36	71.00±6.32	65.28±6.03
Cd	µg/L	0.32±0.012	0.21±0.01	0.39±0.012	0.45±0.012	0.46±0.99	0.59±0.032	0.69±0.02	0.78±0.021	1.02±0.13	0.57±0.01
Co	µg/L	2.36±0.12	3.69±0.22	4.06±2.22	2.13±0.21	3.98±0.03	1.11±0.09	0.52±0.003	1.82±0.06	2.39±0.03	3.14±0.07
Cr	mg/L	0.12±0.001	0.019±0.008	0.29±0.06	0.36±0.009	0.016±0.002	0.024±0.001	0.010±0.006	0.015±0.007	0.010±0.003	0.17±0.0.5
Cu	mg/L	0.19±0.01	0.29±0.06	0.53±0.11	0.18±0.06	0.128±0.08	0.153±0.58	0.015±0.001	0.36±0.01	0.27±0.12	0.23±0.01
Fe	mg/L	0.72±0.005	0.46±0.004	0.78±0.01	1.62±0.009	0.79±0.004	0.63±0.005	0.49±0.005	0.56±0.009	0.79±0.009	0.81±0.006
Ga	µg/L	2.36±0.05	3.04±0.008	12.48±0.007	11.04±0.001	4.26±0.04	3.56±0.04	2.58±0.004	7.32±0.04	8.56±0.01	4.45±0.04
Ge	µg/L	0.23±0.01	0.18±0.001	0.23±0.007	0.54±0.006	0.30±0.001	0.41±0.001	0.35±0.007	0.28±0.003	0.12±0.01	0.16±0.008
In	µg/L	0.76±0.007	0.53±0.04	< LoQ	< LoQ	< LoQ	1.22±0.58	2.05±0.01	1.23±0.005	0.54±0.001	0.69±0.05
Li	µg/L	14.06±2.15	9.89±1.25	14.79±2.26	26.79±2.48	34.19±5.89	21.47±0.01	36.89±5.78	23.26±0.04	56.89±2.59	61.57±5.87
Mg	mg/L	28.89±2.56	74.59±3.69	65.89±7.18	116.32±8.19	12.17±0.06	49.33±4.48	51.06±4.03	215.08±4.89	217.16±4.18	145.06±12.30
Mn	mg/L	0.63±0.005	1.68±5.89	1.15±4.26	0.79±0.009	0.55±0.012	0.94±0.36	0.99±0.006	0.76±0.005	0.56±0.006	0.23±0.009
Mo	µg/L	2.58±1.06	0.99±0.48	0.91±0.001	1.43±0.14	1.89±0.006	2.47±0.009	2.17±0.006	6.35±0.04	5.89±0.006	2.14±0.96
Na	mg/L	6.32±1.29	7.26±3.28	46.08±6.89	32.58±4.19	31.22±4.62	21.15±9.65	3.58±2.17	8.16±1.96	2.26±2.18	3.62±1.14
Ni	mg/L	0.026±0.001	0.036±0.005	0.089±0.006	0.013±0.006	0.016±0.003	0.049±0.007	0.051±0.003	0.028±0.009	0.036±0.005	0.048±0.005
P	mg/L	113.02±8.46	96.32±8.79	271.56±21.16	89.36±4.05	91.08±8.91	126.03±9.48	214.79±4.69	189.13±9.18	147.34±9.18	68.94±9.88
Pb	µg/L	6.00±0.006	9.14±1.17	9.18±2.06	14.91±0.03	4.79±0.002	14.09±2.05	4.98±0.14	8.46±0.25	9.63±0.009	14.10±3.67
Rb	mg/L	2.63±1.03	1.27±0.006	2.22±1.39	1.24±0.005	1.63±0.28	1.59±0.05	1.48±0.12	1.96±1.29	2.36±0.09	1.48±0.01
S	mg/L	63.16±4.06	78.19±9.01	321.06±9.16	254.06±1.06	214.79±2.16	147.06±6.32	102.32±4.16	258.94±3.06	214.19±9.16	217.16±6.13
Sb	µg/L	1.25±0.69	0.87±0.01	0.59±0.06	0.63±0.01	0.12±0.01	0.42±0.06	0.56±0.08	0.31±0.01	0.49±0.01	0.52±0.01
Se	µg/L	2.14±0.02	1.03±0.01	1.49±0.02	1.14±0.01	1.00±0.03	1.54±0.01	2.78±0.59	1.61±0.023	1.18±0.02	1.17±0.03
Si	mg/L	21.14±3.96	9.60±0.45	14.06±2.14	18.19±1.11	19.48±2.49	14.56±2.39	11.23±2.17	9.69±1.45	19.25±5.23	22.48±6.31
Sn	µg/L	2.05±1.02	1.68±0.005	15.02±4.18	11.95±1.02	6.32±0.001	14.98±0.006	1.02±0.047	5.32±0.65	4.12±0.01	1.32±0.005
Sr	mg/L	0.47±0.004	0.47±0.063	0.87±0.001	0.54±0.011	1.47±0.001	0.48±0.03	0.25±0.009	0.14±0.006	0.89±0.002	0.45±0.001
Te	µg/L	0.24±0.003	0.39±0.01	0.48±0.01	0.56±0.01	0.89±0.01	0.59±0.01	0.15±0.01	0.89±0.01	0.65±0.01	0.46±0.01
Ti	µg/L	3.65±1.89	5.17±3.02	2.11±0.91	3.56±0.001	2.88±0.073	1.19±0.07	1.58±0.59	2.36±0.18	2.31±0.08	4.89±0.16
Tl	µg/L	0.61±0.11	0.84±0.29	0.90±0.17	0.26±0.003	0.49±0.01	0.53±0.01	0.69±0.01	0.78±0.016	0.63±0.01	0.64±0.12
V	µg/L	0.59±0.03	0.16±0.05	0.63±0.01	0.36±0.07	0.45±0.012	0.39±0.03	0.69±0.03	0.71±0.021	0.63±0.01	0.44±0.09
Zn	mg/L	0.64±0.01	0.59±0.01	0.36±0.091	0.44±0.011	0.12±0.003	0.78±0.01	0.62±0.0033	0.87±0.019	0.23±0.09	0.42±0.36

El. – element.

The behavior of Li in wine resembles that of alkaline-earth metals and particularly the one of Mg. When aging the bottled wine a reducing environmental is created, causing the Li to be expelled out of the wine.

The concentration of trace elements (In, Sr, Tl, U, Rb, Se, Zn, Ag, Al, Be, Ba, Cr, Cs and Ga) found in Romanian wines agreed with literature data (Kment et al 2005; Fiket et al 2011, Ivanova-Petropulos et al 2013; Geana et al 2013). The results indicated that Romania red wines are moderately rich in In, Ni, Sr, Rb, Se, Tl, U, Zn, Ag, Al, Be, Bi, Ba, Cr, Cs and Ga while white wines are moderately rich In, Sr, Zn, Al, Be, Bi and Ba.

Regarding the concentration of toxic elements (Pb, As, Cd) found in Romanian wines agreed with literature data (Avram et al 2014; Đurđic et al 2017). The As concentration was higher than in published data (Kment et al 2005; Lara et al 2005; Iglesias et al 2007; Fiket et al 2011; Alkiș et al 2014), while the Pb concentration was lower than that in Czech (Kment et al 2005) and Romanian wines (Geana et al 2013).

The higher concentration of some elements may be due to viticultural practices, the use of fertilizers for cultivation of vine (Cu, Ca, K) the winemaking process or addition of substances for wine clearing as bentonite (Fe, Ca, Na). Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analyzed wine samples were below the maximum permissible limits (MPL), respectively as published by the Organization of Vine and Wine (OIV 2016).

Conclusions. Fast and accurate method for sample preparation followed with ICP-MS for multi-element analysis of wine was optimized and developed. The method resented satisfactory linearly LoQ, LoD, accuracy, repeatability and reproducibility for 35 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V and Zn). In this study the characterization of Romanian wines according to their elemental composition was performed. Potassium, magnesium and calcium were the most abundant elements in all investigated wine samples. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in the analyzed wine samples were below the MPL.

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