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 µg.dm⁻³ and 73 µg.dm⁻³, respectively. The Cd content was 1.60 µg.dm⁻³ and 1.79 µg.dm⁻³, respectively and the content of Cu was 183 µg.dm⁻³ and 262 µg.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 µg.dm⁻³, Cu 220 µg.dm⁻³ and Fe 390 µg.dm⁻³ in white and 66 µg.dm⁻³ Pb, 420 µg.dm⁻³ Fe and 195 µg.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 µg.dm⁻³) as Australian wines (average 28 µg.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 modifiers are used in AAS. The optical emission spectrometry methods with inductively coupled plasma (ICP-OES) and ICP/MS have commonly been
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 Czech 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, Fe, 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 vinárské 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 famous Slovakia wineries 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 (Rhinriesling) vintage 2020 (taken from Hubert J. E.) was applied in this work. Working standard solutions were prepared from standards produced by Merck. Nitric acid, modifier 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
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 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; moreover 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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alcohol</th>
<th>Acids</th>
<th>SO$_2$</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red 1</td>
<td>12.07</td>
<td>6.2</td>
<td>147</td>
<td>1.8</td>
<td>77.7</td>
<td>281</td>
</tr>
<tr>
<td>Red 2</td>
<td>12.06</td>
<td>5.8</td>
<td>180</td>
<td>1.8</td>
<td>69.3</td>
<td>243</td>
</tr>
<tr>
<td>Average</td>
<td>12.065</td>
<td>6.0</td>
<td>163</td>
<td>1.8</td>
<td>73.5</td>
<td>262</td>
</tr>
<tr>
<td>White 1</td>
<td>12.61</td>
<td>5.3</td>
<td>107</td>
<td>1.4</td>
<td>62</td>
<td>186</td>
</tr>
<tr>
<td>White 2</td>
<td>12.80</td>
<td>4.3</td>
<td>114</td>
<td>1.7</td>
<td>55</td>
<td>180</td>
</tr>
<tr>
<td>Average</td>
<td>12.71</td>
<td>4.7</td>
<td>111</td>
<td>1.6</td>
<td>59</td>
<td>183</td>
</tr>
</tbody>
</table>

*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 µg.dm$^{-3}$.  

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alcohol</th>
<th>Acids</th>
<th>SO$_2$</th>
<th>Cu</th>
<th>Pb</th>
<th>Fe*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red 1</td>
<td>12.7</td>
<td>6.1</td>
<td>149</td>
<td>194</td>
<td>67</td>
<td>421</td>
</tr>
<tr>
<td>Red 2</td>
<td>12.8</td>
<td>5.9</td>
<td>145</td>
<td>196</td>
<td>65</td>
<td>419</td>
</tr>
<tr>
<td>Red</td>
<td>12.75</td>
<td>6.0</td>
<td>146</td>
<td>195</td>
<td>66</td>
<td>420</td>
</tr>
<tr>
<td>White 1</td>
<td>12.69</td>
<td>6.0</td>
<td>114</td>
<td>218</td>
<td>10.4</td>
<td>400</td>
</tr>
<tr>
<td>White 2</td>
<td>12.60</td>
<td>6.2</td>
<td>118</td>
<td>230</td>
<td>10.6</td>
<td>390</td>
</tr>
<tr>
<td>White</td>
<td>12.64</td>
<td>6.1</td>
<td>116</td>
<td>224</td>
<td>10.5</td>
<td>395</td>
</tr>
</tbody>
</table>

*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 µg.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
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 highlight 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.

REFERENCES