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QUALITY EVALUATION OF WINES FROM KOSOVO AND METOHIJA: POLYPHENOLS CONTENT, ANTIOXIDANT ACTIVITY AND ELEMENTAL COMPOSITION

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ABSTRACT

Wine is a very rich source of polyphenols and essential elements which have multiple biological activities. This study evaluates the total phenolic content (TPC), antioxidant activity (AA) of sixteen wine samples made from different grape varieties in the territory of Kosovo and Metohija, mostly from the area of Orahovac and Velika Hoča. The obtained results, determined by using the Folin-Ciocalteu assay, showed that wines from territory of Kosovo and Metohija are rich in polyphenols, with TPC ranges from 276±16 to 371±46 (white wines) and 1467±32 to 2823±43 mg gallic acid equivalents GAE/L (red wines). The total antioxidant activities, determined by ABTS method, range from 8.7±0.4 to 22.8±0.7 mmol trolox equivalents TE/L for red wines and from 1.3±0.1 to 3.8±0.3 mmol TE/L for white wines. Elemental content of studied wines showed certain difference between wines from nearby regions.

Keywords: Polyphenols, Antioxidant activity, Wine, Elemental composition.

INTRODUCTION

Viticulture and enology are very long-standing in Kosovo and Metohija. This region is located in the central part of the Balkan Peninsula, in southeastern Europe with an average altitude of about 800 m, but with a pronounced height change of the relief and morphology. The importance of wine cultivation and wine production in the territory of Kosovo and Metohija is not at random because the aforementioned territory, especially Metohija, has exceptional climatic and geographical conditions for its cultivation (Ivanišević & Jakšić, 2012). Climatic conditions and soil type are favorable for autochthonous grape varieties which are specific for this part of Balkan Peninsula (Prokupac, Vranac, Smederevka, Župljanka, Kraljica, Žilavka), while other European grape varieties like Gamay, Italian riesling, Cabernet sauvignon, Merlot, are also adopted to this area.

Phenolic compounds have long been considered to be basic components of wines and over 200 compounds have been identified. Wine composition, including the contents of phenolic compounds, varies markedly depending on the grape cultivar, soil, nutrition, climatic conditions, weather, winemaking procedure, and conditions of maturation and storage (Stratil et al., 2008). Different grape varieties also show a distinct sensory appeal, chemical composition, different quantities of native antioxidants and therefore different biological activity (Menković et al., 2014). The anti-oxidant activity of wines has been related to their polyphenolic constituents and is mainly based on their free radical scavenging capacity (Sánchez-Moreno et al., 1999). The total phenols in wines are mainly determined by spectrophotometric Folin-Ciocalteu assay (Waterhouse, 2016.) while HPLC is widely used for individual identification and quantification of polyphenols (Rastija & Medić-Šarić, 2009; Šeruga, 2011). Various methods for determination of antioxidant activity could be used (mostly spectrometry, then electrochemical techniques and chromatography) (Pisoschi & Negulescu, 2011; Stratil, 2008).

It is well known that metals effect on sensorial characteristics, flavor and aroma of wine. Chemical composition of wine provides viticulturists to control the process of vinification in order to obtain high quality wine. The presence of some metals in wines such as Al, Zn, Cu, Fe, Pb is important for efficient alcoholic fermentation (Stafilov & Karadjova, 2006). When considering winemaking and quality assurance of branded wines, knowledge of metal is of special economic importance (Pohl, 2007) Evaluation of amounts of major and trace elements is important for establishment of elemental profiles of studied wines.

According to literature, there is only study of Metohian wines in terms of spectrophotometric color characterization (Babincev et al., 2016), but there is no report about wine quality, considering polyphenols content, antioxidant activity

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and chemical composition of wines from territory of Kosovo and Metohija. Comparison of this results and literature data for wines from neighboring regions and countries, bearing in mind varieties of grapes from which the wines were made, could offer interesting and important facts.

EXPERIMENTAL

Chemicals and apparatus

Gallic acid (3,4,5-trihydroxybenzoic acid), Folin-Ciocalteu reagent, trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and ABTS (2,2'-azinobis-(3-ethylbenzothiazoline)-6-sulfonic acid) were products of Sigma Aldrich, Germany. All the other chemicals were analytical grade.

Spectrophotometric measurements of colour, TP and AA determination of wine samples were done on Rayleigh VIS-7220G/UV-9200 Spectrophotometer (Beijing Beifen-Ruili Analytical Instrument Group Co. Ltd.

Inductively Coupled Atomic Emission Spectrometer, ICP-OES (iCAP 6500 Duo Thermo Scientific, UK) and inductively coupled plasma mass spectrometer (ICP-Q-MS, Thermo Scientific Xseries 2, UK) were used for determination of major and trace elements, respectively. ICP multi-element stock solutions (VHG standards, Manchester, UK) containing 1000 mg/L were used as stock solution for calibration. Mix of ^{6}Li, ^{45}Sc, ^{115}In and ^{159}Tb (VHG standards, Manchester, UK) were used as internal standards for ICP MS measurements.

Wine samples

The basic data about wine samples (vintages 2012, 2013 and 2015) are presented in Table 1. Most of samples are from Velika Hoča and Orahovac. Four white wines are analyzed (samples 2, 4, 5, and 16), one is rose (12) and the others are red. Two wines are commercially available: sample No 12, Duša Metohije, from private winery of Lj. Đurišić and sample No 13, Manastirsko Dečansko. Other wines are produced in domestic production or small private (or monastery) wineries. All wines are stored in the refrigerator to +4 °C, and filtered through syringe filter before determination. pH of wine samples ranged from 3.19-3.84.

For determination of elements content in wine, samples were diluted (1:10) with water containing 2 % (v/v) of nitric acid (Merck, Germany). Standards were prepared with 1% (v/v) ethanol and 2% (v/v) nitric acid and in order to provide the same matrix as in samples.

Determination of total phenolic content

The total phenolic content of wines was determined by using the Folin-Ciocalteu assay. The standard solutions of gallic acid (50, 100, 150, 250 and 500 mg/L) were prepared. Folin-Ciocalteu's phenol reagent and 25% Na_2CO_3 solution were added according the procedure (Waterhouse, 2016.) to each standard solution and to the reagent blank. After incubation for 90 min at room temperature in the darkness, the absorbance against prepared reagent blank was determined at 750 nm. Total phenolic content of wines was expressed as mg of gallic acid equivalents GAE/L. 20μL of sample was added for red wines determination, and 200μL for white wines. All samples were analyzed in triplicates.

Table 1. Basic facts about wine samples.

Sample	Wine color	Grape variety	Area, winery
1	Red	Vranac	Velika Hoča
2	White	Smederevka	Velika Hoča
3	Red	Prokupac, Vranac	Velika Hoča
4	White	Župljanka	Velika Hoča
5	White	Italian riesling	Orahovac
6	Red	Prokupac, Vranac, Gamay	Orahovac
7	Red	Cabernet sauvignon	Velika Hoča
8	Red	Vranac	Velika Hoča Hoča wine d.o.o.
9	Red	Gamay	Velika Hoča Hoča wine d.o.o.
10	Red	Merlot	Velika Hoča
11	Red	Tamjanika / (Muscat)	Kosovska Kamenica
12	Red	Vranac, Cabernet sauvignon, Gamay, fruit aromas	Velika Hoča Hoča wine d.o.o.
13	Red	Cabernet sauvignon, Merlot, Gamay, Vranac	Orahovac Monastery winery
14	Red	Prokupac	Orahovac
15	Red	Vranac	Gračanica Monastery winery
16	White	Kraljica, Žilavka, Tamjanika/ (Muskat)	Gračanica Monastery winery

Determination of antioxidant activity

ABTS test was performed according to the literature (Cavuldak et al., 2013). ABTS radical is obtained by incubating an aqueous solution of 7 mmol/L ABTS with 2.45 mmol/L $K_2S_2O_8$ for 12-16 hours in the dark, at room temperature. ABTS$^{\bullet}$+ radical solution was prepared freshly on the day of analysis by diluting the stock solution with phosphate buffer (PBS), to an absorbance of 0.70 ± 0.02 at 734 nm. The sample volume of 0.1 cm^3 (differently diluted depending on the sample) was added to 3.9 cm^3 of the working solution of ABTS radical, the solution was mixed well and allowed to stand for 6 minutes in a dark place, and absorbance was measured. Standard Trolox solutions (5–20 mmol/L) were also evaluated against the radical in order to obtain a calibration curve. Results are expressed as Trolox Equivalent Antioxidant Capacity (TEAC).

Determination of elemental composition

Seventeen elements, including major (Ca, Mg, Na, K, Rb, Fe) and trace (Mn, Cu, Zn, V, Co, Ni, Cd, Ba, Cr, Se and Pb) elements, in a set of 16 wine samples were analysed. The analytical lines used for each element, the limit of detection (LOD) as well as ICP OES instrumental conditions are shown in Table 2. Also, measured isotopes and instrument operating conditions for ICP MS determination are given in Table 2.

Table 2. Instrument operating conditions for ICP-OES and ICP-Q-MS.

ICP- OES	
Nebulizer	Concentric
Spray chamber	Cyclonic
Rf power (W)	1150
Principal argon flow rate (L/min)	12
Auxiliary argon flow rate (L/min)	0.5
Nebulizer argon flow rate (L/min)	0.5
Sample flow rate (mL/min)	1
Selected wavelengths (nm)	Fe (259.9); Na (589.5); Ca (373.6); Mg (279.5); K (766.4); Rb (780.0)
Detection limits (μg/L)	Fe (0.2); Na (0.2); Ca (0.3); Mg (0.2); K (0.4); Rb (0.1)
ICP-Q-MS	
Rf power (W)	1548
Gas flows (L/min)	13.9;1.09;0.8
Acquisition time	3 x 50s
Points per peak	3
Dwell time (ns)	10
Detector mode	Pulse
Measured isotopes	^{51}V, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{111}Cd, ^{137}Ba, ^{208}Pb, ^{52}Cr, ^{55}Mn, ^{78}Se
Detection limits (μg/L)	V (0.02), Co (0.02), Ni (0.3), Cu (0.2), Zn (0.4), Cd (0.05), Ba (0.02), Pb (0.1), Cr (0.3), Mn (0.4), Se (0.2)

RESULTS AND DISCUSION

Determination of elemental composition

Results for total phenol content expressed in gallic acid equivalents and antioxidant activity expressed as TEAC for studied wine samples were presented in Table 3. TPC in red wines varied from 1467±32 to 2823±43 mg/L of GAE, and the highest value was for wine produced from Vranac grape variety in 2012. The reason could be that 2012 year was very successful enology year in this area. Sample No 1 with 2595±22 mg/L of GAE was also made from Vranac grape variety in 2015, while wine No 12, Duša Metohije, had a highest TPC for year 2013, and it was made from Vranac, Cabernet sauvignon, Gamay and fruits. Hence, all the red wines, with the exception of two samples made from varieties Merlot and Cabernet Sauvignon, have a polyphenol content between about 1900 and almost 2900 mg/L GAE. As usual, white wines had a much lower TPC then red ones, and TPC was in the range of (276±16 - 371±46 mg/L GAE). The highest content of TPC for white wines was found for wine made from Župljanka grape variety. Should be noted that the sample number 11, made from Tamjanika (domestic name for Muscat de Frontignan variety), have properties of rose wine, because its colour and phenolics content are between red and white wines. It is interesting that wine from native cultivar Prokupac at Metohija territory showed much higher TPC then it was reported for Prokupac wine from central Serbia and the phenolic content was higher than in wines from Merlot and Cabernet Sauvignon cultivators, contrary to Atanacković et al. (Atanacković et al., 2012). Merlot from Istria region, Croatia (2005/2006), had a TPC of 1260±23 (Šeruga et al., 2011) while for Cabernet Sauvignon (1998) and Merlot (1998) grown in Croatia were fond 2402 and 3087 mg/L GAE, respectively (Katalinić et al., 2004). Croatian wines like Ivan Dolac and Dingač, made from native variety Plavac mali had a TPC greater than 3000 mg/L GAE (Šeruga et al., 2011; Katalinić et al., 2004).

Table 3. Total phenolic content and antioxidant activity of wines from Kosovo and Metohija.

Sample	TPC mg/L GAE	AA, TEAC mmol TE/L
1	2595±22	19±0.5
2	315±35	2.7±0.4
3	1909±28	12±0.8
4	371±46	3.8±0.3
5	295±18	1.8±0.6
6	2400±37	17.2±0.7
7	1613±25	9.8±0.3
8	2823±43	22.8±0.7
9	1918±19	12.5±0.5
10	1467±32	8.7±0.4
11	808±11	4.2±0.2
12	2203±26	16±0.5
13	2041±32	15.8±0.6
14	1901±34	15±0.2
15	2099±27	15.2±0.4
16	276±16	1.3±0.1

TPC contents of Metohija wines made from Smederevka, and Vranac cultivator were higher than reported in neighboring Macedonia (1382±38.2 and 1515±27.6 mg/L GAE) (Ivanova et al., 2010). Based on these results, it can be concluded that conditions in Metohija are very appropriate for Vranac, Gamey, Prokupac, Župljanka and Smederevka cultivars, and wines from Vranac variety certainly had highest content of polyphenols.

Antioxidant activity (AA) is strongly dependent of the type and structure of poliphenols present in wines. AA for studied red wines ranged from 9.8±0.3 to 22.8±0.7 TEAC and for white wines from 1.3±0.1 to 3.8±0.3 mmol TE/L. The lowest antioxidant activity was found for wine samples 7 and 10, made from Cabernet sauvignon and Merlot grape variety. There was a strong correlation between total phenol content (correlation coefficients was R=0.9727).

Elemental profile of wines

Seventeen elements, including major (Ca, Mg, Na, K, Rb, Fe) and trace (Mn, Cu, Zn, V, Co, Ni, Cd, Ba, Cr, Se and Pb) elements, in a set of 16 wine samples were analysed. The results together with summarized parameters (mean, median, minimum, maximum value and standard deviation) obtained for element content in wine samples presented in Table 4 and 5.

The most abundant element in all analysed wine samples was potassium, with content ranging from 300 mg/L (sample 16, white wine from Gračanica Monastery winery) to 657 mg/L (sample 7, red wine from winery Velika Hoča). The obtained results are in accordance with values reported in the literature (Ražić & Onjia, 2010; Đurđić et al., 2017). The highest concentration of potassium in wines could be explained by the fact that it is an essential element for plants, as well as the application of fertilizers on the basis of this metal (Rodrigues et al., 2011). The content of K in the wine also depends on the grape variety, climatic conditions, soil and fermentation temperature. The elements Mg and Ca showed high mean concentrations 89.1 and 62.7 mg/L, respectively. Values obtained for Mg and Ca are similar with results obtained for Macedonian (Ivanova-Petropulos et al., 2013), other Serbian (Đurđić et al., 2017) and Croatian wines (Vinković Vrček et al., 2011).

In this study, results for Rb ranged from 2.08 to 6.27 mg/L, which are higher compare to results obtained by (Geana et al., 2013) for Romanian red and white wines (0.783 mg/L and 1.050 mg/L, respectively) and for other Serbian wines (0.28 to 4.70 mg/L) (Đurđić et al., 2017). Alkaline earth metals and Rb are less affected by technological factors, so they could be the most relevant elements for geographical origin authentication (Pohl, 2007).

Sodium was present with mean value of 13.29 mg/L. These results are lower than literature data where high concentrations of Na in wines explained by small distance from the sea (Iglesiaset al., 2007) but in agreement with results obtained for Macedonian wine (Ivanova-Petropulos et al., 2013), other Serbian (Đurđić et al., 2017) or German wine (Thiel & Danzer, 1997) report that the different elemental content might provide for differences in the process of vinification, difference occurs due to longer contact skin and seeds of grapes with juice during the production of red wines.

Table 4. Results of major elements composition in wine samples.

mg/L	**Fe**	**K**	**Mg**	**Ca**	**Na**	**Rb**
1	2.9 ± 0.03	452 ± 3	116.4 ± 0.1	79.5 ± 0.6	4.2 ± 0.4	5.2 ± 0.2
2	0.75 ± 0.03	452 ± 2	50.3 ± 0.3	67.5 ±0.5	3.8 ± 0.3	4.1 ± 0.2
3	0.23 ± 0.01	573 ± 4	105.7 ± 0.2	59.5 ± 0.6	5.5 ± 0.4	4.3 ± 0.2
4	0.19 ± 0.03	462 ± 4	72.6 ± 0.3	48.1 ± 0.6	4.1 ± 0.4	3.5 ± 0.2
5	1.86 ± 0.03	451 ± 3	70 ± 0.3	74.8 ± 0.5	6.2 ± 0.4	3.1 ± 0.2
6	3.32 ± 0.02	618 ± 5	89.7 ± 0.2	42.6 ± 0.5	1.5 ± 0.4	2.1 ± 0.2
7	9.00 ± 0.01	657 ± 5	137.3 ± 0.1	44.4 ±0.6	2.8 ± 0.4	6.3 ± 0.2
8	2.62 ± 0.03	588 ± 3	105.2 ± 0.1	58.3 ± 0.1	2.4 ± 0.4	4.7 ± 0.2
9	2.17 ± 0.01	379 ± 3	116.1 ± 0.1	70.7 ± 0.5	1.9 ± 0.5	4.4 ± 0.2
10	2.37 ± 0.01	426 ± 4	102.6 ± 0.1	77.5 ± 0.4	2.2 ± 0.4	4.4 ± 0.2
11	0.44 ± 0.05	623 ± 5	75.0 ± 0.3	125.6 ± 0.1	91.9 ± 0.1	4.3 ± 0.2
12	3.14 ± 0.03	502 ± 6	73.7 ± 0.3	54.7 ± 0.1	2.7 ± 0.4	3.4 ± 0.2
13	2.34 ± 0.03	456 ± 4	87.7 ± 0.3	48.1 ± 0.5	7.5 ± 0.4	5.1 ± 0.2
14	2.64 ± 0.03	486 ± 5	72.8 ± 0.2	47.2 ± 0.6	50.8 ± 0.4	4.7 ± 0.2
15	2.69 ± 0.03	548 ± 6	86.0 ± 0.1	28.9 ± 0.4	7.2 ± 0.4	4.8 ± 0.2
16	2.47 ± 0.03	300 ± 3	64.9 ± 0.3	76.2 ± 0.4	17.9 ± 0.4	4.4 ± 0.2
mean	2.45	499	89.1	62.7	13.3	4.3
median	2.42	475	86.8	58.9	4.1	4.4
max	9.00	656	137.3	125.6	91.9	6.3

For Zn and Mn the mean values were 864.3 and 1176 µg/L, respectively. The content of Zn and Mn could be influenced by agricultural practices or by metal containers used during ageing stages. White wine from Orahovac has high content of Zn compared to other samples (4413.0 µg/L). It can be explained with long contact of the equipment and wine during the process of vinification, as well as with the use of pesticides in agricultural practices (Greenough et al., 2005). The variation of Cu content in wine samples is relatively high (Table 5), ranged from 28 µg/L (sample 15) to 1108 µg/L (sample 7), red wine from Gračanica Monastery winery and red wine from Velika Hoča, respectively. This may originate mainly from Cu accumulation in soil of using Bordeaux mixture or other copper-based fungicides (Ražić & Onjia, 2010). We do not have information on whether the used Bordeaux mixture, but assume it is used because it is the most common tool used in agriculture. Copper can also be found in the wines from the use of equipment based on this metal (Ivanova-Petropulos et al., 2013).

Table 5. Results of trace elements composition in wine samples.

μg/L	Ba	Cd	Co	Cr	Se	Ni	Pb	Mn	Cu	Zn	V
1	159.6 ±0.1	2.15 ±0.03	0.02 ±0.02	6.06 ±0.03	0.83 ±0.02	133.1 ±0.4	45.3 ±0.8	1389 ±6	686 ±6	712.9 ±0.5	0.82 ±0.02
2	111.1 ±0.1	13.51 ±0.03	4.59 ±0.06	5.26 ±0.02	0.20 ±0.02	101.3 ±0.4	54.6 ±0.8	1845 ±5	338 ±6	146.5 ±0.5	5.08 ±0.02
3	124.1 ±0.1	1.67 ±0.03	2.07 ±0.02	6.23 ±0.03	0.86 ±0.02	94.8 ±0.4	93.1 ±0.8	881 ±9	194 ±6	153.5 ±0.5	2.31 ±0.02
4	38.6 ±0.1	1.42 ±0.03	0.59 ±0.08	3.59 ±0.02	1.29 ±0.02	68.0 ±0.4	28.4 ±0.8	761 ±7	170 ±6	710.3 ±0.5	0.67 ±0.02
5	40.1 ±0.1	1.94 ±0.03	2.32 ±0.06	5.26 ±0.02	0.89 ±0.02	59.1 ±0.4	50.7 ±0.8	1051 ±6	235 ±6	4413.0 ±0.5	0.77 ±0.02
6	60.0 ±0.1	1.01 ±0.03	4.26 ±0.02	7.23 ±0.01	1.21 ±0.02	44.0 ±0.4	52.1 ±0.8	750 ±6	60 ±6	596.2 ±0.5	0.02 ±0.02
7	86.8 ±0.1	1.69 ±0.03	1.96 ±0.02	10.32 ±0.02	2.60 ±0.02	56.9 ±0.4	133.4 ±0.8	1405 ±5	1108 ±6	822.7 ±0.5	1.22 ±0.02
8	101.8 ±0.1	1.42 ±0.03	3.04 ±0.02	6.89 ±0.04	1.56 ±0.02	60.4 ±0.4	39.1 ±0.8	1360 ±5	351 ±6	765.3 ±0.5	0.86 ±0.02
9	94.8 ±0.1	1.86 ±0.03	2.09 ±0.03	6.85 ±0.04	1.30 ±0.02	75.6 ±0.4	64.3 ±0.8	1365 ±6	88 ±6	604.2 ±0.5	0.02 ±0.02
10	92.4 ±0.1	1.83 ±0.03	0.47 ±0.06	8.98 ±0.04	0.27 ±0.02	66.5 ±0.4	45.6 ±0.8	1246 ±6	64 ±6	2381.0 ±0.5	0.56 ±0.02
11	128.3 ±0.1	3.03 ±0.03	0.04 ±0.02	3.74 ±0.02	0.20 ±0.02	26.8 ±0.4	59.6 ±0.8	755 ±8	312 ±6	284.4 ±0.5	2.39 ±0.02
12	90.9 ±0.1	1.45 ±0.03	3.64 ±0.02	17.61 ±0.02	0.20 ±0.02	87.5 ±0.4	30.8 ±0.8	1422 ±3	29 ±6	181.5 ±0.5	4.96 ±0.02
13	129.8 ±0.1	1.21 ±0.03	5.11 ±0.03	14.49 ±0.02	0.18 ±0.02	98.2 ±0.4	26.7 ±0.8	1257 ±6	65 ±6	258.1 ±0.5	1.75 ±0.02
14	170.6 ±0.1	1.66 ±0.03	6.65 ±0.03	5.57 ±0.02	0.20 ±0.02	76.0 ±0.4	56.4 ±0.8	1313 ±6	45 ±6	35.8 ±0.5	0.02 ±0.02
15	76.1 ±0.1	5.33 ±0.03	3.33 ±0.02	12.31 ±0.02	2.26 ±0.02	31.0 ±0.4	78.1 ±0.8	989 ±6	28 ±6	419.3 ±0.5	0.89 ±0.02
16	49.5 ±0.1	7.60 ±0.03	2.63 ±0.02	7.41 ±0.02	0.05 ±0.02	54.6 ±0.4	145.9 ±0.8	1024 ±5	124 ±6	1345.0 ±0.5	1.19 ±0.02
mean	97.2	3.05	2.85	7.99	1.11	70.9	62.7	1176	205	864.4	1.81
median	93.6	1.76	2.63	6.87	1.05	67.2	53.3	1252	106	600.2	1.19
max	170.6	13.5	6.65	17.61	2.60	133.1	145.9	1845	1108	4413	5.09
min	38.6	1.01	0.02	3.59	0.05	26.8	26.7	750	28	35.8	0.56
sd	39.3	3.28	1.82	3.90	0.78	27.6	34.7	305	265	1107	1.54

CONCLUSION

In summary, for the first time characterization of wine samples from this region was given. It is shown that these wines are rich with polyphenols, especially cultivar Vranac, often presented in this region as variety for domestic, small wine producers. This region could be also favorable for the autochthones cultivars such as Župljanka (white wine) and Prokupac (red wine) which results shows higher content of important nutrients compared with these wines from other Balkan regions. Quality data of wines produced in this historically important viticulture region could significantly contribute to the nowadays development, certification and commercialization of wines bearing in mind that existing small private wineries and wine producers which produce high-quality wine mainly have domestic or local significance and rarely place their wines in the European markets.

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REFERENCES

Atanacković, M., Petrović, A., Jović, S., Bukarica, L. G., Bursać, M. & Cvejić, J. 2012. Influence of winemaking techniques on the resveratrol content, total phenolic content and antioxidant potential of red wines. Food Chem. 131, pp. 513-518. doi.org/10.1016/j.foodchem.2011.09.015

Babincev Lj. M., Gurešić D. M. & Simonović R. M. 2016. Spectrophotometric characterization of red wine color from the vineyard region of Metohia, Journal of Agricultural Sciences Belgrade 61(3), pp. 281-290. https://doi.org/10.2298/JAS1603281B

Cavuldak, O. A., Anli, R. E. & Vural, N. 2013. Phenolic Composition and Antioxidant Capacity of Some Red Wines from Turkey. International Journal of Food Science and Nutrition Engineering 3(3), pp. 40-47. DOI:10.5923/j.food.20130303.04

Đurđić, S., Pantelić, M., Trifković, J., Vukojević, V., Natić, M., Tešić, Ž. & Mutić, J. 2017. Elemental composition as a tool for the assessment of type, seasonal variability, and geographical origin of wine and its contribution to daily elemental intake. RSC Advance, 7, pp. 2151-2162. http://doi.org/10.1039/C6RA25105F

Geana, I., Iordache, A., Ionete, R., Marinescu, A., Ranca, A. & Culea, M. 2013. Geographical origin identification of Romanian wines by ICP-MS elemental analysis. Food Chemistry, 138, pp. 1125-1134. DOI:10.1016/j.foodchem.2012.11.104

Greenough, J. D., Mallory-Greenough, L. M. & Fryer, B. J. 2005. Geology and Wine 9: Regional Trace Element Fingerprinting of Canadian Wines. Geoscience Canada, 32(3), pp. 129-137. https://journals.lib.unb.ca/index.php/GC/article/view/2712

Iglesias, M., Besalu E. & Anticó, E. 2007. Internal Standardization−Atomic Spectrometry and Geographical Pattern Recognition Techniques for the Multielement Analysis and Classification of Catalonian Red Wines. J. Agric. Food Chem., 55, pp. 219-225. https://doi.org/10.1021/jf0629585

Ivanišević, D. & Jakšić, D. 2012. Viticulture in Serbia according to statistics and viticulture zoning, Final Conference, Application Census of Agriculture 2012 in the situation of agriculture and in the planning of agricultural policy in the Republic of Serbia. http://media.popispoljoprivrede.stat.rs/2014/Dokumenta/Radovi/Viticulture%20in%20Serbia%20according%20to%20statistics%20and%20viticulture%20zoning.pdf

Ivanova, V., & Stefova, M. 2010. Chinnici, F. Determination of the polyphenol contents in Macedonian grapes and wines by standardized spectrophotometric methods. J. Serb. Chem. Soc., 75(1), pp. 45-59. https://doi.org/10.2298/JSC1001045I

Ivanova-Petropulos, V., Wiltsche, H., Stafilov, T., Stefova, M., Motter, H., & Lankmayr, E. 2013. Multielement analysis of Macedonian wines by inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–optical emission spectrometry (ICP-OES) for their classification. Macedonian Journal of Chemistry and Chemical Engineering, 32(2), pp. 265-281. DOI:10.20450/mjcce.2013.447

Katalinić, V., Milos, M., Modun, D., Music, I. & Boban, M. 2004. Antioxidant effectiveness of selected wines in comparison with (+)-catechin. Food Chem., 86, pp. 593-600. https://doi.org/10.1016/j.foodchem.2003.10.007

Menković, N., Živković, J., Šavikin, K., Gođevac, D., Zdunić, G., 2014. Phenolic composition and free radical scavenging activity of wine produced from the Serbian autochthonous grape variety Prokupac – A model approach. J. Serb. Chem. Soc. 79(1), pp. 11-24. https://doi.org/10.2298/JSC130511089M

Pisoschi, A. M. & Negulescu, G. P. 2011. Methods for Total Antioxidant Activity Determination. A Review, Biochem & Anal Biochem, 1, pp. 1-10. DOI: 10.4172/2161-1009.1000106

Pohl, P. 2007. What do metals tell us about wine? Trends in Analytical Chemistry, 26(9), pp. 941-949. https://doi.org/10.1016/j.trac.2007.07.005

Rastija, V. & Medić-Šarić, M., 2009. Chromatographic Methods for the Analysis of Polyphenols in Wines. Journal of Chemists and Chemical Engineers, 58(03), pp. 121-128. https://hrcak.srce.hr/32964

Ražić, S. & Onjia, A. 2010. Trace element analysis and pattern recognition techniques in classification of wine from central Balkan countries. American Journal of Enology and Viticulture (ASEV) 61(4), pp. 506-511. DOI: 10.5344/ajev.2010.10002

Rodrigues, S. M., Otero, M., Alves, A. A., Coimbra, J., Coimbra, M. A., Pereira, E. & Duarte A. C. 2011. Elemental analysis for categorization of wines and authentication of their certified brand of origin. J. Food Compos.Anal.24,pp. 548-562. DOI: 10.1016/j.jfca.2010.12.003

Šeruga, M., Novak, I. & Jakobek, L. 2011. Determination of polyphenols content and antioxidant activity of some red wines by differential pulse voltammetry, HPLC and spectrophotometric methods . Food Chem. 124, pp. 1208-1216. https://doi.org/10.1016/j.foodchem.2010.07.047

Sánchez-Moreno, C., Larrauri, J. A. & Saura-Calixto, F. 1999. Free radical scavenging capacity of selected red, rose and white wines. J. Sci. Food Agric., 79, pp. 1301-1304. https://doi.org/10.1002/(SICI)1097-0010(19990715)79:10<1301::AID-JSFA367>3.0.CO;2-Y

Stafilov, T. & Karadjova I. 2006. Methods for determination and speciation of trace elements in wine (review). International Journal of Pure and Applied Chemistry (IRJPAC),1,2, pp. 273-305. http://hdl.handle.net/20.500.12188/13830

Stratil P, Kuban V. & Fojtova J. 2008. Comparison of the phenolic content and total antioxidant activity in wines as

determineted by spectrophotometric methods. Czech J. FoodSci.26, pp. 242-253. https://www.agriculturejournals.cz/publicFiles/01961.pdf
Thiel G. & Danzer Fresenius K. 1997. Direct analysis of mineral components in wine by inductively coupled plasma optical emission spectrometry (ICP-OES). J. Anal. Chem. 357, pp. 553-557. https://doi.org/10.1007/s002160050212
Vinković Vrček I., Bojić M., Žuntar I., Mendaš G. & Medić-Šarić M. 2011. Phenol content, antioxidant activity and metal composition of Croatian wines deriving from organically and conventionally grown grapes. Food Chem. 124, pp. 354-361. https://doi.org/10.1016/j.foodchem.2010.05.118
Waterhouse A., Folin-Ciociocalteu micro method; Department of Viticulture and Enology; University of California, Davis. https://waterhouse.ucdavis.edu/folin-ciocalteau-micro-method-total-phenol-wine