Short Note:

The Impact of Vintage on Copper Levels in Slovakian Wines

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Abstract

The article explores the effects of climate change on the copper content in Slovakian wines. The aim was to quantify the copper content in red and white wines of different vintages from southern Slovakia with the protected designation of origin "Južnoslovenská". The white wine varieties "Rizling vlašský" (RV) from the 2007 vintage and "Rizling rýnsky" (RR) from the 2016, 2020, 2021 and 2022 vintages as well as the red wine variety "Frankovka modrá" (FM) from the 2016, 2020, 2021 and 2022 vintages from the same region were analysed using ETA-AAS. The copper content in the white wines was between 183 µg/l and 255 µg/l, while values between 262 and 295 µg/l were found in the red wine variety "Frankovka modrá". The main aim of the study was to determine whether the increasing evidence of global warming could be linked to higher copper levels in wines. The available data suggest that there is a potential correlation between global warming and copper levels in wines.

Keywords: Metals in wine, Cu determination, Cu content of different vintages

Zusammenfassung

Der Einfluss des Jahrgangs auf den Kupfergehalt in slowakischen Weinen. In dem Artikel werden die Auswirkungen des Klimawandels auf den Kupfergehalt in slowakischen Weinen untersucht. Ziel war es, den Kupfergehalt in Rot- und Weißweinen verschiedener Jahrgänge aus Südslowakei mit der geschützten Ursprungsbezeichnung "Južnoslovenská" zu quantifizieren. Analysiert wurden die Weißweinsorten "Rizling vlašský" (RV) aus dem Jahrgang 2007 und "Rizling rýnsky" (RR) aus den Jahrgängen 2016, 2020, 2021 und 2022 sowie die Rotweinsorte "Frankovka modrá" (FM) aus den Jahrgängen 2016, 2020, 2021 und 2022 aus derselben Region mittels ETA-AAS. Der Kupfergehalt in den Weißweinen lag zwischen 183 µg/l und 255 µg/l, während bei der Rotweinsorte "Frankovka modrá" Werte zwischen 262 und 295 µg/l festgestellt wurden. Hauptziel der Studie war es zu ermitteln, ob die zunehmenden Hinweise für die globale Erwärmung mit höheren Kupferwerten in Weinen in Verbindung gebracht werden können. Die verfügbaren Daten deuten darauf hin, dass ein potenzieller Zusammenhang zwischen der globalen Erwärmung und den Kupfergehalten in Weinen besteht.

Schlagwörter: Metalle in Wein, Cu-Bestimmung, Cu-Gehalt verschiedener Jahrgänge

Introduction

A considerable part of the copper contained in the grapes precipitates as sediment during fermentation, which means that its content in the wine is lower than in the must. Knowledge of the heavy metal content, especially the copper content, is important because it can affect both the stability of the wine and the health of the consumer (Banovic et al., 2009; Svancarova et al., 2022). Both the soil and the climate in the vineyard play a decisive role in the flavour of the wine. The chemical and physical composition of the soil, including minerals, rocks and other soil components, significantly influence the flavours of the wine.

In terms of technological aspects, the presence of metal ions plays a decisive role in the redox-reactions that lead to the browning of wine. The most reactive metals in this context are copper, iron and manganese (Cacho et al., 1995). Cu^{2+} is significantly involved in oxidative transformations that favour the oxidation of iron and could possibly lead to brown colouration and turbidity. However, high copper concentrations in wine can cause reactions or precipitation that can have a negative impact on sensory properties such as colour or taste (Wang et al., 2023).

The importance of copper in viticulture is emphasised by the results of numerous studies like Ambrosini et al. (2018), as it is used against the Peronospora fungal disease. The application of fosetyl to plants, which can leave phosphoric acid residues in the fruit, could lead to an increase in the copper content in the wine. A variety of foliar treatments could mimic the effect of these residues (Malusa, 2005).

The biological efficacy and selectivity of mandipropamide plus copper oxychloride and iprovalicarb plus copper oxychloride (Melody Compact, Bayer Crop Science, Leverkusen, Germany) were studied and no phytotoxic effect on the fruit was observed (Fanigliulo, 2009). The total copper (Cu) concentration in soils varies considerably and depends on the application of mandipropamid and other agrochemicals. The use of copper-containing pesticides on the surface of the fruit as a potential source of copper in grapes has also been investigated (Sedláčková, 2004). Most copper deposits were detected in leaves and stems, while less was present in the roots.

In addition, the copper content also depends on the maceration time. As a result, the skin contact technique can improve the quality of a wine by increasing flavour extraction from the skins (Gómez-Míguez et al., 2007; Ihl et al., 2023). Therefore, a comprehensive control of skin contact conditions related to the potential increase of copper content in wine is of great importance (Fabianowicz et al., 2021).

Copper sulphate or citrate is often added in wine production to remove hydrogen sulphide (H2S). As a result, quantities of copper can also enter the wine and lead to the formation of precipitates (Bekker et al., 2017). Due to this practice, the International Organisation of Vine and Wine (OIV) has set the limit for Cu^{2+} ions in wine at 1,0 mg/l. It is therefore crucial to detect, quantify and avoid copper in grapes and wine as much as possible.

Material and methods

Electrothermal atomization and AAS with Flame are common methods for the determination of Cu.

Background compensation in Atomic Absorption Spectroscopy is sophisticated and widely used for solving interference problems generated by real wine samples. During evaluation of different background compensation methods in flame and furnace operation Deuterium (^{2}H), HighSpeed Self Reversal (SR) and Zeeman methods have been used (Oppermann, 2007). Up to now several methods for the determination of copper content in wine are suitable, not only AAS methods, inductively coupled plasma (ICP-MS), but also the fluorescence detection method was developed to detect Cu^{2+} ions in wine by using coumarin derivatives (Xiuxiu Dai et al., 2022).

Slovakian wines with a protected designation of origin (PDO) were collected over a period of five vintages and analysed to determine the copper content using ETA-AAS (atomic absorption spectrometry with electrochemical atomisation). The dry red and white wines came from renowned Slovakian wine producers such as Vinárske závody Topoľčianky, s.r.o. and HUBERT J.E., s.r.o., and were collected in different vintages. The samples were certified by the CCTIA (Central Control and Testing Institute in Agriculture) in an accredited laboratory.

For the analysis, copper was measured after filtration of the wine sample through a 0,45 µm membrane and direct injection of 20 µl of the sample into a graphite furnace. This method was carried out using an AA-6800 with graphite furnace (Fy Shimadzu) with background correction and autosampler. A Halow cathode lamp for copper with a resonance line of 324,8 nm was used as the light source. Argon was used as the carrier gas and the atomisation temperature was 2600 °C. The working standard solutions were prepared from Merck standards, nitric acid, modifier Pd+$Mg(NO_3)_2$ and demineralised water. The advantage of this method lies in the accuracy of the calibration curve and the possibility of following the atomisation process with a camera.

Results and discussion

Different results were obtained for the copper content in white and red wines. (Tab. 1).

Tab. 1: Determination of the parameters alcohol, total sugar and total SO2 according to the OIV methods as well as the measurement of copper content using AAS-ETA

Sample	alcohol [% vol.]	sugar[g/l]	Total SO_2 [mg/l]	Cu [µg/l
FM2016	12,1±0,1	1,6±0,1	187,0±6	262,0±7
FM2020	12,6±0,2	2,3±0,2	149,0±4	195,0±6
FM2021	12,5±0,1	2,8±0,2	163,0±5	251,0±7
FM2022	12,8±0,2	3,3±0,3	173,0±5	295,0±8
RV2007	11,9±0,1	4,0±0,3	111,0±4	183,0±6
RR2016	12,4±0,1	1,9±0,2	109,0±4	218,0±4
RR2020	12,7±0,2	2,5±0,2	114,0±4	248,0±6
RR2021	12,5±0,2	3,3±0,2	95,0±5	221,0±7
RR2022	12,4±0,2	4,5±0,3	123,0±5	255,0±8

FM=Frankovka modrá (Blaufränkisch), RR=Rizling rýnsky (Rheinriesling), RV=Riesling blanc

The OIV methods MA-AS312-01, MA-AS313-01, MA-AS311 and MA-AS323-04 were used to measure alcohol, total acids, sugars and total SO2. The AAS-ETA results showed a potential correlation between copper content and total SO2 content, with higher SO2 levels associated with higher copper content.

A copper content of 195 µg/l was measured in the red wine of the 2020 vintage, which was slightly lower than in the white wine of the same vintage. In the 2021 vintage, the copper levels in red and white wine were almost identical. However, the red wine of the 2022 vintage had a higher copper content. These results are in line with an earlier study on Australian and Portuguese wines, which showed that copper levels in red wines are usually slightly higher than in white wines (Catarino et al., 2018).

The excellent correlation between the calibration standards illustrates the value of the automatic AAS-ETA measurement. The calibration curve for copper shows an equation of y = 0,011249x-0,0056 and a correlation coefficient of R^2 = 0,9994 (see Fig. 1). This method proves to be suitable for the precise determination of the copper content in wine and beer. The EU and OIV limits for the trace elements lead, copper and zinc in wine are 0,15 mg/l, 1,0 mg/l and 5,0 mg/l respectively. In all cases analysed, the copper content in the wine was below the limit value of 1,0 mg/l.

A significant factor for the copper content in wine is the soil of the vineyard, where the copper is absorbed via the roots of the vines (Vasiliki et al., 2023).

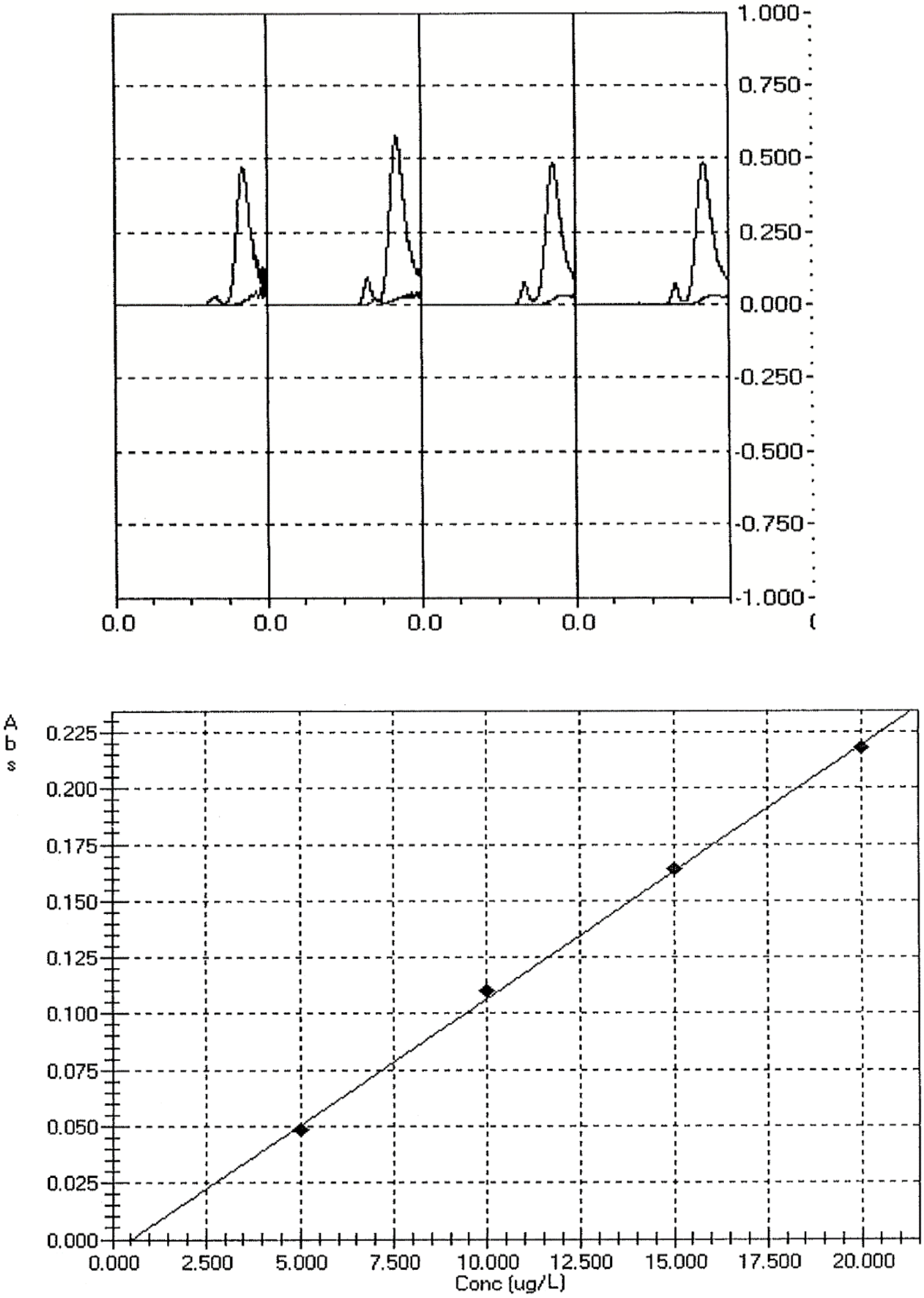
However, research analysing wines and the soils of their origin is rare. Information on the metallic composition of Slovak wines and their classification by geographical origin is also limited. In this context, a study was designed to examine whether the protected designation of origin “Južnoslovenská” can serve as a tool for traceability of different geological formations by including different vineyards within the same region.

Although there was no notable increase in the copper content in the wines, careful monitoring of the chemical parameters, especially the metal content, is essential. Various factors such as the processing of the grapes, problems during fermentation, improper use of copper as an H2S fining agent or various cultivation factors such as the use of copper as a fungicide and the soil situation can potentially lead to increased levels. The situation regarding copper in the wine industry is extremely diverse and complex, and the forms of copper present vary greatly. This makes it fundamentally difficult to accurately measure the copper content in wines (Wang et al., 2023).

Conclusions

The aim of this study was to determine the copper content in wines of different vintages from the same region of origin, PDO "Južnoslovenská" (southern Slovakia). The study investigated whether there is a connection between global warming and the copper content in the wines. The results showed that Slovakian quality wines have a copper content below the limit value of 1 mg/l. This work demonstrates the ability of the AAS spectrometer to accurately measure the copper content of wines.

	Action	Sample ID	X	True Value (ug/mL)	Conc. (ug/mL)	Abs.	BG	Pos.	VOL	Diluent R1	Reagent 1 R2	Reagent 2 R3	Reagent 3 R4	Total Volume	VF	DF	Actual Conc.	Actual Conc. Unit
52	AUTOZER																	
56	BLK-AV					0.0210	0.0118	R1	20	0	0	0	10	30				
59	STD-AV			5.0000		0.0482	0.0151	R2	5	15	0	0	10	30				
62	STD-AV			10.0000		0.1100	0.0143	R2	10	10	0	0	10	30				
65	STD-AV			15.0000		0.1642	0.0144	R2	15	5	0	0	10	30				
68	STD-AV			20.0000		0.2176	0.0117	R2	20	0	0	0	10	30				
83	UNK6-AV	vino			12.7845	0.1382	0.0221	R3	10	0	0	0	10	20	2.00	10.00	255.6900	NONE



Abs=0,011249c-0,0056

R=0,9994

Fig. 1: Calibration curve for Cu measurement.

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