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Original Article

Estimation of heavy metals in wines using atomic absorption spectrometry

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ABSTRACT

Some heavy metals like Cu, Cd, Co, Pb, Zn, and Fe are indispensable for us in very small quantities and are essential for human life in low concentrations, but at higher content in foods they are hazardous and toxic for people. The article presents the estimation of heavy metal content in red and white varietal wines in different vintages from south Slovakia with protected designation of origin (PDO) "Južnoslovenská". The white wine variety "Rizling vlašský" vintage 2007 (Riesling blanc), as well as the red variety "Frankovka modrá" vintage 2007 (Blaufrankisch), was determined by atomic absorption spectrometry (AAS). The amounts of Pb were found to be 59 $\mu g.dm^{-3}$ and 73 $\mu g.dm^{-3}$, respectively. The Cd content was 1.60 $\mu g.dm^{-3}$ and 1.79 $\mu g.dm^{-3}$, respectively and the content of Cu was 183 $\mu g.dm^{-3}$ and 262 $\mu g.dm^{-3}$, respectively. After 13 years the white wine variety "Rizling rýnsky" vintage 2020 (Rheinriesling) from the same PDO "Južnoslovenská" was tested and determination of the metals Pb, Cu, and Fe by Atomic Absorption Spectrometry with Electrothermal Atomization (AAS-ETA) was performed. The red wine variety "Frankovka modrá" vintage 2020 was tested by AAS-ETA. The metal amounts were Pb 10 $\mu g.dm^{-3}$, Cu 220 $\mu g.dm^{-3}$ and Fe 390 $\mu g.dm^{-3}$ in white and 66 $\mu g.dm^{-3}$ Pb, 420 $\mu g.dm^{-3}$ Fe and 195 $\mu g.dm^{-3}$ Cu in red wine. This study aimed to examine whether the wines in the different vintages vary according to the content of heavy metals. Data analysis showed no statistically significant differences and no contamination was found.

KEYWORDS: metals in wine, Cu, Cd, Pb, Fe determination, atomic absorption spectrometry.

1. INTRODUCTION

Cadmium, Copper and Lead are common and dangerous contaminants in the environment [1] and their determination in samples with high amounts of salts or sugars is not easy. These elements are naturally occurring in wine grapes and, as such, are normally present in the wine produced from them. Concentrations of these elements can vary from region to region and from variety to variety due to the presence of nutrients in the soil. EU survey shows that industrialized countries in Europe influence the concentrations of heavy metals in wine and European wines contain twice as much lead (average 63 $\mu g.dm^{-3}$) as Australian wines (average 28 $\mu g.dm^{-3}$) [2]. Contamination of wine is not desirable; therefore it is very useful to determine heavy metals by suitable methods.

To reduce the interferences in spectral lines many methods and procedures, including the Zeeman effect, background correction, and modificators are used in AAS. The optical emition spetrometry methods with inductively coupled plazma (ICP-OES) and ICP/MS have commonly been

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developed for the determination of As, Cd, Cu, Ni, and Pb in the range 0.5-50 mg/kg by mass spectrometer with microconcentric nebulizer Calibration was carried out routinely with standard solutions (20 μg.dm^{-3} analyte) and blank solutions as proposed by Owen T. Butler [3] but this method is rather expensive and time-consuming. Determination of Cu by AAS-F in Czechishe wines vintage 2007-2009 was done and the content varied from 0.03 mg.dm^{-3} Cu to 0.48 mg.dm^{-3} Cu [4]. The authors used the method OIV/MA-E-AS322/06 with an uncertainty of 0.04 mg.dm^{-3} and with a limit of detection (LOD) of 0.009 mg.dm^{-3}. Stripping chronopotentiometry is also a very useful method for the determination of Cd, Pb, and Zn in must and wines. Stripping chronopotentiometry with microwave sample preparation is a suitable method for the determination of heavy metals in wine. The guaranteed accuracy of the method checked against reference material of wine TITRIVIN is lower than 10% for the μg.dm^{-3} concentration level with very low limit of detection (LOD) limits [5]. Atomic Absorption Spectrometry with Electrothermal Atomization (AAS-ETA) and AAS with Flame are common methods for the determination of heavy metals [6]. Mineral compounds in wine with content of only a few mg.dm^{-3} (Fe, B, Si, Mn, Zn) and metals indispensable for us like essential ions (Al, Cu, F, Co, As, Pb, Cd) with content of only a few μg.dm^{-3} are crucial for the nutrition of yeasts during fermentation of wine and give the wine important odour and taste characteristic [7]. The study aims to determine and compare heavy metal content in red and white quality variety wines from the Slovakian "Južnoslovenská" region.

2. MATERIALS AND METHODS

Quality variety wines (red and white) with protected designation of origin (PDO) defined in law Commission Regulation No 607/2009 from south Slovakia wine growing region "Južnoslovenská" were chosen from famous winemakers: BSC Slovakia s.r.o., HUBERT J.E. s.r.o. and vinárske závody Topoľčianky s.r.o. In the vintage 2007 red variety Frankovka modrá (Blaufrankisch) and white variety Rizling vlašský (Riesling blanc) wines were taken from famoust Slovakia vineries and Cd, Pb, and Cu in them were determined by Atomic Absorption Spectrometry; also the Organisation Internationale de la Vigne et du Vin (OIV) methods were used for determining common parameters in these wines (Compendium of International Methods of Wine Analysis).

AAS-ETA method, using AA-6800 with graphite furnace Fy Shimadzu, for determination of Cu, Fe, and Pb in the white wine variety Rizling rýnsky (Rhienriesling) vintage 2020 (taken from Hubert J. E.) was applied in this work. Working standard solutions were prepared from standards produced by Merck. Nitric acid, modificator $Pd+Mg(NO3)_2$, demineralized water, Halow Cathode lamps with the resonance lines Pb = 283, 3 nm, Cu = 324, 8 nm and Fe = 248, 3 nm, Argon, atomization temperature 2600 °C and 20 μl of the sample were used.

AAS-F (AA220 Flame-Varian) for determination of Fe in the red wine variety Frankovka modrá (Blaufrankisch) vintage 2020 (sample taken from Topoľčianky s.r.o.) as well as AAS-ETA (SpectrAA240-Varian with Zeeman effect) determination of Cu and Pb in this red wine were used.

3. RESULTS AND DISCUSSION

The results from atomic absorptin spectrometry show (see Table 1) a little higher content of Cu in the red wine than in the white wine. The average Cu in red wine was found to be 0.262 mg.dm^{-3} and that in white wine was 0.183 mg.dm^{-3}. The role of copper in wine is multifold, as it is involved in oxidative transformations in wine ageing and if its content is too high, the wine undergoes oxidation-reduction reactions leading to browning of the wine, turbidity and astringency. The content of Pb was 73.5 μg.dm^{-3} in red and 59 μg.dm^{-3} in the white wine and is comparable with other European countries like Bulgaria (67 μg.dm^{-3} Pb) [8] and Croatia (101 μg.dm^{-3}) [9]. The maximum acceptable limit for Pb in wine is 0.15 mg.dm^{-3}, for As is 0.2 mg.dm^{-3}, for Cd is 0.01 mg.dm^{-3} and that for Cu is 1 mg.dm^{-3} [10-12]. The Cd content in Slovak wines is usually below the limit of quantification. The Cd content we determined in white wine was 1.6 μg.dm^{-3} and that in red wine was 1.8 μg.dm^{-3} Cd. This AAS method is suitable and very precise for the

Table 1. Determination of Cd, Pb, and Cu in the red and white wine vintage 2007.

Sample	Alcohol	Acids	SO_2	Cd	Pb	Cu*
Red 1	12.07	6.2	147	1.8	77.7	281
Red 2	12.06	5.8	180	1.8	69.3	243
Average	12.065	6.0	163	1.8	73.5	262
White 1	12.61	5.3	107	1.4	62	186
White 2	12.80	4.3	114	1.7	55	180
Average	12.71	4.7	111	1.6	59	183

*Alcohol is given in % vol., total acids in $g.dm^{-3}$, total SO_2 in $mg.dm^{-3}$ and Cd, Cu, and Pb are given in unit $\mu g.dm^{-3}$.

Table 2. Determination of Fe, Pb, and Cu in the red and white wine vintage 2020.

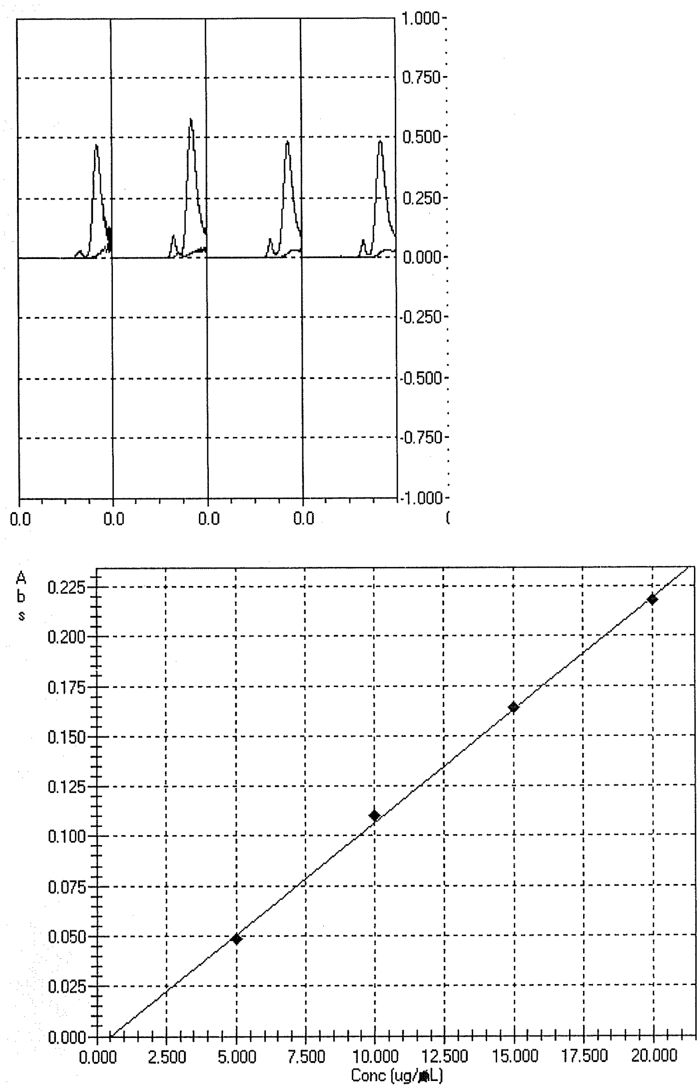
Sample	Alcohol	Acids	SO_2	Cu	Pb	Fe*
Red 1	12.7	6.1	149	194	67	421
Red 2	12.8	5.9	145	196	65	419
Red	12.75	6.0	146	195	66	420
White 1	12.69	6.0	114	218	10.4	400
White 2	12.60	6.2	118	230	10.6	390
White	12.64	6.1	116	224	10.5	395

*Alcohol is given in % vol., total acids in $g.dm^{-3}$, total SO_2 in $mg.dm^{-3}$, Cu, Pb, and Fe are given in unit $ug.dm^{-3}$.

measurement of Cd, Cu and Pb. The atomization process of metal determination in wine samples and vaporization process at 2600 °C could be seen on a computer monitor through a camera using SpectrAA240-Varian with Zeeman effect. Common parameters in this red and white wine vintage 2007 were measured by OIV methods [13].

This OIV methods MA-AS312-01, MA-AS313-01, MA-AS323-04, MA-AS313-02 and MA-AS323-04B were used for measuring common parameters like alcohol, total acids and SO_2 in wines. The levels of heavy metals in the red and white wine vintage 2020 determined by AAS-ETA are shown in Table 2. The content of Cu in red and white wine vintage 2020 was found to be almost same (average Cu 0.195 $mg.dm^{-3}$ in red and 0.224 $mg.dm^{-3}$ in white wine).

The excellent correlation between the calibration standards demonstrates the value of the automatic in-line sample and standard dilution available on the ETA-AAS. The calibration curve of Cu measurement is shown in Figure 1. The content of Pb was lower in white wine (0.010 $mg.dm^{-3}$) and higher in red wine (0.066 $mg.dm^{-3}$). The content of Fe was almost the same in red and white wine vintage year 2020 (average of 0.4 $mg.dm^{-3}$). Limits for Cu, Fe, and Mn in wine are 1, 8, and 2 $mg.dm^{-3}$, respectively. The limits by Commission Regulation (EC) No 606/2009 and by OIV resolutions for Pb, Cu, Zn, and Fe are 0.15 $mg.dm^{-3}$, 1 $mg.dm^{-3}$, 5 $mg.dm^{-3}$ and 10 $mg.dm^{-3}$, respectively. The advantage of AAS-ETA (SpectrAA-240Varian) is that the calibration process is automatic and that the atomization process can be viewed through a camera. AAS-ETA is a suitable method for Pb and Cu determination in dry wines. AAS with flame is suitable for measuring Cu, and Fe; more over AAS-F could determine Fe in wine very fast and this is an advantage because this metal contributes to haze formation in wines and should be determined very fast. Grapes have the potential to



Abs=0,011249c-0,0056

R=0,9994

Figure 1. Calibration curve of Cu determination in wine by ETA-AAS.

produce great wines under the right circumstances, but the choices made by growers and winemakers are key, as are factors like soil and climate.

4. CONCLUSIONS

Grape must and wine always contain relatively large amounts of heavy metals that come from vines and grapes, but most of it originates from sprays used to treat vines, soil, agricultural insecticide or atmospheric pollution [14]. Most of the heavy metals (Fe, Pb, Cu, Cd) in the grapes precipitate during fermentation into the sediments. Therefore their content is lower in the wine than in the must. The objective of this study was to compare heavy metal content in wines from the same place "Južnoslovenská" during 2007 and 2020 harvest. No contamination was found after 13 years. Our aim is to share knowledge on heavy metal measurement and on the technological aspects that higlight the important role of metal ions.

This work demonstrated the ability of AAS spectrometers to accurately measure Cu, Pb, and Cd in the quality variety wines at low levels. The estimation of total metal content is also useful for characterizing wine and classifying it according to geographical origin. Metals in wine have an impact on wine quality and the health of the consumer. Therefore the maximum acceptable limits for trace elements in wine have been established in each national legislation in almost all countries.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest. Authors declare that the funders had no role in the design of the study, in the collection, analyses, or interpretation of data, or in the writing of the manuscript.

REFERENCES

1. Tokahoglu, S. and Gurbuz, F. 2010, Food Chemistry, 123, 183.
2. Ribéreau-Gayon, P., Glories, Y., Maujean, A. and Dubourdieu, D. 2001, Handbook of Enology, Vol. 2, The Chemistry of Wine Stabilization and Treatment, WILEY.
3. Butler, O. T., Cairns, W. R. L., Cook, J. M. and Davidson, C. M. 2017, J. Anal. Atom. Spectrom., 32, 11-57.
4. Knápek, J., Buchtová, R. and Vošmerová, D. 2010, Proceedings of the 14. Česko-Slovenské Spektroskopické Konference, Litomyšl 31.5.-3.6. 2010, Univerzita Pardubice, Cz., ISBN 978-80-7395-282-2.
5. Lastincova, J., Beinrohr, E. and Pospíšilová, Ľ. 2011, J. Life Sci., 5, 768-771.
6. Spivey, N. and Thompson, P. 2016, Application Note Atomic Absorp., 2016 Perkin Elmer Inc., Shelton, CT.
7. Šprláková, K. 2011, Influence of grapevine growing methods on the quality of the wine. Bachelorś thesis, Brno University of Technology, Faculty of Chemistry, Institute of Food Science and Biotechnology, Cz.
8. Angelova, V., Ivanov, A., Braikov, D. and Ivanov, K. 1999, J. Int. Sci. Vigne. Vin., 33(3), 119-131.
9. Banovič, M., Kirin, J., Čurko, N. and Kovačevič Ganič, K. 2009, Czech J. Food Sci., Vol. 27, Special Issue, pp. 401-403.
10. Blanka, T. 2011, Biological Trace Element Research, Vol. 144, 143-156. doi:10.1007/s12011-011-9052-7.
11. Commission Regulation (EC) No 606/2009 from 10.7.2009.
12. Commission Regulation (EC) No 607/2009 from 10.7.2009.
13. Compendium of International Methods of Wine Analysis-OIV, Vol. 2, Edition 2009, Paris.
14. Florin-Dumitru Bora, Claudiu-Ioan Bunea, Teodor Rusu and Nastasia Pop, 2015, Chem. Cent. J., 9, 19. doi:10.1186/s13065-015-0095-2.