Assessment of Copper Content in Wines from Tohani-Dealul Mare by Flame Atomic Absorption Spectrometry

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Knowledge of the content of microelements from wine is important due to their influence on wine quality and also from toxicological point of view. The presence of heavy metals in wine is a consequence of different factors as metal content in vineyard soil, application of fertilizers and pesticides and also is a result of environmental pollution. Our study was undertaken in order to assess by FAAS means the copper content of some wine samples from Tohani-Dealul Mare. The analyses indicated that average copper concentrations range between 0.286-0.347 mg/L for Târâioasă Romanesca, 0.255-0.342 mg/L for Sauvignon Blanc, 0.373-0.482 mg/L for Riesling Italian, 0.463-0.538 mg/L for Fetească Albă, 0.295-0.454 mg/L for Buzioaeacă de Bohotin and 0.122-0.214 mg/L for Fetească Neagră. All values were below 1 mg/L, maximum allowable limit set by OIV.

Keywords: copper, wine, FAAS

Wine is a natural product with a complex chemical composition: tartaric acid, malic acid, phenolic compounds, vitamins, minerals, microelements, water, sugar and alcohol. The quantitative level of various compounds of wine allows oenologists to control the process of obtaining high quality wine with desired properties: taste, bouquet, flavor, transparency, and colour.

Some metals influence clarity, aroma and sensorial properties of wine [1]. For example, Cu, Fe, Mn participates in destabilization of wine and in their oxidative evolution [2], meanwhile Fe, Al, Zn, Ni produce undesirable changes of aroma and taste [3]. Cu, Fe and Mn are involved in oxidoreductive reactions resulting from wine browning, case, turbidity or astringency [4]. The mineral content is often used to characterize the wines by their authenticity and geographical origin [5].

The concentrations of metals and trace metals in wines depend primarily on the metal content in the vineyard soil, which influence the degree of metal uptake by the vine [6]. Contamination of grapes in a vineyard could be originating from soil which means that depend on geographical location or could have environmental origin (atmospheric deposition of airborne particulate matter) [7-8]. Others like usage of fertilizers could affect the metallic content of wines. Application of some pesticides could influence the higher contents of Cu, Mn and Zn in wines [9].

In different studies, the content of metallic elements has been evaluated from nutritional and toxicological purposes [10-11]. Moderate wine consumption contributes to the daily intake of many essential elements, such as Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Zn [12].

The aim of this paper was to establish the copper concentration in some wines and to compare with limits set by OIV. As the official methods for determination of metals in wine recommended by OIV are based on atomic absorption spectrometry, we chose this analytical technique to assess copper content.

Copper is widely distributed in nature and is an essential microelement for humans. It functions as a part of many enzymes involved in oxidoreductive processes [13]. The variety of enzymes includes cytochrome c oxidase, tyrosinase and p-hydroxyphenylpyruvate hydratase [14].

The copper content is correlated with wine quality. High levels of copper can cause spoilage leading to pinking of red wine as well as haze formation [15].

Apart from the bitter metallic taste caused by the presence of excessive amount of copper in wine, copper it is considered toxic above some daily intake [16]. Symptoms of copper poisoning include nausea, vomiting, abdominal and muscle pain [17]. Copper becomes toxic in amounts higher than 2-3 mg/day. It has been shown that musts generally contain 1-4 mg/L due to pesticidal treatments [18].

The research was developed during 2009-2011 and was undertaken in order to assess the copper content of some wine samples from Tohani-Dealul Mare. Agrochemical soil analyses were presented elsewhere [19].

Because copper deficiency and also copper excess produce adverse effects on humans, we consider that is important to monitor copper levels in wine, moreover in our country is a tradition to produce and consume wine. According to OIV [20], the maximum allowable limit of copper in wine is 1 mg/L.

The study was undertaken considering that copper possesses an important role in wine processes and to our knowledge, similar studies regarding copper content for Romanian wines are poorly represented.

Experimental part

Description of the area

Tohani is a locality in Prahova County, Romania. From geographical point of view, Tohani is located in a downy area covered by the Curvature Sub-Carpathians and it became known over time because of the important wine-growing areas.

In Tohani area, the most common soils are cambisol, luvisol, regosol. These are soils with medium texture in the upper horizon and are characterized by moderate natural fertility.

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The climate is temperate continental with cold winters and hot summers. The average annual temperature is 11.3°C and the recorded mean annual precipitation is 642 mm.

**Wine samples**

There were analyzed 4 wine samples (bottled) from each variety (6 varieties) every year. 50 mL sample of wine has been calcinated at 450°C and brought down to 10 mL volume with nitric acid, 0.1 mol/L. The sample preparation was made according to SR EN 14082:2003 [21].

**Reagents and materials**

All used reagents were ultrapure grade. High purity water from a Milli-Q apparatus was used to prepare the standard solutions. The calibration curve for copper is linear for the studied ranges and was plotted by running different concentrations of standard solutions prepared from a stock solution of 1000 mg/L copper provided by Merck.

All glassware that were used were kept at least 24 h in HNO₃ 10% and rinsed with ultrapure water before use.

**Equipment**

Measurements were carried out using Zeenit700 Analytic Jena atomic absorption spectrometer. Working parameters are, as it follows: wavelength for copper-324.8 nm, slit width 1.2 nm, air-acetylene flame, fuel flow 40L/h.

**Results and discussions**

Copper is indispensable trace element for normal functions of plant issues. At low concentration is involved in oxidative transformations that occurs in red wine ageing, promotes oxidation of iron and white casse. At the concentrations around 1 mg/L causes turbidity. At high doses it is toxic, which justifies the legal limit of 1 mg/L [22].

During vegetation period, every year in vineyard were applied treatments that contained copper free products (for example, Mancozeb, Fenazaquin, Dinocap, Metiram, Pyraclostrobin, Cypermethrin, Tetcobanazol, sulphur) but also copper hydroxide, copper oxychloride. It is widely known that in viticulture, copper compounds are used to control downy mildew (Plasmopara viticola), botrytis (Botrytis cinerea) [23].

Soil chemical analyses, presented in a previous study [19] revealed that total copper content, higher than maximum allowable limit (20 mg/kg) but below alert level (100 mg/kg) [24], it is accumulated mainly in the surface layer (0-20 cm). With an exception, the same variation was found for the mobile form of copper in soil.

A set of 72 wine samples (white, red, rosé) obtained from six grape varieties were analyzed in order to determine the copper content. It was analyzed Tâmâioasă Româneasca, Sauvignon Blanc, Riesling Italian, Fetească Albă (white wine), Busuioacă de Bohotin (rosé wine) and Fetească Neagră (red wine), produced by Tohani Dealu Mare. From each wine variety have been 4 samples/year analyzed, totalizing 12 samples of each type.

During the vinification process, copper content may vary, decreasing because of the formation of insoluble precipitates or increasing due to corrosion processes from used equipment [18].

Regarding crops, some authors reported that no correlation was observed between total and/or extractable copper concentrations and its contents in plants or plants organs [25].

The results are presented in table 1 and table 2. Low CV values indicate that the average is representative for all series.

Wine’s copper content assessment revealed that all concentrations were below 1 mg/L. The highest value was recorded for Fetească Albă with an average of 0.538 mg/L for samples obtained in 2011. Our study showed that white wines contain higher doses of copper than Fetească Neagră, red wine. Literature studies indicated that red wines undergo higher must aeration during the winemaking process and their higher oxygen content may increase copper oxidation and copper salt precipitation.
This causes, usually a higher copper content in white wines as reported in [26].

Copper content found in analyzed wine samples present almost the same variation with wines from different countries (table 3).

High residual copper can contribute to the phenomena called “browning”, met particularly in white wines. This represent one of the most acute enological problem for wine producers and copper is one of the metallic ions that are activators of the “browning”. It supposes a process of continuous oxidation, a loss of aromatic freshness, the appearance of precipitates of condensed phenolic material in the bottled wine.

To minimize the occurrence of these problems, it is generally recommended to maintain copper concentration in the range 0.3-0.5 mg/L or lower [36]. Analyzed white wines from Tohani-Dealu Mare accomplish this recommendation and there is no danger to appear undesired “browning”.

Conclusions

A research regarding copper content in six wines (white, rosé and red) from Tohani-Dealu Mare was developed and revealed that in all cases, the copper level was below 1 mg/L, limit set by OIV. As copper content in wines could be affected by phytosanitary vineyard treatments, soil processes of red wines. The analytical values were in agreement with those reported in literature and there is no toxicological danger regarding consuming of these wine sorts.

The occurrence of “browning” in white wines is minimal. So, no doubt their copper content is situated at recommended levels.

Knowledge of the metal content of wine is crucial for not only winemakers but also for consumers. Certainly, because of the nutritional value of metals in wine, analysis of the total contents of major, minor and trace metals is of a particular interest with respect to quality and safety of wine.

All analyzed wine samples meet the OIV requirements concerning maximum allowable limit of copper and pose no danger for consumers, from this point of view.

References