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Mineral element content of some Georgian wines

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A B S T R A C T

The purpose of this study was to determine mineral element composition in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. All sample wines are made from grapes variety grown in Adjara region and were from 2015 to 2017 vintages. Plasma-atomic emission spectrometer ICPE-9820 has been used for qualitative and quantitative determination of the elements in the required concentration range, because of a high sensitivity, a wide dynamic range and a high sample throughput of this spectrometer. The ICPE-9820 provides axial view plasma observation in a direction coaxial to the plasma, and in addition to axial view, provides radial view plasma observation in the perpendicular direction. This dual view capability allows measurements to switch automatically between high-sensitivity axial view and high-accuracy radial view, enabling analysis of elements across a broad concentration range with a single method. In this study, sixteen mineral elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) were analyzed. The analysis was performed by diluting wine samples 10 times with deionized water, without any prior preparation, followed by sequential determination of the elements by ICPE. The higher concentrations were noted for major elements as follows: potassium, magnesium, calcium, sodium and iron. The lowest concentrations were noted for minor elements: manganese, aluminium, barium, zinc and copper. Such trace elements as nickel, chromium and lithium were found under the limit of quantitation. Plumbum, cadmium and cobalt were under the limit of detection. Analyzing concentration levels of elemental composition, it can be concluded that depending on the color of the wine, the content of the individual element was different. Data obtained showed that none of the wine samples surpassed the toxic levels reported for metals in the literature and were within the allowed metals levels in wines for human consumption.

Keywords: major elements, minor elements, concentration, multielement analysis, wine, ICPE-9820.

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Introduction

Georgia is one of the oldest winemaking nations in the world and by some experts even considered as the birth-place of wine. This is supported by 8000 years old archeological findings of grape-stones inside antique clay pots. In Georgia the conditions are well suited for winemaking, as the climate is moderate and extreme weather conditions are rare. The summers are not too hot and the winters are mild. Also, the surrounding mountains are full of natural springs, with rivers providing mineral-rich waters into the valleys. Nowadays, approximately 530 native Georgian sorts of grapes are known. More than 425 sorts are preserved today and are kept is special nurseries. 30-35 sort of Georgian grapes are used today in wine production [1].

A lot of scientific researches have been conducted to confirm that the moderate consumption of wine improves good health and longevity when it is combined with a balanced diet [2]. Wine is a complex matrix and it contains low level concentration of mineral elements. Determination of the mineral element content of wines is important for many reasons. Firstly, the concentration of elements in wine is useful information to vine grower and oenologists for controlling the process of obtaining high and quality wines, also the element content could be used as a wine fingerprint and represents one of the criteria for evaluating the authenticity of wine [3,4]. Secondly, their content should be determined and controlled, because excess is undesirable, and in some cases prohibited, due to potential toxicity. In addition, the wine industry does not require control of the metal content in wine, thus, the knowledge of their content in this alcoholic beverage is very important [5-7].The level of the major elements (Ca, K, Na, Mg and Fe) that are related to the grape variety and maturity, type of soil in the vineyard, and ecoclimatic conditions, usually ranges between 10 and 1000 mg/L. The minor elements (Al, Cu, Mn, Ba, and Zn) depends on external impurities during the growth of grapes and vinicultural and winemaking practices, are present in the range of 0.1 to 10 mg/L. Trace elements (Cd, Co, Cr, Ni, Li and Pb) are in the range of 0.1-1000 μg/L [8]. Some factors, such as application of fungicides, pesticides and fertilizers during the growing season, can lead to an increase these elements in wine [9-11]. The allowed levels of metal in wines are prescribed by the International Organization of Vine and Wine (OIV) [12].

The goal of this study is to measure and analyze the mineral components in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. Inductively coupled plasma-atomic emission spectrometer (ICPE-9820) was used for qualitative and quantitative determination of mineral elements in wine samples [13].

Materials and Methods

Three samples of wines, including one sample of red wine (Aladasturi), one sample of rose wine (Chkhaveri) and one sample of white wine (Tsolikouri) were analyzed. All sample wines are made from grapes variety grown in Adjara region and were from 2015 to 2017 vintages. Aladasturi is dry red wine made from Aladasturi grapes, cultivated in Western Georgia. Wine has pomegranate color and is characterized with distinctive bouquet and harmonious taste. Chkhaveri is dry rose wine made from rare Georgian grape variety – Chkhaveri, harvested in mountainous area of Adjara region. Chkhaveri is described as light and pleasant wine in “Ampelography of Georgia” – a book issued in 1960, being one of the most valuable books in Georgian winemaking. Nowadays, wine professionals and winemakers fairly think that such interpretation is not sufficient and Chkhaveri varietal needs further observation and research. Tsolikouri, dry white wine, has been manufactured since 1890. The wine made from grapes variety of the same name cultivated in Western Georgia. Tsolikouri is of pale-straw colour and has strong bouquet, at fresh harmonious taste. The alcohol in each wine samples ranges from 10 to 12.5%vol, sugar - from 18 to 22% and titratable acidity - from 7 to 9‰ [1].

For the determination of elemental composition of wines, it is required to properly prepare the samples. Taking into consideration that wine is a complex water-ethanol mixture, containing various inorganic and organic substances at different levels, the sample preparation stage is very important in the analysis of particular wine components. The wine samples have been simply diluted 10 times with deionized water, without any prior preparation. It was sufficient for the elimination of matrix effects, especially the amount of salts and organic components introduced into the ICP plasma. Lower dilution factors significantly hindered determination of elements in wine samples. The similar observation was found in the study of wine analysis by A.Gonzálvez [14]. The containers used for storage or treatment of the samples were cleaned to avoid contamination with any metals. The containers were treated with nitric acid and washed with deionized water [14,15].

The ICPE-9820 spectrometer (Shimadzu, Japan) was used for the analysis of sixteen elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) in selected wine samples.

The Shimadzu ICPE-9820 is a simultaneous spectrometer with CCD (charge-coupled device) detector, which has been used for all determinations. The ICPE-9820 provides axial view plasma observation in a direction coaxial to the plasma, and the radial view plasma observation in the perpendicular direction. This dual view capability allows measurements to switch automatically between high-sensitivity axial view and high-accuracy radial view, enabling analysis of elements across a broad concentration range with a single method. This series features Shimadzu’s mini-torch system and Eco mode, which reduces argon gas consumption and power consumption during measurement standby by approximately half in comparison to previous models. Furthermore, performance is ensured even with 99.95 % pure argon gas, not the 99.999 %, or purer gas generally used for ICP systems which helps to reduce operating costs. In addition, a vertically-oriented torch reduces memory effects and shortens rinse time. The adoption of this torch and vacuum spectrometer enables highly stable, high-throughput analysis. ICPE solution control software features intuitive operation for easy creation and optimization of complicated methods, allowing for a smooth analysis process from the start [14,16,17]. Table 1 shows a summary of the system parameters and the analytical lines for each element are shown in table 2.

For spectrometry measurements, series of calibration solutions with proper concentrations were made. For calibration solution preparations following standards (Sigma-Aldrich, Switzerland) were used:

-Multielement Standard Solution 6 for ICP, 100mg/L each element in 5% HNO_3;

-Internal Yttrium Standard (Y) for ICP, 1001 mg/L±4mg/L in 2% HNO_3.

1% HNO_3 was used to prepare calibration standards immediately before usage. Concentrations of calibrations were from 5μg/L to 5 mg/L for every element and 0.1mg/L for an internal yttrium standard.

Deionized water with the maximum resistivity of 18.2 MΩ/cm obtained from the Purity Labwater system D340 (Oxfordshire, United Kingdom) were used for sample pretreatment and dilution. All the solutions were prepared in high-density polyethylene containers and were of analytical reagent grade [14].

Table 1. *ICPE-9820 instrumental parameters for determination of elements in wine*

Parameters	Setting
Radio frequency power	1.20 kW
Gas Type	Argon
Argon	6 L/min
Gas purity	99.95%
Auxiliary gas	0.60 L/min
Plasma gas	7.00 L/min
Carrier gas	0.70 L/min
Nebulizer	Coaxial
Plasma observation	Axial/Radial
Detector	CCD (charge coupled device)
Spectral range	167 – 800 nm
Exposure time	15 sec.
Attached Instrument	Mini-torch

Table 2. *The analytical lines for determination of each element*

Elements	Detection wavelength (λ/nm)
Aluminium	396.153
Barium	455.403
Calcium	315.887
Copper	327.396
Iron	259.940
Potassium	766.490
Magnesium	383.231
Manganese	344.297
Sodium	589.592
Zinc	213.856
Nickel	231.604
Plumbum	220.353
Cadmium	226.502
Cobalt	237.862
Chromium	206.149
Lithium	610.364

Result and discussion

This research was intended to characterize the wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region and made from different types of grapes, in terms of metals content. Sixteen elements were analyzed by plasma-atomic emission spectrometer (ICPE-9820). The method proposed is simple and sensitive, allowing the adequate and simultaneous determination of major and minor elements by ICPE. Depending on the elements, their quantity varied in wine from μg/L to mg/L. It needs to be noted that all metals content in the analyzed wine samples was much smaller than the maximum concentrations permitted according to the OIV [12].

Major elements like potassium, magnesium, calcium, sodium and iron were abundant in our wine samples (Table 3). The concentration levels of these elements in our study were close to the values found in other researches [18,19,20,21].

Potassium exhibited higher concentrations (255 to 425 mg/L) than the rest of the elements in our wine samples. The highest level of K (425 mg/L) was detected in the white wine (Tsolikouri). Potassium is the main positive ion in wine. A number of factors affect the amount of potassium in wine, including the variety of grapes, soil and climatic conditions, time of harvest, the temperature of fermentation and storage, and the pH and he use of ion-exchange resins. The high level of potassium in wine has great nutritional values.

Magnesium was detected in concentrations between 77.2 mg/L to 110 mg/L in our wines. Red wine (Aladasturi) contents higher concentration of magnesium (110 mg/L). Magnesium content in wines correlates with the natural Mg content of grapes, its content also can be attributed to a number of factors including the soil composition, pH, the time and temperature of storage, and the rate of pressing.

Calcium, sodium and iron were 57.7 to 80 mg/L, 1.77 to 5.51 mg/L, 1.43 to 4.26 mg/L, respectively, in wine samples. High concentration levels of these elements were in rose wine sample (Chkhaveri). Vineyard soil is a natural source of calcium in musts, however, wines with a calcium level above 80 mg/L are considered to be at risk of instability. However, calcium leads to no problems under normal circumstances, and the fining process can be a pathway for calcium entry in wine. Sodium is the main extracellular cation. It participates in the maintenance of the acid-base balance and in osmotic regulation. This principal component can be related to soil composition and winemaking process. Iron play an important role in chemical processes with acetaldehyde, it catalyzes acetaldehyde combination with phenol compounds.

Minor elements such as manganese, aluminium, barium, copper and zinc were found in lowest concentrations (0.48 to 1.07 mg/L, 0.42 to 1.22 mg/L, 0.42 to 0.57 mg/L, 0.14 to 0.46 mg/L, and 0.14 to 0.38 mg/L, respectively) that were under Maximum Permissible Limits (MPL). The results revealed the trace elements concentration such as nickel, chromium, lithium to be extremely low, under the limit of quantitation (ULOQ) (<0.0105μg/L, <0.0162μg/L, <0.0792μg/L, respectively) in our wines. Plumbum, cadmium and cobalt were under the limit of detection (ULOD) (Table 3). This can be explained by the limited industrialization in the area grapes were cultivated.

Figures 1-5 demonstrate the calibration curves of major and minor elements (K, Mg, Ca, Na, Fe, Mn, Al, Ba, Zn and Cu). The calculated calibration curves show good linearity range for all tested analytes with coefficient of determination in the range from 0.974 to 0.999; limit of quantity (LOQ) and the limit of detection (LOD) for each element were obtained.

Figures 6-9 show the spectral lines of major and minor elements in selected wines (Aladasuri, Chkhaveri and Tsolikouri).

The results of quantitative analysis of elemental concentrations in different wine samples determined by ICPE-9820 are listed in Table 3.

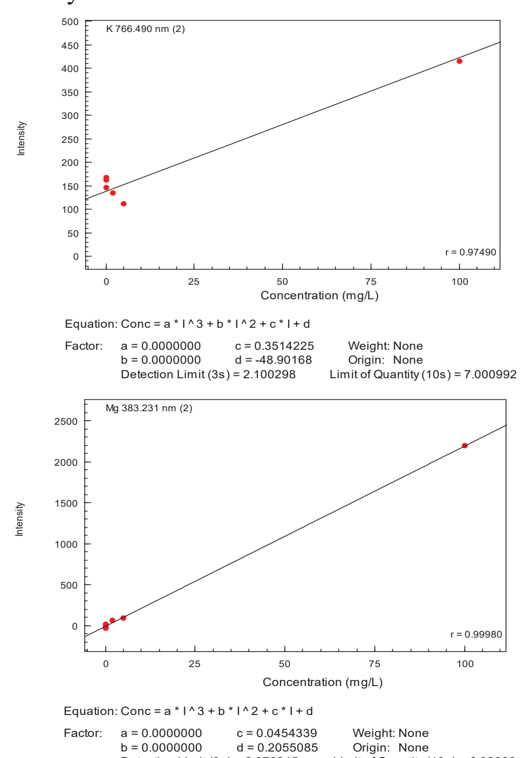
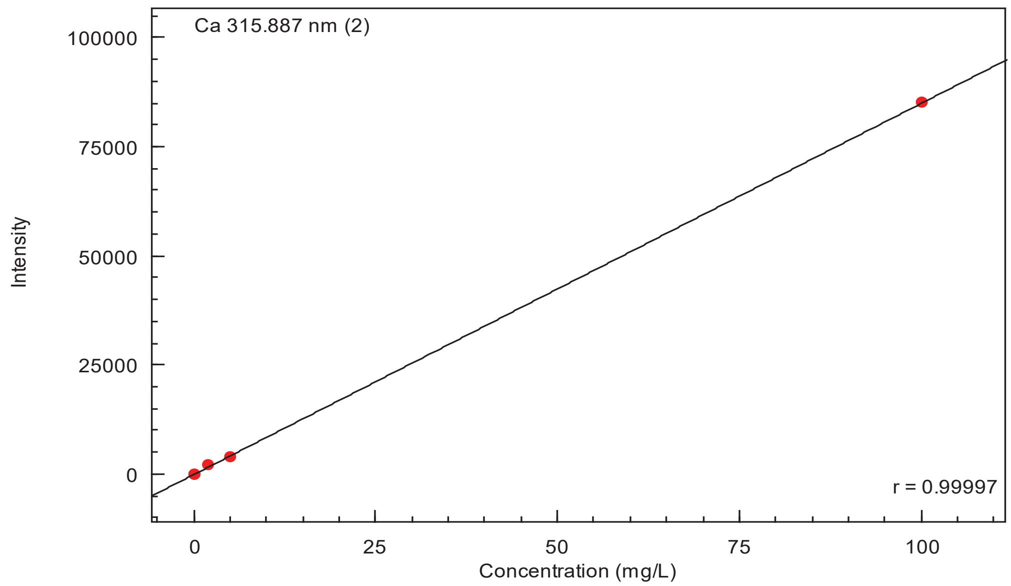
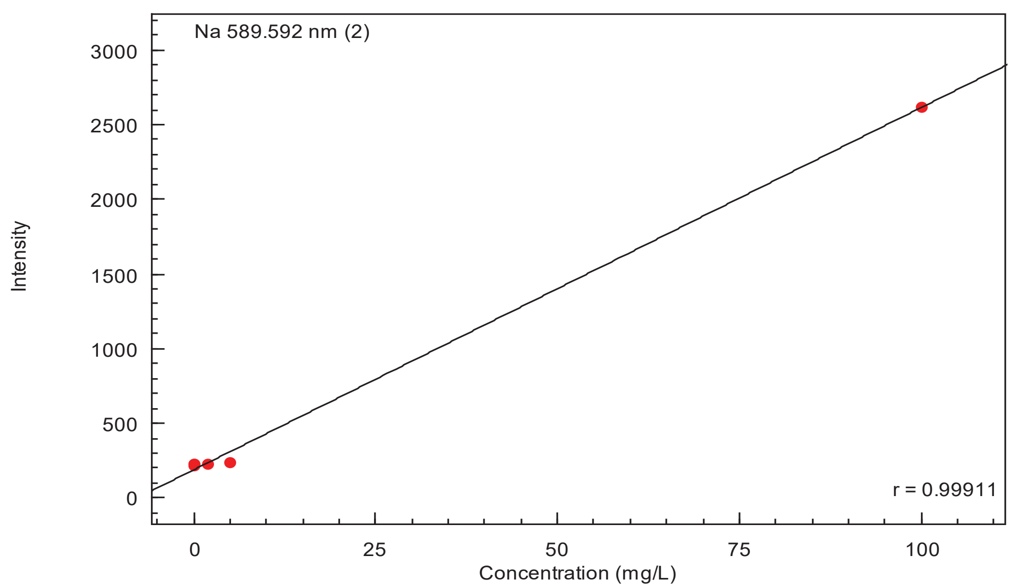


Fig. 1. *The calibration curves of major and minor elements*



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

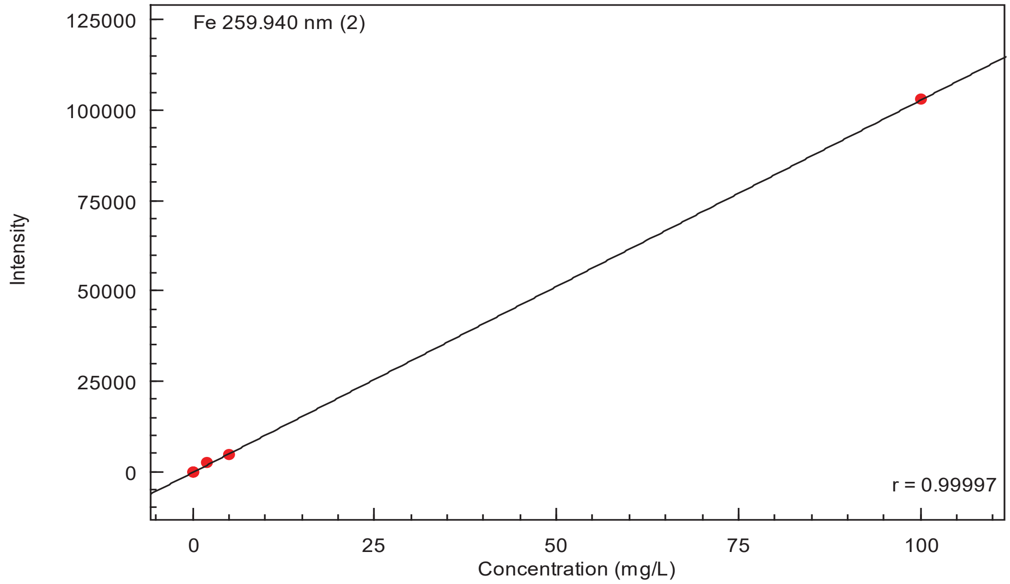
Factor: a = 0.0000000 c = 0.0011753 Weight: None
b = 0.0000000 d = -0.0402528 Origin: None
Detection Limit (3s) = 0.0595058 Limit of Quantity (10s) = 0.1983526



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

Factor: a = 0.0000000 c = 0.0411979 Weight: None
b = 0.0000000 d = -7.969392 Origin: None
Detection Limit (3s) = 2.088058 Limit of Quantity (10s) = 6.960195

Fig. 2. *The calibration curves of major and minor elements*



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

Factor: a = 0.0000000 c = 9.712104e-004 Weight: None
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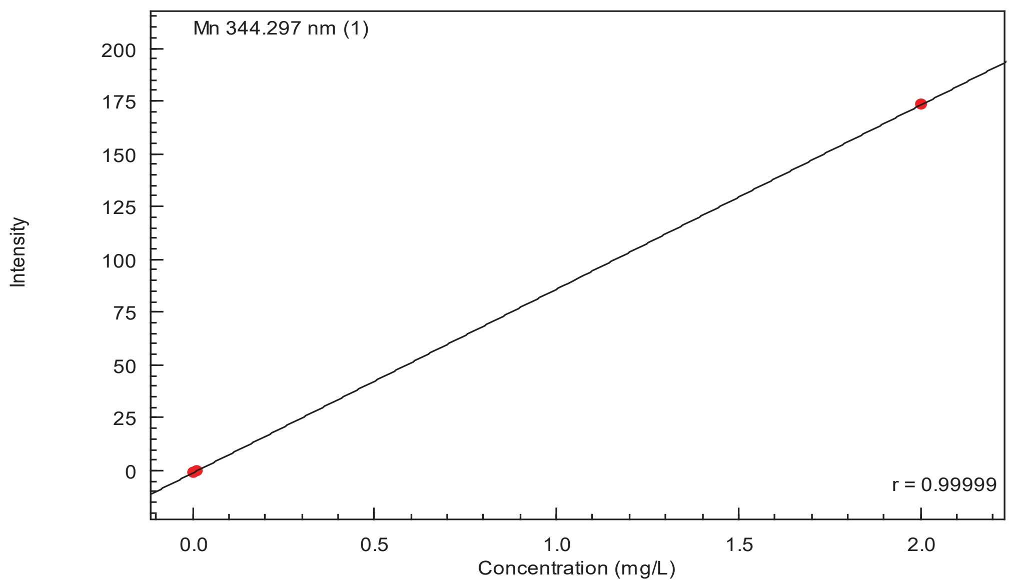
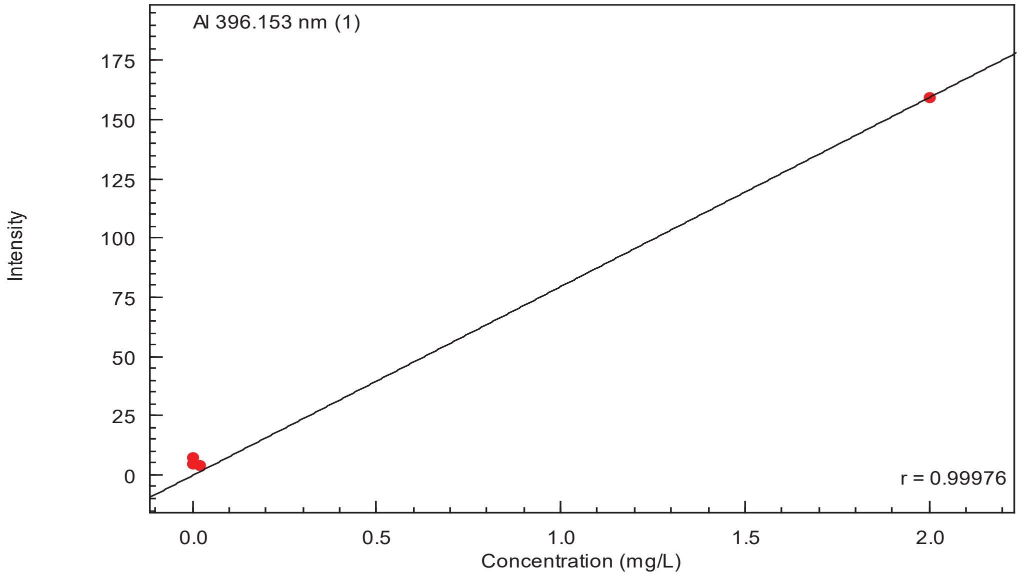


Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

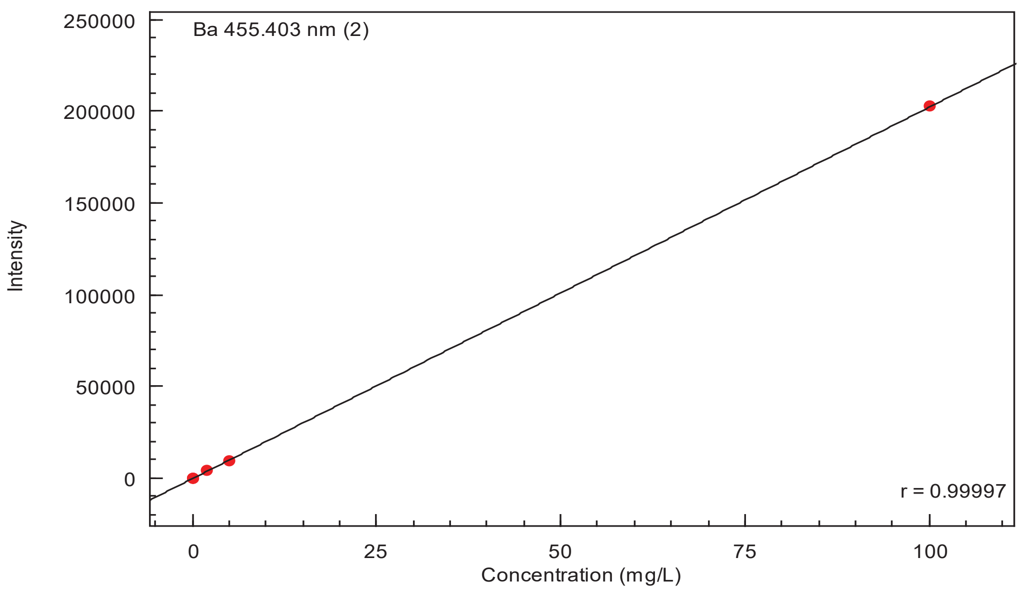
Factor: a = 0.0000000 c = 0.0114759 Weight: None
b = 0.0000000 d = 0.0100922 Origin: None
Detection Limit (3s) = 8.859409e-004 Limit of Quantity (10s) = 0.0029531

Fig. 3. *The calibration curves of major and minor elements*



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

Factor: a = 0.0000000 c = 0.0125266 Weight: None
b = 0.0000000 d = 0.0000000 Origin: Passed
Detection Limit (3s) = 0.0350671 Limit of Quantity (10s) = 0.1168905



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

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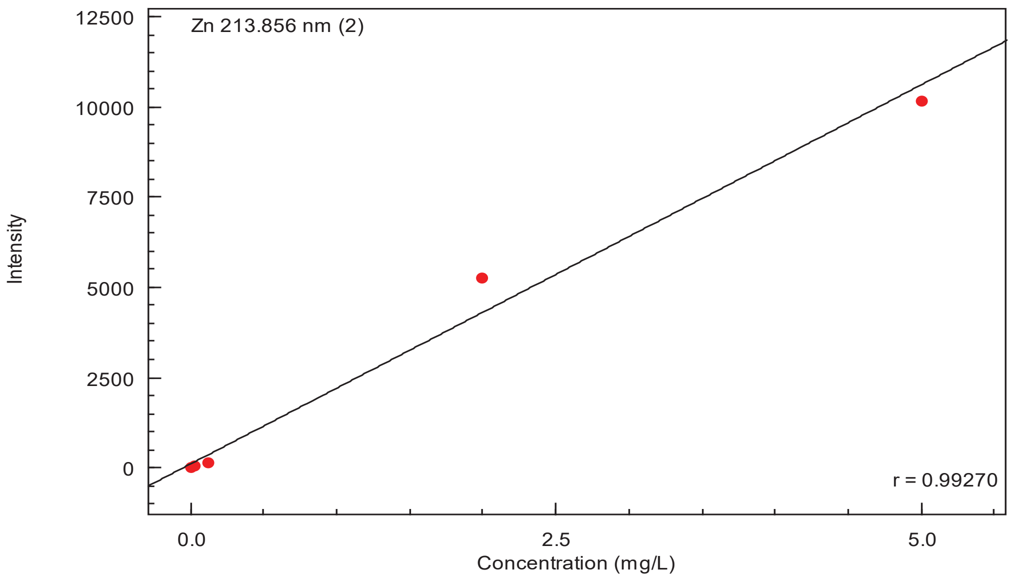
Detection Limit (3s) = 0.0277817 Limit of Quantity (10s) = 0.0926056

Fig. 4. *The calibration curves of major and minor elements*



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

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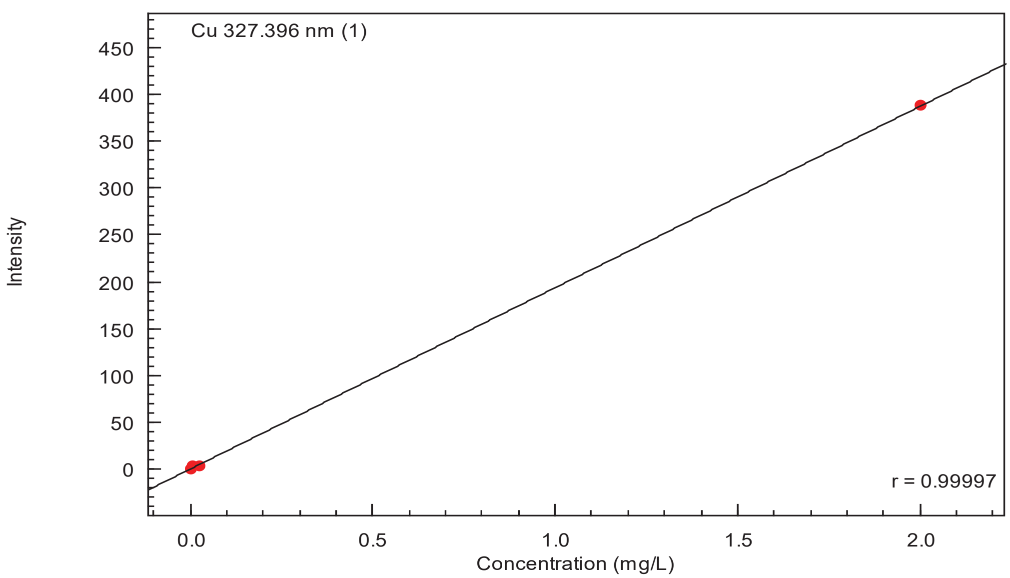
Detection Limit (3s) = 0.0092475 Limit of Quantity (10s) = 0.0308248



Equation: Conc = a * I ^ 3 + b * I ^ 2 + c * I + d

Factor: a = 0.0000000 c = 0.0051703 Weight: None
b = 0.0000000 d = -0.0047623 Origin: None
Detection Limit (3s) = 6.711194e-004 Limit of Quantity (10s) = 0.0022371

Fig. 5. *The calibration curves of major and minor elements*

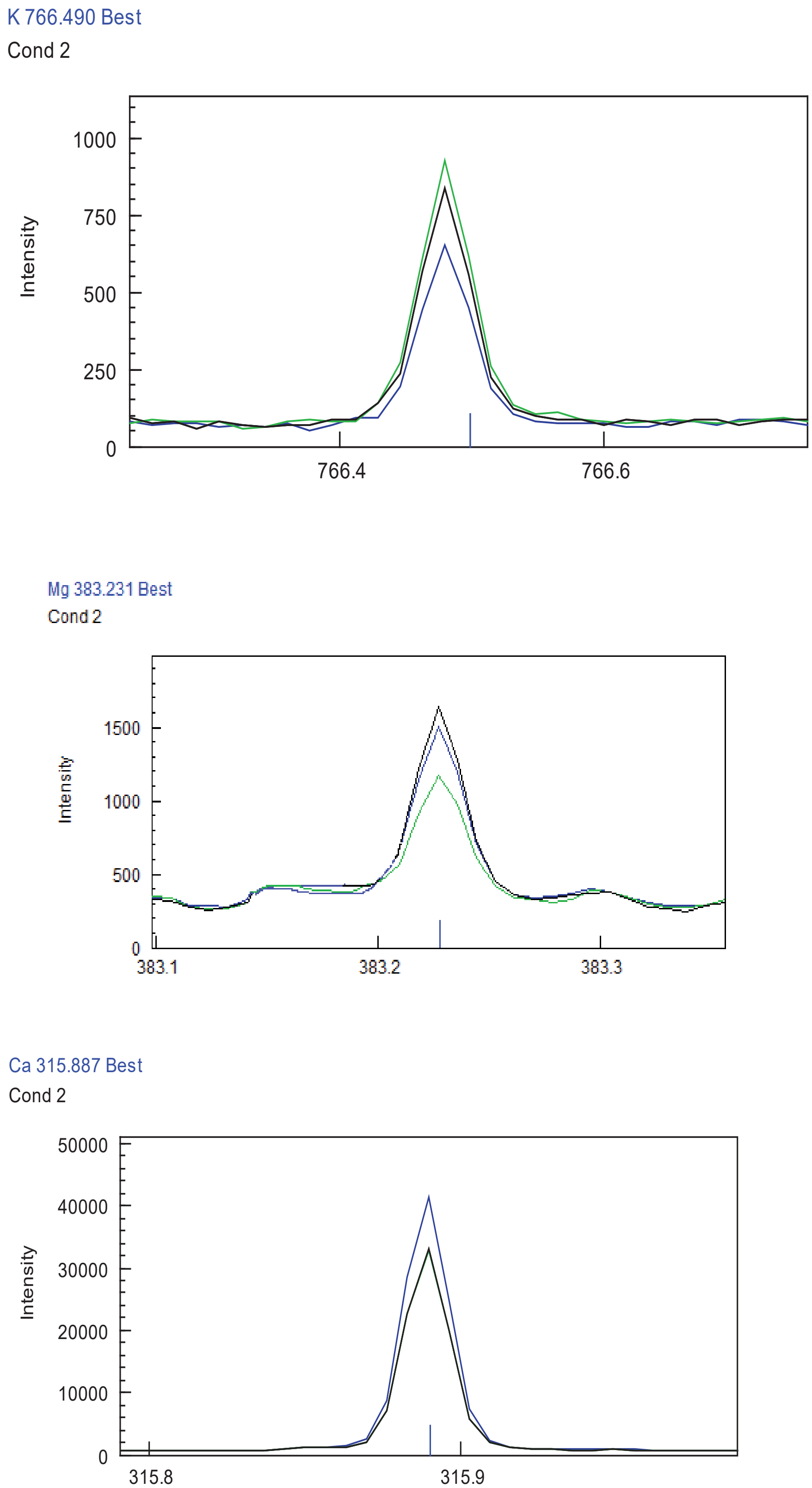


Fig. 6. *The spectral lines of major and minor elements in wine samples (Aladasturi, Chkhaveri, Tsolikouri)*

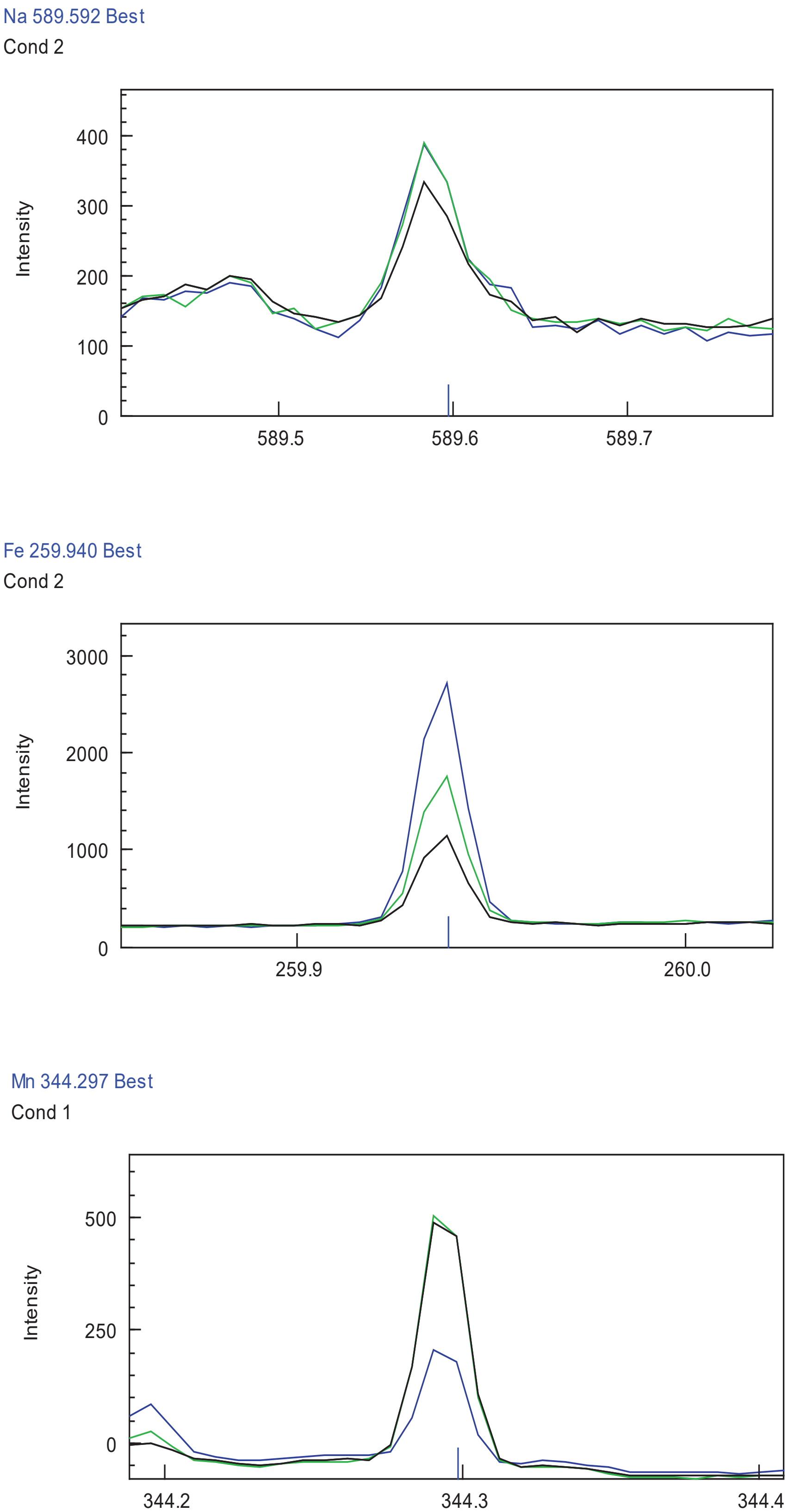


Fig. 7. *The spectral lines of major and minor elements in wine samples (Aladasturi, Chkhaveri, Tsolikouri)*

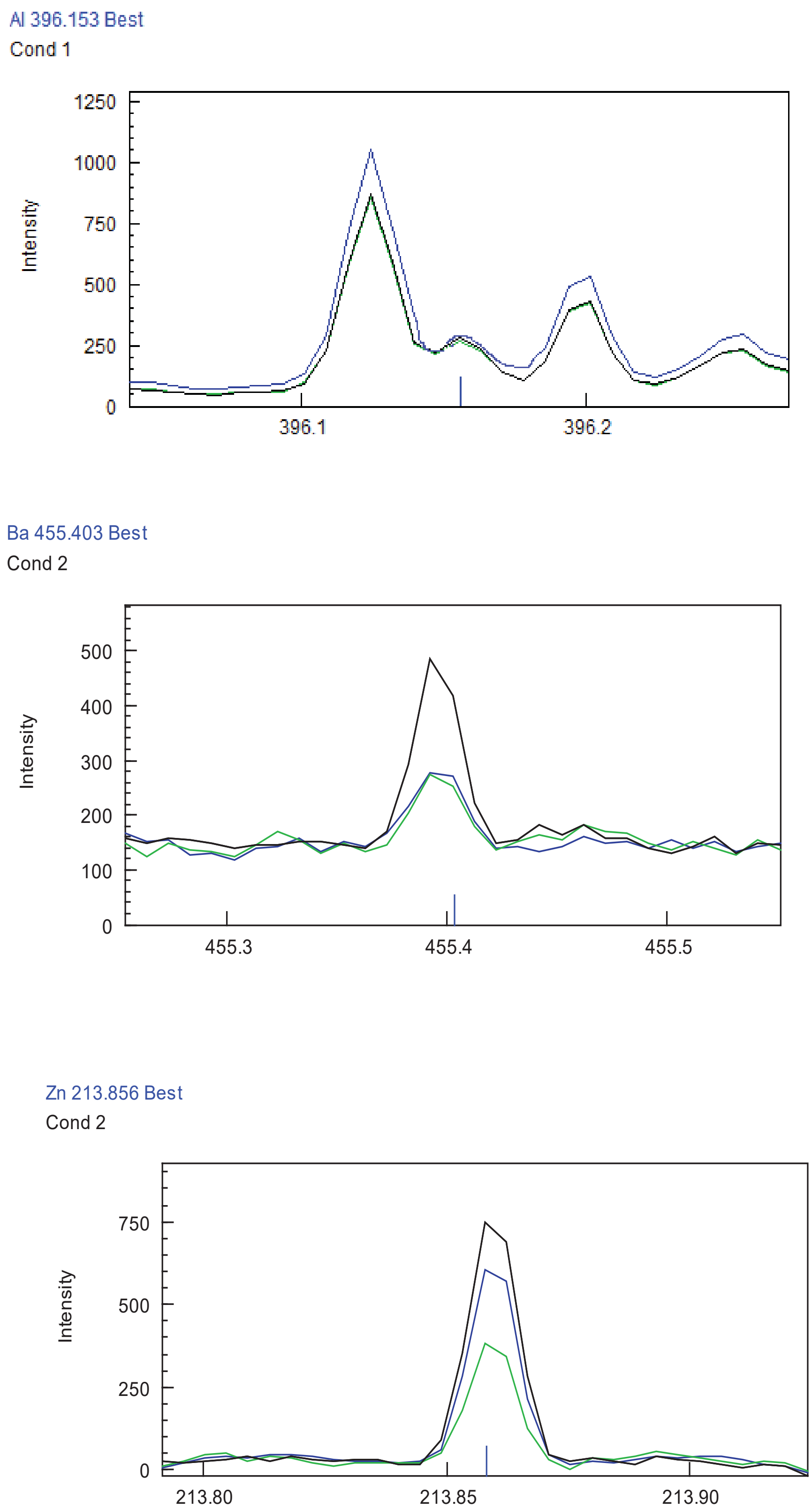


Fig. 8. *The spectral lines of major and minor elements in wine samples (Aladasturi, Chkhaveri, Tsolikouri)*

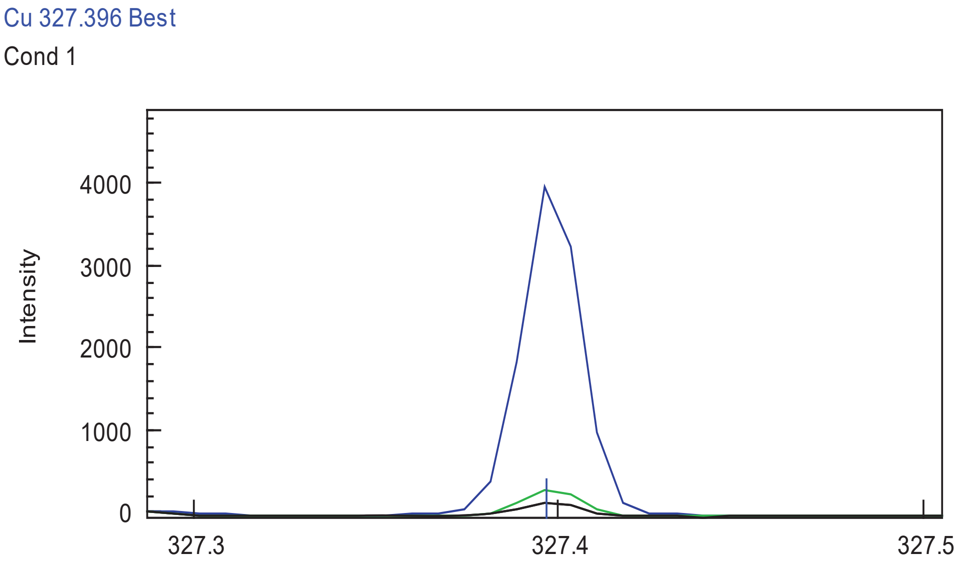


Fig. 9. *The spectral lines of major and minor elements in wine samples (Aladasturi, Chkhaveri, Tsolikouri)*

Table 3. *Element content of wine samples*

№	Element	Aladasturi (red wine)	Chkhaveri (rose wine)	Tsolikouri (white wine)
		Concentration (mg/L)		
1	Al	0.45	1.22	0.42
2	Ba	0.42	0.43	0.57
3	Ca	57.7	80.0	64.1
4	Cu	0.14	0.46	0.17
5	Fe	1.43	4.26	2.63
6	K	318	255	425
7	Mg	110	101	77.2
8	Mn	1.06	0.48	1.07
9	Na	1.77	5.51	5.35
10	Zn	0.38	0.33	0.14
		Concentration (µg/L)		
11	Ni	<0.0524	<0.0105	<0.0496
12	Pb	ULOD	ULOD	ULOD
13	Cd	ULOD	ULOD	ULOD
14	Co	ULOD	ULOD	ULOD
15	Cr	<0.0162	<0.0172	<0.0243
16	Li	<0.0792	<0.1250	<0.0938

ULOD –under the limit of detection

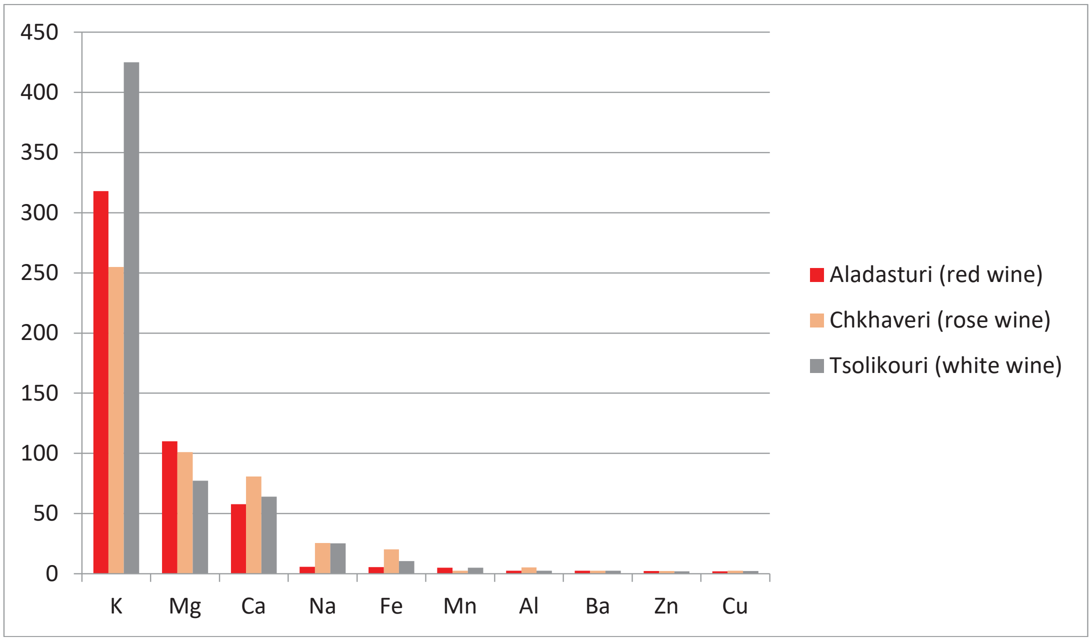


Fig.10. *Results for element concentration in the wine samples (in mg/L)*

Figure 10 clearly shows the ratio of major and minor elements in determined wines.

If relative abundances of the mineral elements in Aladasturi are compared, the tendency at the ranking is as follows: K>Mg>Ca>Na>Fe>Mn>Al>Ba>Zn>Cu;

in Chkhaveri –

K>Mg>Ca>Na>Fe>Al>Mn>Cu>Ba>Zn;

in Tsolikouri –

K>Mg>Ca>Na>Fe>Mn>Ba>Al>Cu>Zn.

These relations are similar in all selected wines: K>Mg>Ca>Na>Fe.

The following general conclusions can be made from data in Table 3:

-Magnesium and zinc content of red wine is higher than those of rose and white wines;

-Calcium, sodium, iron, aluminium and copper content of rose wine is higher than those of red and white wines;

-Potassium, manganese and barium content of white wine is higher than those of red and rose wines.

Analyzing concentration levels of determined mineral elements, it can be concluded that depending on the color of the wine, the content of the individual element is different.

Based on the amount of concentration in wine, the elements were classified into four categories:

- K, Mg, Ca, Na and Fe – elements in the high concentrations;
- Mn, Al, Ba, Zn and Cu - elements in the low concentrations;
- Ni, Cr and Li - under the limit of quantitation;
- Pb, Cd and Co - under the limit of detection.

Conclusion

Inductively coupled plasma-atomic emission spectrometer (ICPE-9820) has been used for qualitative and quantitative determination of sixteen mineral elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Zn, Ni, Pb, Cd, Co, Cr and Li) in three selected wine samples (Aladasturi, Chkhaveri and Tsolikouri) produced in Adjara region of Western Georgia. The results show that ICPE-9820 is preferable for elemental determination in wine, for its fastness and simplicity of analysis. Moreover, multielement analysis using this spectrometer requires little sample preparation and gives good precision analysis with low detection limits.

Potassium, magnesium, calcium, sodium and iron quantitatively dominate in all determined wine samples. Manganese, aluminium, barium, zinc and copper have been under Maximum Permissible Limits (MPL). A remarkable finding of this study was that in all wine samples the heavy metals nickel, chromium and lithium have been under the limit of quantitation. Plumbum, cadmium and cobalt have been under the limit of detection. The established content of metals showed that none of our wine samples surpassed the toxic levels of metals as published by the OIV. Analyzing concentration levels of elemental composition, it can be concluded that depending on the color of the wine, the content of the individual element was different.

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