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IZVORNI ZNANSTVENI RAD

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Abstract
To investigate the effect of different maceration techniques on the mineral composition of Malvazija istarska wines, five different maceration treatments were carried out. Maceration techniques of two days at 8 °C (CRYO), and seven (M7), 14 (M14), 21 (M21), and 42 days (M42) at 16 °C, were studied and compared to control treatment without maceration (C). Analysis of macro- and microelements was conducted by inductively coupled plasma-optical emission spectrometry (ICP-OES). According to the obtained results, the longest maceration treatments (M21 and M42) resulted with the highest concentration of almost all macroelements. A proportional increase with maceration time was observed in the concentration of all analyzed microelements, with M42 treatment wine resulting in significantly highest concentrations.

Key words: Malvazija istarska, white wine, maceration, mineral composition, ICP-OES

Introduction
The overall wine quality depends on many factors, including its metal composition (Tariba, 2011). Metals affect wine flavor, freshness, aroma, color and taste (Pohl, 2007). Some macroelements (K, Ca, Mg and Na) are responsible for regulating yeast cellular metabolism by maintaining adequate pH and ionic balance (Pohl, 2007). Moreover, precipitation of K and Ca salts of tartaric acid influences taste and mouthfeel properties by altering pH which enhances the oxidation of Cu and Fe and the formation of clouding (Pohl, 2007). The information about wine mineral composition is essential for several reasons. Elements such as Al, Cu, Fe and Mn, may induce haze formation and result in undesirable changes in wine aroma and taste (Tariba, 2011), hence metal analysis is an important tool in wine quality control (Grindlay et al., 2011). Mineral content may also serve for characterization of the wines by their authenticity and geographical origin (Banović et al., 2009). Additionally, moderate daily wine consumption contributes to the requirements of the human organism for essential elements, such as Ca, Cr, Co, K, Se, Zn (Vrček et al., 2011), while other metals (Cu, Zn, As, Cd and Pb) can be potentially toxic when consumed in excess (Tariba, 2011). The concentration of metals in wine must be controlled according to health-protection regulations (Pohl, 2007). The legal threshold limit values for metals in wine are established by the International Organization of Vine and Wine (OIV, 2015) and Croatian Regulation on wine production (Official Gazette, Regulation on wine production, NN 2/2005), ensuring the wine metal content is within the toxicological safety limits. There are two main sources of metals in wine: primary source – soil on which vines are grown, and secondary source – external impurities that are in contact with grapes during growth or that occur in the process of winemaking (Pohl, 2007). To affect the sensory quality and increase the bioactive properties of white wines, many producers apply the grape maceration process. Since metals

are mainly extracted from the solid parts of the grape berry, their content may increase during maceration (Soto Vázquez et al., 2013; Shimizu et al., 2020). Several authors reported an increase in mineral content with a longer maceration duration (Shimizu et al., 2020, Rossi et al., 2022). While a lower temperature causes precipitation of K and Ca tartrates (Pohl, 2007), long macerations at high temperatures cause a greater extraction of metals from the grape berry (Soto Vázquez et al., 2013). The aim of this study was to investigate the effect of applying different maceration techniques on the mineral composition of wines produced from the Malvazija istarska grape variety (*Vitis vinifera* L.), an autochthonous white variety originating from the Istria region of Croatia.

Materials and methods

The grapes of *cv*. Malvazija istarska used for this experiment were produced in 2019, in the experimental vineyard of the Institute of Agriculture and Tourism in Poreč located in the viticultural region Croatian Istria and Kvarner. Grapes were harvested, destemmed, and crushed at the experimental cellar of the Institute of Agriculture and Tourism Poreč. Five out of six grapes must treatments were homogeneously transferred into 220 L stainless steel fermenters, each reproduced in three replicates (n = 3). Control treatment (C) was pressed immediately after crushing, while other treatments proceeded with the maceration processes of different duration periods as follows: pre-fermentative two days maceration at 8 °C (CRYO), seven days maceration at 16 °C (M7), and prolonged post-fermentative maceration at 16 °C for 14 days (M14), 21 days (M21), and 42 days (M42). The pectolytic enzyme of 4 g/hL (Endozym Aromatic, AEB, Brescia, Italy) was added to the juice of C treatment before it was cold settled for 24 hours, and to the mashes of the maceration treatments immediately after crushing. Each of the six treatments was inoculated with 30 g hL^{-1} of selected dry yeast (Fermol Arome Plus, *Saccharomyces cerevisiae*, AEB) and yeast supplement (Fermoplus floral, AEB), and the maceration/fermentation temperature was set to 16 °C. Before yeast inoculation, CRYO treatment was subjected to a temperature of 8 °C during the two days maceration process. During the maceration period, the caps of all maceration treatments were punched down three times a day. After the end of the maceration process, each treatment was pressed, racked off the sediment, and transferred into a clean tank and infused with nitrogen gas. The level of free and bound SO_2 was monitored throughout the whole process and corrected accordingly. Approximately 6 months after bottling, wines were subjected to analysis of macro- and microelements. Determination of macro- and microelements (Al, Cu, Fe, Mn, K, Ca, Mg, Na) was conducted using Optima DV 2000 inductively coupled plasma – optical emission spectrometer (PerkinElmer, Shelton, Connecticut, USA) equipped with a Meinhard spray chamber, nebulizer, and peristaltic sample delivery system, with the working conditions previously described by Rossi et al. (2022). Analyzed elements were identified in line with ICP-OES using the WinLab 1.35 PerkinElmer software and quantified by a direct calibration method. Statistical analysis was performed using Statistica 10.0. Software (Stat-Soft Inc. Tulsa, OK). Fischer's least significant difference test (LSD) was performed using a one-way analysis of variance (ANOVA).

Results and discussion

The mineral compositions of different Malvazija istarska treatment wines are presented in Figure 1 and Table 1. Total macroelements content ranged from 881.5 ± 3.66 to 1023.6 ± 2.02 mg L^{-1} (Figure 1). Significantly the highest concentration was found in the maceration treatments (M42, M21, M14 and M7) with no significant differences between those treatments, while a lower concentration was found in CRYO treatment wine. Control wine (C) obtained the lowest concentration of total macroelements: potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na). According to Grindlay et al. (2011), among all macroelements, K usually reaches the highest concentration levels in wines (500-1500 mg L^{-1}), which is in agreement with the concentrations found in this study. Potassium in wine, especially in higher concentration, has a great nutritional value (Karataş et al., 2015). The concentration of Ca, Mg and Na in wine are usually ranging from 10 to 200 mg L^{-1} (Grindlay et al., 2011), which is accordant with our results. Magnesium (Mg) concentration increased with longer maceration treatments, being the highest in M21 and M42 treatment wines and the lowest in C wine. Prolonged post-fermentation maceration treatments, M21 and M42, showed the highest concentration of almost all analyzed macroelements, K, Mg and Ca, respectively. Such results correspond to those of Rossi et al., (2022), who also noted an increase in K, Mg and Ca concentrations resulting from the prolonged maceration process in Teran red wine. In an earlier study (Shimizu et al., 2020), K and Ca concentration decreased after 2nd day of maceration, while a proportional increase with maceration length was observed in our study. Sodium (Na), the extracellular cation, helps to maintain the acid-base balance and osmotic regulation (Karataş et al., 2015). The highest sodium concentration in our study was observed in M7 treatment wine, while the lowest concentration was found in M42 treatment wine, meaning a longer maceration duration promotes sodium decrease.

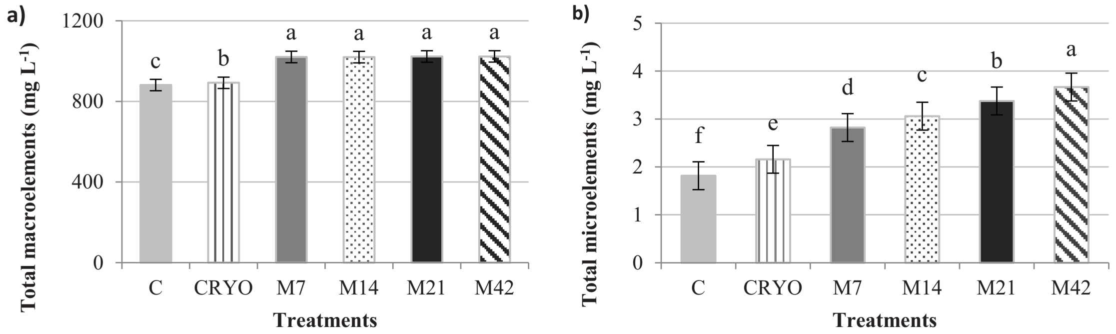

Figure 1 **a)** total concentration (mg L^{-1}) of macroelements in different Malvazija istarska treatments, **b)** total concentration of microelements (mg L^{-1}) in different Malvazija istarska treatments; C - control treatment, CRYO - pre-fermentative two days cryomaceration treatment, M7 - seven days maceration treatment, M14 - prolonged post-fermentative 14 day maceration treatment; M21 - prolonged post-fermentative 21 day maceration treatment, M42 - prolonged post-fermentative 42 day maceration treatment. Different lowercase superscript letters represent statistically significant differences between treatments at $p < 0.05$ obtained by one-way ANOVA and least significant difference (LSD) test.

The concentration of total microelements (aluminium (Al), copper (Cu), iron (Fe) and manganese (Mn)), ranged from 1.82 ± 0.02 to 3.67 ± 0.03 mg L^{-1} and was significantly the highest in M42 treatment wine, containing 2-fold higher total microelements concentration than C treatment wine. Those elements are usually present in concentrations ranging from 0.1 to 10 mg L^{-1} (i.e. trace elements) (Grindlay et al., 2011). The concentration of Fe was the highest of all microelements and the values increased proportionally with maceration time, being 3-fold higher in M42 than in C treatment wine. Such results are in concordance with Rossi et al., (2022), who reported a correlation between Fe concentration and maceration duration. Other microelements showed a similar trend, meaning their concentration increased with longer maceration duration but were contained below the maximum acceptable levels in wine according to the national Official Gazette (Regulation on wine production, NN 2/2005). Seeds contain three times as much manganese as skins and thirty times as much as grape flesh (Ribéreau-Gayon et al., 2006), which can explain a proportional increase in manganese with the progression of maceration time, being the highest in M42 treatment wine. Cu, Zn, and Fe are essential metals, important for various physiological processes and have certain nutritional benefits (Tariba, 2011). Prolonged maceration with grape skins may also increase the concentration of Cr, Cu, Fe and Zn in wine (Shimizu et al., 2020), which agrees with our results and the concentrations of Fe and Cu found in prolonged maceration treatments.

Table 1. Concentration (mg L^{-1}) of macro- and microelements of different Malvazija istarska wine treatments

	Treatments					
	C	**CRYO**	**M7**	**M14**	**M21**	**M42**
Macroelements						
K	716.57 ± 1.1^{d}	720.57 ± 1.01^{c}	817.63 ± 0.83^{b}	818.63 ± 0.83^{b}	820.47 ± 1.25^{a}	821.83 ± 1.07^{a}
Ca	32.77 ± 1.84^{d}	36.2 ± 0.95^{c}	56.83 ± 0.67^{b}	57.17 ± 0.67^{b}	59.47 ± 0.95^{a}	59.47 ± 0.95^{a}
Mg	97.83 ± 0.57^{e}	100.53 ± 0.42^{d}	105.63 ± 0.21^{c}	106.87 ± 0.15^{b}	108.47 ± 0.21^{a}	109.03 ± 0.21^{a}
Na	34.33 ± 0.21^{d}	35.37 ± 0.31^{c}	40.53 ± 0.40^{a}	37.57 ± 0.35^{b}	34.9 ± 0.10^{c}	33.27 ± 0.35^{e}
Microelements						
Al	0.653 ± 0.03^{d}	0.833 ± 0.03^{c}	0.906 ± 0.01^{b}	0.916 ± 0.01^{b}	0.926 ± 0.01^{ab}	0.956 ± 0.01^{a}
Cu	0.016 ± 0.00^{f}	0.026 ± 0.00^{e}	0.035 ± 0.00^{d}	0.042 ± 0.00^{c}	0.049 ± 0.00^{b}	0.063 ± 0.00^{a}
Fe	0.52 ± 0.01^{f}	0.65 ± 0.01^{e}	1.1 ± 0.02^{d}	1.3 ± 0.03^{c}	1.54 ± 0.01^{b}	1.76 ± 0.02^{a}
Mn	0.629 ± 0.00^{f}	0.650 ± 0.00^{e}	0.777 ± 0.00^{d}	0.797 ± 0.00^{c}	0.869 ± 0.00^{b}	0.886 ± 0.00^{a}

Results of macro- and microelements are expressed in mg L^{-1} as means ± standard deviations; C - control treatment, CRYO - pre-fermentative two-days cryomaceration treatment, M7 - seven days maceration treatment, M14 - prolonged post-fermentative 14 day maceration treatment; M21 - prolonged post-fermentative 21 day maceration treatment, M42 - prolonged post-fermentative 42 day maceration treatment. Different lowercase superscript letters represent statistically significant differences between treatments at $p < 0.05$ obtained by one-way ANOVA and least significant difference (LSD) test.

Conclusion

The composition of both macro- and microelements in different Malvazija istarska wines was highly affected by the maceration treatment. Total macroelements concentration was the highest in maceration treatment wines, particularly those with longer maceration time and higher maceration temperature. Total microelement concentration increased proportionally with maceration time, being significantly the highest in the longest post-fermentative maceration treatment. When observing the individual mineral concentration, almost all minerals increased with maceration time, especially when maceration time increased to 21 and 42 days. According to the increase in mineral composition of several maceration treatments, obtained results may serve wine producers choose the appropriate winemaking technology for improving the quality of their products.

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Utjecaj duljine maceracije na mineralni sastav vina ´Malvazije istarske´ (*Vitis vinifera* L.)

Sažetak

U svrhu ispitivanja utjecaja različitih tretmana maceracije masulja na mineralni sastav vina sorte ´Malvazija istarska´, postavljeno je pet različitih tretmana maceracije. Tretmani maceracije u trajanju od dva dana na 8°C (CRYO), te sedam (M7), 14 (M14), 21 (M21) i 42 dana (M42) na 16 °C uspoređivani su s kontrolnim tretmanom (C) bez maceracije. Analiza makro- i mikroelemenata provedena je tehnikom optičko-emisijske spektroskopije induktivno spregnute plazme (ICP-OES). Prema dobivenim rezultatima, tretmani produljene maceracije (M21 i M42) rezultirali su najvišim koncentracijama gotovo svih makroelemenata. Uočen je porast koncentracije svih mikroelemenata proporcionalno s duljinom trajanja maceracije, a kod tretmana M42 signifikantno najviše vrijednosti.

Ključne riječi: Malvazija istarska, bijelo vino, maceracija, mineralni sastav, ICP-OES