



Determination of Elements Composition in Vranec Wines Produced with Different Maceration Time

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Abstract. Vranec (*Vitis Vinifera* L.) is the most widespread red grape variety in Republic of N. Macedonia, which is grown in all vineyards, but mostly it is located in the main Tikveš wine region. In the present study, Vranec wines have been produced applying 4, 7, 14 and 30 days for maceration, in order to determine the influence of maceration time on the elements profile of wines. Inductively coupled plasma–atomic emission spectrometry (ICP-AES) technique was used to perform the analyses of 18 elements, including Al, Ba, Bi, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sr, V and Zn. The results demonstrated that K, P, Mg and Ca were the predominant elements in wines, regardless the maceration time applied for vinification. Concentration of the most of the elements, such as Al, Ba, Bi, Mg, Mn, Na, Ni, P, Sr, P and Zn, increased during the maceration. Copper was determined in a highest concentration in the wine macerated for 4 days (average value: 0.026 mg/L), followed by decreasing of the content during maceration, as it was expected. In general, the content of toxic elements Cu and Fe was lower than the maximal allowed concentrations, concluding that studied Vranec wines were safe for consumption and possessing a nutritional value as a result of the high level of K, P, Mg and Ca.

Keywords: Maceration · Elements · Vranec wine · ICP-AES

1 Introduction

Wine contains various organic and inorganic substances, such as carbohydrates, organic acids, proteins, polyphenols, volatile compounds, as well as elements (metals and non-metals), which influence the quality [1]. Elements are important constituents of wine, which has already been proven that possess nutritional value (e.a. Ca, Cr, Co, K, Mg, Mn,

Na, Se, and Zn). Some of them have potential toxic effects on the human body, such as heavy metals As, Cd, and Pb. According to the regulation published at the International Code of Oenological Practices, established by OIV (International organization of vine and wine), maximum acceptable limits for some metals have already been set as following: 0.2 mg/L for As, 0.01 mg/L for Cd, 1 mg/L for Cu, 0.15 mg/L for Pb, 80 mg/L for Na, and 5 mg/L for Zn. Therefore, their content have to be controlled during vinification [2].

Many factors influence the concentration of elements in wines, starting from the vineyards conditions, such as vine variety, soil content, fertilization practices used, climate changes, etc., continuing to the end of fermentation and vinification (addition of selected yeasts, maceration time, content of proteins and tartarates, addition of fining agents (i.e. bentonite, especially for white wines) [2–7]. Maceration is a technological phase important for production of high quality red wines. Longer maceration leads to increased color stability and complexity, improves the taste and flavor as well as overall wine quality. During maceration, the metals concentration increases, followed by decreasing throughout the fermentation process, as a result of precipitation [3, 8]. In addition, the prolonged maceration time can increase concentrations of some elements, such as Cd, Cr, Cu, Fe, Pb and Zn, since some of them can be released from cellar equipment produced from brass and stainless steel materials.

Elements can directly or indirectly affect the clarity and sensory characteristics of wines, due to the formation of precipitates during various phases of vinification (fermentation, maturation and storage). Moreover, Ca, K, Mg, and Na are considered as important elements for effective and successful alcoholic fermentation, while Cu, Fe, Mn, Zn are important elements for yeasts activity [8].

Various analytical techniques, such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been used for determination of metals and nonmetals content in wines from various countries in the world [3, 8–17]. Actually, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been introduced for the first time in the year 2011, in the booklet of the International Organization of Vine and Wine (OIV) as recommended methods for wine elemental analysis and control [18, 19].

Several studies on the elemental composition of Macedonian wines have been performed and published applying ETAAS, ICP-OES, ICP-AES and ICP-MS techniques [3, 10, 20]. Thus, systematic study on the elemental's concentration and composition of Macedonian wines has been performed in distinguishing red and white wines as well as in determination of their geographical origin. Analyses were carried out with inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–optical emission spectrometry (ICP-OES) for wines classification [10]. In addition, the contents of Pb and Cd have been determined in *Vitis Vinifera* L. white wines (Smederevka, Chardonnay and Riesling, vintage 2011) grown at two different territories in the Tikveš region: Disan and Negotino, using electrothermal atomic absorption spectrometry (ETAAS) [3]. Moreover, multi-element composition of red Vranec wines fermented with autochthonous and commercial yeast strains, have been quantified, applying microwave

digestion method for wine sample preparation, followed by ICP-MS analyses of the elements [20].

However, to the best of our knowledge, there has been no report on the concentration of elements in red Vranec wines produced with different maceration time, applying inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for analysis. Considering this, the aims of the present work were twofold: (1) to report and use a simple and fast ICP-AES method for determination of elements, after dilution of wines (1:1 with 1M HNO₃) and (2) to study the influence of maceration time on the elements composition of red wines from Vranec grape variety, the most important variety in Republic of N. Macedonia and Balkan countries.

2 Materials and Methods

2.1 Chemicals and Reagents

All reagents and standard solutions were p.a. grade. Bi-distilled water was used to prepare all solutions. Basic standard solution with a concentration of 1,000 mg/L for 23 elements in diluted nitric acid (ICP multi-element standard solution IV was purchased from Merck. Basic standard solutions with a concentration of 1,000 mg/L for Mo, P, S and V were purchased from Solution Plus.

2.2 Grape and Wine Samples

Grapes from Vranec variety, *Vitis vinifera* L. cultivated at Disan location in the Tikveš wine region, R. N. Macedonia, were harvested at optimal maturity (23–24° Brix, vintage 2010). Grapes were collected early in the morning from nine years old vineyards (area of 6 ha, at 560–580 m altitude) and were transported to the wine cellar “Elenov”, located in Demir Kapija. The distance between the rows was 2.4 m and the distance between the vines was 0.9 m.

Harvested grapes were processed with electrical inox crusher/destemmer, followed by addition of SO₂ in a form of 5% sulphurous acid (ca. 50 mg/L total concentration of SO₂), addition of commercial yeast Lalvin ICV-D254, *S. cerevisiae* (25 g/hL, supplied from Lallemand, Montreal, Canada) after two hours in order to start the fermentation and addition of nutrients (25 g/hL, Go-Ferm, obtained from Lallemand, Canada). Then, the grape mash was divided into 4 sets, applying maceration of 4, 7, 14 and 30 days (abbreviations: V-4d, V-7d, V-14d and V-30d, respectively). During the maceration and alcoholic fermentation at 25 °C, “pumping over” was applied, three times a day. When fermentation finished, wines were separated from the pomace, stabilized at temperature of 15 °C for a period of three days, bottled and stored in a wine cellar at 6–8 °C. Elements profile was determined after three years wine aging.

Wine samples were diluted in ration 1:1 with 1M HNO₃ before the ICP-AES analyses.

2.3 ICP-AES Conditions

All analyzed elements (Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr, Tl, V, Zn) were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian, 715-ES). In this spectroscopic method, inductively coupled plasma was used as the source for excitation of atoms. The test solution was fed by a peristaltic pump through an atomizer into the quartz burner (torch), which consists of three concentric tubes with separate inlets for the solution and the working gas argon. The torch was located in an induction coil connected to a high-frequency generator to produce a strong electromagnetic field that allows the generation of a plasma in which excitation occurs. At a temperature of about 7000 K, excitation of all elements present in the test solution was possible.

The following emission lines were used in ICP-AES: Al: 396.152 nm, As: 188.980 nm, Ba: 493.408 nm, Bi: 223.061 nm, Ca: 370.602 nm, Cd: 214.439 nm, Co: 238.892 nm, Cr: 267.716 nm, Cu: 327.395 nm, Fe: 238.204 nm, K: 769.897 nm, Li: 670.783 nm, Mg: 883.829 nm, Mn: 257.610 nm, Mo: 202.032 nm, Na: 589.592 nm, Ni: 231.604 nm, P: 213.618 nm, Pb: 220.353, S: 181.972 nm, Sr: 407.771 nm, Tl: 351.923 nm, V: 292.401 nm, Zn: 213.857 nm. The data on the operating conditions are given in Table 1.

Table 1. Instrumental parameters for ICP-AES analyses of elements.

RF generator			
Operating frequency: 40.68 MHz free-running, air-cooled RF generator			
Power output of RF generator: 700–1700 W in 50 W increments			
Introduction area			
Sample nebulizer: V-groove			
Spray chamber: Double-pass cyclone			
Peristaltic pump: 0–50 rpm			
Spectrometer			
Optical arrangement: Echelle optical design			
Polychromator: 400 mm fo cal length			
Echelle grating: 94.74 lines/mm			
Polychromator purge: 0.5 l min ⁻¹			
Megapixel CCD detector: 1.12 million pixels			
Wavelength coverage: 177 nm to 785 nm			
Conditions for the program			
RFG power	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 l min ⁻¹	Stabilization time	30 s
Auxiliary Ar flow rate	1.5 l min ⁻¹	Rinse time	30 s
Nebulizer Ar flow rate	0.75 l min ⁻¹	Sample delay	30 s

Calibration solutions were used for construction of calibration curves ($y = ax + b$) for each element. The linearity of the calibration curves was tested and correlation factor $R^2 > 0.99$ was considered as acceptable.

The lowest concentration that can be quantitatively determined with an acceptable level of accuracy is defined as limit of detection (LOD). LODs were determined for each elements: 0.25 $\mu\text{g/L}$ for Al, 10 $\mu\text{g/L}$ for As, 0.5 $\mu\text{g/L}$ for Ba, 1 $\mu\text{g/L}$ for Bi, 0.5 $\mu\text{g/L}$ for Ca, 0.1 $\mu\text{g/L}$ for Cd, 1 $\mu\text{g/L}$ for Co, 1 $\mu\text{g/L}$ for Cr, 0.25 $\mu\text{g/L}$ for Cu, 0.12 $\mu\text{g/L}$ for Fe, 100 $\mu\text{g/L}$ for K, 1 $\mu\text{g/L}$ for Li, 0.5 $\mu\text{g/L}$ for Mg, 0.03 $\mu\text{g/L}$ for Mn, 4 $\mu\text{g/L}$ for Mo, 40 $\mu\text{g/L}$ for Na, 5 $\mu\text{g/L}$ for Ni, 10 $\mu\text{g/L}$ for P, 10 $\mu\text{g/L}$ for Pb, 50 $\mu\text{g/L}$ for S, 0.5 $\mu\text{g/L}$ for Sr, 10 $\mu\text{g/L}$ for Tl, 1 $\mu\text{g/L}$ for V and 0.06 $\mu\text{g/L}$ for Zn.

2.4 Statistical Analyses

Each wine was analyzed in three replicates. Statistical analysis was performed, including calculation of means, standard deviation and relative standard deviation, using the XLSTAT software, version 7.5.2, Addinsoft (Paris, France). In addition, the ANOVA test of Student–Newman–Keuls of multiple comparisons of mean values was applied to the results for the concentration of each element in order to reveal differences or similarities between the studied wines. Significant difference was considered at level of $p < 0.05$.

3 Results and Discussion

The results related to the determination of 18 elements (Al, Ba, Bi, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sr, V, Zn) in Macedonian red Vranec wines produced with different maceration time of 4, 7, 14 and 30 days are presented in Table 2. The elements As, Cd, Co, Mo, Pb and Tl, which are heavy and harmful, were detected at concentrations lower than the determined LOD, and therefore, they are not presented in the table. Elemental analysis demonstrated that K, P, Mg, S and Ca were the dominant elements in the wines, regardless the maceration time, followed by Na, Fe, Mn, Sr and Al.

Potassium was the major element in all analyzed Vranec wines regardless the maceration time, ranging from 298 to 332 mg/L. This element is considered as a natural component present in the grapes that passes into the wine during fermentation. The content of potassium in wine is an indication for its concentration in the grape berries at the final stages of ripening [10]. High potassium contents lead to precipitation of tartaric acid and then, increasing of the pH value, causing wine instability. In our study, the content of potassium was not very high, which confirms the tartarate stability of the wines, regardless the duration of maceration time applied for winemaking. Phosphorous, which is naturally present macroelement and essential for life, was ranging between 71.3 and 105 mg/L in the wines. High content of this element in the wines confirms their nutritional value [20]. Sulfur was detected in the wines in the range of 47.3 to 61.5 mg/L. In fact, S is expected to be present since SO_2 is used in winemaking to prevent oxidation and browning of wine (enzymatic and nonenzymatic oxidation of phenolic compounds, especially phenolic acids, carbohydrates and amino acids). The content of S in the analyzed wines confirms that wines were sufficiently protected from oxidation and ensures their stability.

Table 2. Concentration (mg/L) of elements in Vranec wines produced with maceration time of 4, 7, 14 and 30 days and determined by ICP-AES.

Elements (mg/L)/Wine samples	V-4d	V-7d	V-14d	V-30d	Min	Max	Average
Al	0.33 ± 0.006	0.51a ± 0.007	0.51a ± 0.007	0.54a ± 0.008	0.33	0.54	0.474
Ba	0.097 ± 0.006	0.125a ± 0.0005	0.123a ± 0.002	0.134a ± 0.003	0.097	0.134	0.120
Bi	0.042 ± 0.001	0.056 ± 0.0028	0.081 ± 0.0021	0.112 ± 0.007	0.042	0.112	0.073
Ca	31.3a ± 0.342	33.5a ± 0.424	32.4a ± 0.326	31.9a ± 0.145	31.3	33.5	32.3
Cr	0.002a ± 0.001	0.004 ± 0.0002	0.001a ± 0.0007	0.010 ± 0.003	0.001	0.010	0.004
Cu	0.026 ± 0.003	0.009 ± 0.003	0.004 ± 0.0007	0.000 ± 0	0.000	0.026	0.010
Fe	0.87a ± 0.034	0.91a ± 0.008	0.57 ± 0.0404	0.84a ± 0.034	0.57	0.91	0.797
K	317 ± 0.598	332 ± 1.29	298 ± 1.677	305 ± 1.813	298	332	313
Li	0.010 ± 0.0002	0.004 ± 0.0002	0.000 ± 0	0.002 ± 0.0002	0.000	0.010	0.004
Mg	51.9 ± 0.143	55.1 ± 0.234	54.9 ± 0.183	61.9 ± 0.218	51.9	61.9	55.9
Mn	0.42a ± 0.003	0.45a ± 0.002	0.44a ± 0.004	0.49a ± 0.030	0.42	0.49	0.45
Na	1.93a ± 0.036	2.08b ± 0.044	1.91a ± 0.048	2.15b ± 0.022	1.91	2.15	2.02
Ni	0.000 ± 0	0.016 ± 0.0004	0.000 ± 0	0.022 ± 0.0002	0.000	0.022	0.010
P	71.3 ± 0.132	88.4 ± 0.031	91.8 ± 0.445	105 ± 0.353	71.3	105	89.2
S	61.5 ± 0.212	53.5a ± 0.084	47.3 ± 0.438	54.8a ± 0.362	47.3	61.5	54.3
Sr	0.39 ± 0.0212	0.48a ± 0.0136	0.48a ± 0.008	0.52 ± 0.043	0.39	0.52	0.467
V	0.056 ± 0.001	0.016 ± 0.002	0.000 ± 0	0.000 ± 0	0.000	0.056	0.018
Zn	0.037 ± 0.0001	0.029 ± 0.0009	0.085 ± 0.001	0.180 ± 0.002	0.029	0.180	0.083
Σ	537	568	529	564	529	568	550

Results represent an average value of three repeated measurements ± SD (standard deviation). Values with indicated letter within a row have been analyzed by the Student–Newman–Keul’s test (ANOVA) and are considered as not significantly different at $p > 0.05$.

In general, high concentrations of macroelements calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) contribute a salty taste in wines. The concentration of Ca (average value: 32.3 mg/L), Mg (average value: 55.9 mg/L) and Na (average value: 2.02 mg/L) were very low compared to other wines from the world [21] which means that the salty character was not present in Vranec wines, as it was expected. Similar contents between elements were noticed for manganese (on average: 0.45 mg/L), strontium (on average: 0.467 mg/L) and aluminum (on average: 0.474 mg/L), regardless the maceration time.

The presence of Al, Cu, Fe, Pb, Zn is important for conducting and completion of an effective alcoholic fermentation and therefore, their contents in wine must be controlled. Moreover, excess content of dissolved iron and copper can change the flavor and appearance of wine since both elements act in oxidation and reduction reactions, changing the flavor and color of wine, detrimenting the overall quality. The iron and copper contents in Vranec wines ranged from 0.567 to 0.912 mg/L (on average: 0.797 mg/L) and from 0.00 to 0.026 mg/L (on average: 0.01 mg/L), respectively, which were very lower compared to maximum allowed concentrations for Fe (5 mg/L) and Cu (1 mg/L) in wine [2].

Heavy metals, such as Cd and Pb, have toxic effects and they deactivate the enzymes. Therefore, their contents in wine must be monitored. In this study, both metals (Cd and Pb) have been not detected in the analysed Vranec wines. In addition, Ni, Bi and Zn were found in very low concentrations (on average: 0.01 mg/L for Ni, 0.073 mg/L for Bi and 0.083 mg/L for Zn) compared to the maximum acceptable levels (for Ni: 0.1 mg/L and for Zn: 5 mg/L). In fact, the potential source of Ni in wine is the presence of nickel alloys in stainless steel equipment.

Considering the influence of maceration time, the content of trace elements is expected to increase during fermentation, and afterwards to decrease, since they are absorbed onto the yeast cell and precipitate or coprecipitate with polyphenols and tannins and then removed. Thus, copper was present in highest concentration in the wine macerated for 4 days (0.026 mg/L), followed by decreasing of the content during maceration, as it was expected. Sr and Fe presented relatively similar concentration regardless the maceration time. In this study, for most of the elements, such as Al, Ba, Bi, Mg, Mn, Na, P, Sr and Zn, a slight increasing of their content was noticed during maceration, observing slightly higher content in wines macerated for 30 days.

In general, analyzed Vranec wines produced with different maceration time contained similar or lower levels of determined elements compared to the literature data [10–16, 21], which confirms their safety for consumption. Moreover, high level of macroelements, such as K, P, Mg and Ca, confirmed the nutritional value of Vranec wines.

4 Conclusion

In this study, fast and simple method based on ICP-AES technique was used to determine 18 elements, including Al, Ba, Bi, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sr, V and Zn, in Vranec wines produced with maceration time of 4, 7, 14 and 30 days, after simple sample preparation (dilution of wines in ratio 1:1 with 1M HNO₃). K, P, Mg, S and Ca were the dominant elements in all wines regardless the maceration duration, followed by elements Na, Fe, Mn, Sr and Al. Concentration of Cu decreased during maceration, while slight increase of Al, Ba, Bi, Mg, Mn, Na, P, Sr and Zn contents were noticed in the wines. All wines presented a good dietary source of macro and micro-nutrient elements.

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