Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. *75* (12) 1701–1709 (2010)
JSCS–4089

UDC 663.2+543.421:546.72+
546.56+546.47(497.11)
Original scientific paper

The concentrations of Fe, Cu and Zn in selected wines from South-East Serbia

DANIJELA KOSTIĆ[#], SNEŽANA MITIĆ[#], GORDANA MILETIĆ, SAŠA DESPOTOVIĆ and ALEKSANDRA ZARUBICA[*#]

Department of Chemistry, Faculty of Science, University of Niš, 18000 Niš, Serbia

(Received 4 January, revised 30 July 2010)

Abstract: Fruits and vegetables constitute the cheapest source of essential trace elements for the majority of people living in developing countries. The Cu, Fe and Zn contents in twenty selected wine samples produced in the South-East region of Serbia were determined by flame atomic absorption spectrometry. The Cu concentrations varied from 0.07 to 0.57 ppm in wines, and the Fe concentrations fluctuated from 2.93 to 36.2 ppm, while the Zn levels were in the range from 0.21 to 0.67 ppm. The established contents of Cu and Zn showed that wines from this part of the world could serve as good dietary sources of the essential trace metals, and the determined values were within the allowed metals levels in wines for human consumption.

Keywords: AAS; Fe, Cu and Zn contents; South-East Serbian wines; wine analysis.

INTRODUCTION

Several spectroscopy techniques can be commonly used for the evaluation of food and/or drink quality[1] as well as of pharmaceutical samples.[2] Wine is a popular and worldwide consumed alcoholic beverage, which has been well-known since the early periods of civilization. The moderate consumption of wine, especially red wines, was shown to improve health and longevity.[3,4] From an analytical chemical point of view, wine is referred to as a complex matrix with a varying content of inorganic compounds (*e.g.*, traces of dissolved alkaline and alkaline earth elements, and transition metals), as well as organic substances (*e.g.*, polyphenols, polyhydroxy alcohols, proteins, amino acids, and polysaccharides) dissolved and/or dispersed in an aqueous solution of ethanol.[5]

---

[*] Corresponding author. E-mail: zarubica2000@yahoo.com
[#] Serbian Chemical Society member.
doi: 10.2298/JSC100104133K

Scientific discussions concerning human exposure to the trace metals contents of various beverages and dietary products, including wines, have received raising attention, since the consumption of wines, especially reasonably large volumes, may significantly contribute to the daily dietary intake of trace elements by humans.[5] Moreover, some of these trace elements (*e.g.*, Cu, Fe, and Mn) have an organoleptic effect, and also contribute to the haze and taste of wines.[6] The regional variations of the content trace metal in wines can also be used for identification purposes, *i.e.* to verify authenticity.[7] Considering all the above points, the determination of toxic (*e.g.*, As, Cd and Pb) and essential trace elements (*e.g.*, Cu) in wines appears to be an important and challenging analytical task, which requires multi-element methods of good selectivity, sensitivity, and robustness. The origin of Cu in wines is associated with copper-based vineyard sprays, whereas the As, Cd and Pb contents reflect differences in grape variety, environmental factors (*e.g.*, soil and climate), and the wine-processing method (an anthropogenic impact).[5]

However, nutritional metals such as Cu and Zn occur naturally in fruits and vegetables, as essential trace elements necessary for good health, but they could be toxic when their concentrations exceed limits of safe exposure.[3,4,8] In addition to toxicity problems, Cu and Zn deficiency may also be experienced; hence, as stated earlier,[3] knowledge of heavy metal contents in crops is important for the identification of adequate, sub-adequate and marginal intake levels for humans and animals, so that diseases related to trace element deficiency can be overcome. A large number of symptoms/ailments, comprising anemia, depressed growth, dermatitis, dwarfism, electrolyte-imbalance, gastro-intestinal and neurological disorders, lethargy and nausea, have been associated with Cu and Zn deficiency in humans, as well as with toxicity due to excessive intake.[6,8–11] Furthermore, the presence of trace elements in fruits and vegetables has been ascribed to their absorption from the soil and sources such as fertilizer, agricultural chemicals and contaminants.[8,12] Other sources of heavy metals contamination of most foodstuffs may also include agricultural mechanization procedures, sprays, seed preservatives,[13] and components from the global pollution process. Hence, the need to determine and/or monitor the Cu and Zn contents of fruits and vegetables have become imperative due to their principal role as essential or detrimental trace elements. A survey of the literature indicates that such a study is scarce, particularly in the southeast region of Serbia.

Trace elements in wine samples can be measured by different techniques, such as stripping voltammetry,[4–6,8–13] instrumental neutron activation analysis,[14] ICP–AES, ICP–MS[15–17] and/or UV–Vis spectrophotometry.[18–21]

However, the official methods for the determination of heavy metals in wine established by the Office International de la Vigne et du Vin and the American Society of Enologists are essentially based on atomic absorption spectrometry

(AAS).[22] Similarly, Flame-AAS is the official method of analysis for the determination of Na, K, Mg, Ca, Fe, Ag and Zn in wine according to EU regulations.[1] Some elements with relatively high concentrations in wine could be analyzed by flame atomic absorption spectrometry (FAAS).[23–25] However, for some elements present in wine in low concentrations, hydride generation techniques using FAAS (HG–AAS)[26–28] or mostly electrothermal atomic absorption spectrometry (ETAAS)[29–31] are used. The ETAAS method was applied in order to directly determine some trace elements (or using simple dilution) in wine.[32,33]

Flame-AAS is largely employed in wine analysis mainly due to the low cost of instrumentation, which makes the technique easily accessible to most oenological laboratories. Considering the compromise between the cost and sensitivity required, flame-AAS can be considered as the technique of choice for determination for alkaline and alkali-earth metal in wine. It is also well suited for Cu, Fe, Mn and Zn determinations, with respect to the concentration ranges of these metals in wines. On the other hand, it is not suitable for the determination of toxic or undesirable elements, such as As, Cd, Cr, and Hg and Pb, with the exception of highly contaminated samples and/or application of preconcentration procedures.

The analysis precision was usually very good, being on average above 1 % for all the elements considered at the mg L^{-1} concentration level.[14,15]

In the present study, a scheme was developed for the determination of Fe, Cu and Zn in different wine fractions. Flame and electrothermal (ET) atomic absorption spectrometry were used for the quantitative determination of the metals, depending on their levels.[4–6,8–13,34]

EXPERIMENTAL

Reagents and materials

All reagents used were of analytical grade (Merck, Germany). Stock standard solutions were prepared daily by the appropriate dilution of Titrisol standards (Merck) containing 1000 mg L^{-1} Fe, Cu or Zn. High purity water from a Milli-Q apparatus was used to prepare the standard solutions.

Sample preparation

Several types of wine samples were investigated: Serbian wine samples were given from vineries and only filtered in the further procedure. Several other commercially bottled wines (Serbian wines) were purchased from the market. Labels descriptions of the analyzed wine samples are presented in Table I. In each case, aliquots of samples were withdrawn with a glass pipette 10 cm below surface level of the liquid.

An aliquot of 5 ml of wine sample was mixed with 1.0 mL of 2 M HCl solution and further diluted to 10 mL with distilled water, and then directly nebulized in an air–acetylene flame under the optimal instrumental parameters (background correction for zinc was required). Fe, Cu and Zn were determined by AAS in the air-acetylene flame using standard calibration curves. All determinations were performed on untreated wine samples; only nitric acid was added to lower the pH (1.0 mL of concentrated acid to 100 mL sample, the resulting pH being 1.5).

TABLE I. Label description of the wine samples

Sample No.	Sample label	Year	Vinery
1	Vranac	2001	Župa
2	Rubinova ružica	2002	Rubin
3	Cabernet Sauvignon	2001	Rubin
4	As	2003	Župa
5	Merlot	2005	Navip
6	Car Lazar	2001	Rubin
7	Medveđa krv	2006	Rubin
8	Pinot Noir	2006	Rubin
9	Kratošija	2003	Župa
10	Međaš crni	2004	Župa
11	Župski rizling	2006	Župa
12	Međaš beli	2001	Župa
13	Vranac	2004	Rubin
14	Navipovo crno Rojal	2001	Navip
15	Rubinovo crno	2003	Rubin
16	Graševina	2005	Rubin
17	Pinot Noir	2001	Navip
18	Terra Lazarica	2006	Navip
19	Jagodinska Ružica	2004	Navip
20	Rose	2002	Župa

Apparatus/analysis

The atomic absorption measurements were realized with a Varian Spectra A 10 atomic absorption spectrometer equipped with a deuterium background corrector and single element hollow cathode lamp of Cu, Fe and Zn. An air–acetylene flame was utilized for all the elements. The calibration range, wavelengths and slit values are reported in Table II.

TABLE II. Calibration range, wavelength and slit value

Characteristics of analysis	Fe	Zn	Cu
Wavelength, nm	248.3	213.9	324.8
Slit, nm	0.2	1.0	0.5
Calibration range, mg L^{-1}	0.06–15.0	0.01–2.0	0.03–10.0

RESULTS AND DISCUSSION

The determined concentrations of heavy metals in the examined wine samples originating from the southeast region of Serbia are reported in Table III.

The measured concentrations of iron (Table III) show that these varied in range from 2.93 (“Cabernet Sauvignon”) to 11.21 mg L^{-1} (“Rose”) with the exception being the wine sample named as “As”. This wine sample had an iron content of 36.2 mg L^{-1}. The concentrations of copper in the different wines also differed a lot, *i.e.*, from 0.07 mg L^{-1} (Graševina and Župski rizling) to 0.57 mg

L$^{–1}$ (“Merlot”), while the zinc concentrations covered a somewhat narrower range, from 0.21 (“Navipovo crno Royal”) to 0.67 mg L$^{–1}$ (“Cabernet Sauvignon”).

TABLE III. Average content of Fe, Cu and Zn in the examined wine samples (*ia* – inaccuracy of measurement (standard deviation at the 95 % confidence level))

Sample No.	Sample label	$c \pm ia$ / mg L^{-1}		
		Fe(III)	Cu(II)	Zn(II)
1	Vranac	6.40±0.19	0.40±0.008	0.48±0.03
2	Rubinova ružica	5.84±0.17	0.39±0.007	0.65±0.04
3	Cabernet Sauvignon	2.93±0.09	0.11±0.002	0.67±0.01
4	As	36.2±1.08	0.14±0.003	0.57±0.03
5	Merlot	6.62±0.19	0.57±0.011	0.62±0.04
6	Car Lazar	4.69±0.14	0.12±0.002	0.61±0.04
7	Medveđa krv	3.17±0.09	0.10±0.001	0.54±0.03
8	Pinot Noir	4.62±0.14	0.17±0.003	0.55±0.03
9	Kratošija	9.78±0.29	0.12±0.002	0.55±0.03
10	Međaš crni	5.03±0.15	0.10±0.001	0.57±0.03
11	Župski rizling	5.37±0.16	0.07±0.001	0.38±0.02
12	Međaš beli	6.82±0.20	0.08±0.001	0.52±0.03
13	Vranac	3.69±0.11	0.16±0.003	0.49±0.03
14	Navipovo crno Royal	4.17±0.12	0.19±0.004	0.21±0.01
15	Rubinovo crno	3.53±0.10	0.22±0.004	0.57±0.03
16	Graševina	4.75±0.14	0.07±0.001	0.47±0.03
17	Pinot Noir	4.22±0.13	0.44±0.009	0.35±0.02
18	Terra Lazarica	6.60±0.19	0.32±0.006	0.64±0.04
19	Jagodinska Ružica	5.51±0.16	0.26±0.005	0.31±0.02
20	Rose	11.21±0.34	0.26±0.005	0.49±0.03

The allowed levels of metal in wines are defined by standards. The established allowed values of the standards differ from country to country, even though there are common standards prescribed by the International Office for Grapes and Wines.[3] An insight into the accepted limits of the content of metals in wines in different countries and also those given by the Office International de la Vigne et du Vin (OIV) are listed in Table IV.

TABLE IV. The accepted limits of the metals content, mg L^{-1}, in wines in different countries

Country	Al	As	Cd	Cu	Na	Pb	Ti	Zn
Australia	–	0.10	0.05	5.00	–	0.20	–	5.00
Germany	8.00	0.10	0.01	5.00	–	0.30	1.00	5.00
Italy	–	–	–	10.00	–	0.30	–	5.00
OIV	–	0.20	0.01	1.00	60.00	0.20	–	5.00

The results obtained in the current study are comparable with previously reported values showing high degree of agreement.[8] Here, the estimated data (Table III) demonstrate that the contents of the major metal, *i.e.*, Fe, and the selected trace elements, *i.e.*, Cu and Zn, in wine samples from different parts of Serbia are considerably smaller than the maximum concentrations allowed according to the OIV, Tables III and IV. In addition, the contents of these trace metals in the studied Serbian wines were significantly lower than in some European wines, but similar to those found in some Slovenian and Hungarian wines.[34,35] Namely, it was reported earlier that the contents of Cu and Zn in some selected Slovenian red wine labels are up to 1.0 and 0.6 mg L^{-1}, respectively.[35] It is obvious that determined metal levels in the present study are completely comparable to the ones in the Slovenian wine samples, whereby the contents of Zn are especially similar, Table III. The estimated concentrations of Zn in Serbian wines are also analogous to those discussed formerly in literature data.[36]

The Hungarian national legislation according to OIV recommendations allows a maximum level of 1 mg L^{-1} Cu in wines and other food products.[34] The corresponding Cu contents varied in the range from 0.02 to 0.64 mg L^{-1} being greatly below the cited limit in all the studied Hungarian wine samples.[34] The results of the present study evidenced fluctuation of Cu contents over a similar range as in Hungarian wines, whereas these contents reported to be a bit higher in the case of later wines. On the contrary, in German red wines,[37] the Cu content was found to be even five times higher than the highest concentration of this element in Hungarian wines and almost the same as in Serbian wines. Similarly, for Australian wines,[38] but white ones, the Cu content ranged within limits almost four times higher than in the selected Serbian wines. Unexpectedly, the Cu level ranged from 0.03 to 0.17 mg L^{-1} in Russian and Italian red and white wines, as well,[39] being noticeably lower than the Cu content in wines originating from other European countries, including Serbian wines. On the other hand, in Russian and Italian wines,[39] the Zn content was reported to be between 0.14 and 0.76 mg L^{-1}, which is completely in accordance to values found in wines produced from other European regions. Opposed to other papers, one review article[1] reported very wide ranges of the Fe, Cu and Zn contents in Italian wines. Somewhat curious is/are the highest/higher value/values of the Fe content/s in selected Serbian wines (Table III), being even higher than all reported values in the review article concerning Canadian wines.

Wine samples from Jordan show relatively high values of metal contents,[40] especially the maximal determined levels, but most of the estimated values were below the toxic limit in food (Swiss Standard, 1993). This may be explained by the homemade production procedure applied.

The presence of some other trace metals, such as: lead, manganese, cadmium and nickel, was not detected in the examined wine samples.

The concentration of metals in alcoholic beverages may vary widely depending on the plant origin and the technology used (home-made or by an official producer). Moreover, it was recently reported that some home-produced alcoholic beverages and spirits contain rather high concentrations of metals.[8] In addition; it was observed that alcoholic beverages from Africa, India and Canada possess higher metal concentrations, *i.e.*, 58, 68 and 245 mg L^{-1} of Cu, Zn and Fe, respectively.[41]

The concentrations of metals and trace metals in wines depend on the metal content in the vineyard soil, which primarily determines the degree of metal uptake by the grape plant. In addition, anthropogenic impact plays a vital role in determining the metal content in wines. Namely, as was stated above before, some home-made wines showed a higher trace element content, probably due to contamination during the wine-making process and/or the mixing/storage procedure, and also additives used.

It is worth emphasizing that the allowed limits for metal contents in alcoholic beverages are higher than those imposed for water envisaged for human consumption.[8] This may be related to the lower predicted intake of alcoholic beverages.

The variation of the discussed levels of metals concentrations in the present study as well as those reported earlier by other authors suggest a necessity for the establishment of common limits.

CONCLUSIONS

Different metals occur in wines at the mg L^{-1} and/or μg L^{-1} level not directly influencing the taste of the end product. Nevertheless, their content should be determined because excess is undesirable due to potential toxicity and risks to human health, consequently imposing the maximal allowed values and/or prohibited limits. The contents of the investigated metals (Fe, Cu and Zn) in wine samples from different areas of Serbia are considerably lower than the maximum concentrations allowed according to the OIV. The contents of selected trace metals were significantly lower than those of some European wines, but similar to the values found in some Slovenian and Hungarian wines. Additionally, these contents were compared with known literature values. Somewhat curious is the relatively high Fe content in the selected Serbian wines (“As” and “Rose”). The variation in the metal content in the studied Serbian wines may be related to the metal content in the vineyard soil, *i.e.*, soil type, and/or an anthropogenic impact arising from the wine-making process and/or storage procedure.

Acknowledgement. The financial support of the Ministry of Science and Technological Development of the Republic of Serbia (Project No. ON 142051) is highly appreciated.

И З В О Д

КОНЦЕНТРАЦИЈА Fe, Cu И Zn У ОДАБРАНИМ ВИНИМА ЈУГОИСТОЧНЕ СРБИЈЕ

ДАНИЈЕЛА КОСТИЋ, СНЕЖАНА МИТИЋ, ГОРДАНА МИЛЕТИЋ, САША ДЕСПОТОВИЋ
и АЛЕКСАНДРА ЗАРУБИЦА

Природно-математички факултет, Универзитет у Нишу, 18000 Ниш

Воће и поврће представљају најјефтинији извор есенцијалних метала, који се јављају у траговима, за највећи део становништва развијеног света. Садржај Cu, Fe и Zn је одређен пламеном атомско апсорпционом спектрометријом у двадесет узорака одабраних вина, пореклом из региона Југоисточне Србије. Концентрација Cu варира од 0,07 до 0,57 ppm у испитиваним винима, гвожђа од 2,93 до 36,2 ppm, док је ниво Zn у интервалу од 0,21 до 0,67 ppm. Установљен садржај Cu и Zn показује да вина из овог дела света могу бити добар дијететски извор есенцијалних метала, заступљених у траговима; одређени садржаји метала су у границама дозвољених вредности у људској исхрани.

(Примљено 4. јануара, ревидирано 30. јула 2010)

REFERENCES

1. M. Aceto, O. Abollino, M. C. Bruzzoniti, E. Mentasti, C. Sarzanini, M. Malandrino, *Food Addit. Contam.* **19** (2002) 126
2. S. Mitić, J. Vučetić, S. Miletić, D. Kostić, *J. Serb. Chem. Soc.* **65** (2000) 595
3. B. Zoecklein, K. Fugelsang, B. Gump, F. Nury, *Wine Analysis and Production*, Chapman & Hall, New York, 1994
4. J. Wang, S. Mannino, *Analyst* **114** (1989) 643
5. C. Marin, P. Ostapczuk, *Fresenius J. Anal. Chem*. **343** (1992) 881
6. H. Eschnauer, P. Ostapczuk, *Wein-Wiss.* **47** (1992) 206
7. S. Ražić, Dj. Čokeša, S. Sremac, *J. Serb. Chem. Soc.* **72** (2007) 1487
8. J. Ibanez, A. Carreon-Alvarez, M. Barcena-Soto, N. Casillas, *J. Food Composition Anal.* **21** (2008) 672
9. M. Arcos, M. Ancin, J. Echeverria, A. Gonzales, J. Garrido, *J. Agric. Food Chem.* **41** (1993) 2333
10. P. Ostapczuk, *Anal. Chim. Acta* **273** (1993) 35
11. E. Zakharova, V. Pichugina, T. Tolmacheva, *Zh. Anal. Khim.* **51** (1996) 918
12. S. Sanllorente, O. Cruz, M. J. Arcos, *Analyst* **123** (1998) 513
13. O. Domingez, S. Sanllorente, M. Arcos, *Electroanalysis* **1** (1999) 1273
14. S. May, J. Leroy, D. Piccot, G. Pinte, *J. Radioanal. Chem.* **72** (1982) 305
15. H. Eschnauer, L. Jakob, H. Meierer, R. Neeb, *Microchim. Acta* **3** (1989) 291
16. J. Goossens, T. De Smaele, L. Moens, R. Dams, *Fresenius J. Anal. Chem.* **347** (1993) 119
17. S. Augagneur, B. Medina, J. Bernard, Szpunar, R.Lobinski, *J. Anal. At. Spectrom.* **11** (1996) 713
18. G. Weber, G. Schwedt, *Anal. Chim. Acta* **134** (1982) 81
19. C. Garcia-Jahres, M. Lage-Yusty, J. Simal-Lozano, *Fresenius J. Anal. Chem.* **338** (1990) 703
20. K. Ohzeki, I. Nukatsuka, K. Ichimura, F. Kumagai, M. Kogawa, *Microchem. J.* **49** (1994) 256
21. S. Cherubin, S. Buiatti, F. Battistutta, R. Zironi, *Wein-Wiss.* **49** (1994) 78
22. T. Stafilov, J. Cvetkovic, S. Arpadjan, I. Karadjova, *BAÜ Fen Bil. Enst. Dergisi* **4.2** (2002) 90
23. R. Farre, M. Lagarda, *J. Micronutr. Anal.* **2** (1986) 201

24. J. Korkisch, A. Sorio, I. Steffan, *Talanta* **23** (1976) 289
25. U. Anders, G. Hailer, *Fresenius J. Anal. Chem.* **278** (1976) 203
26. D. Siemer, R. Vitek, P. Koteel, H. Prabhakaran, W. Houser, *Anal. Lett.* **10** (1977) 357
27. J. Sanz, P. Basterra, J. Galban, J. R. Castillo, *Mikrochim. Acta* **1** (1989) 271
28. M. Segura, Y. Madrid, C. Camara, *J. Anal. At. Spectrom.* **14** (1999) 131
29. M. Segura, J. Grgic, Z. Grgic, B. Segura, *Dtsch. Lebensm.-Rundsch.* **94** (1998) 336
30. E. Lendinez, M. Lopez, C. Cabrera, M. Lorenzo, *J. AOAC Int.* **81** (1998) 1043
31. C. Cabrera-Vigne, P. Teissedre, M. Cabanis, J. Cabanis, *Am. J. Enol. Vitic.* **51** (2000) 103
32. B. Kildahl, W. Lund, *Fresenius J. Anal. Chem.* **354** (1996) 93
33. C. Cabrera-Vique, P.-L. Teissedre, M.-T. Cabanis, J. Cabanis, *J. Agric. Food Chem.* **45** (1997) 1808
34. Z. Ajtony, S. Zoboszlai, E. Klaudia Susko, P. Mezei, K. Gyorgy, L. Bencs, *Talanta* **76** (2008) 627
35. J. Kristl, M. Veber, M. Slekovec, *Acta Chim. Slov.* **50** (2003) 123
36. K. Bauer, S. Hinkel, R. Neeb, R. Eicher, H. Eschnauer, *Vitic. Enol. Sci.* **49** (1994) 209
37. C. Wiese, G. Schwedt, *Fresenius J. Anal. Chem.* **358** (1997) 718
38. L. Sauvage, D. Frank, J. Stearne, M. B. Millikan, *Anal. Chim. Acta* **458** (2002) 223
39. Kh. Z. Brainina, N. Yu. Stozhko, G. Belysheva, O. Inzhevatova, L. Kolyadina, C. Cremisini, M. Galletti, *Anal. Chim. Acta* **514** (2004) 227
40. F. Al Nasir, A. Jiries, M. Batarseh, F. Beese, *Environ. Monit. Assess.* **66** (2001) 253
41. C. Reilly, *J. Sci. Food Agric.* **23** (1972) 1143.