

Prevention of browning development in white wine by Se addition

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Abstract. Oxidation of white wines implies modification of their organoleptic characteristics and in most cases degradation of their overall quality. The development of oxidative browning is associated with polyphenol oxidation, and it can be accelerated by the presence of metal ions such as Fe²⁺ while it may be delayed by the addition of antioxidants, such as selenium (Se) and SO₂. The aim of this study was to study the browning capacity of Assyrtiko white wines after Se addition at two temperatures (35 and 50°C) employing the accelerated browning test. For this purpose, two concentrations of Se were added at the wine, either alone or with the simultaneous presence of Fe²⁺, and the absorbance at 420 nm was monitored for twelve days. It was also of interest to evaluate the changes of other analytical parameters which are implicated in wine oxidation such as: SO₂ content (free and total). Browning was approached from a kinetic point of view and the study was focused on the implication of oxidants and antioxidants on browning rate. The results showed that the addition of Se protected wine color and preserved total SO₂ at 35°C while at 50°C these effects were not any longer observed. GSH content of the samples containing Se after 12 days of accelerated ageing was similar with that of the control.

1 Introduction

Browning in white wines is due to a complex series of reactions that take place during processing, ageing and storage, as a result of oxygen exposure. Browning development increases both color intensity and browning index while simultaneously decreases brightness [1]. It exerts a detrimental effect on wine sensory properties and compromises the shelf life of bottled wines since it is often accompanied by loss of freshness and fruity notes, appearance of oxidized character and increase in bitterness [2].

Browning development mainly follows a zero-order kinetics [1] and it has been attributed to the oxidation of polyphenolic compounds. In more detail, oxidizable substrates such as o-diphenols and hydroxycinnamic acids have been associated with the oxidation reactions while several studies have reported the significant implication of the appearance of quinones [3].

These oxidation reactions result in the generation of H₂O₂ which in association with ferrous ions (Fe²⁺) may lead to the formation of reactive oxygen species (such as hydroxyl radicals and hydroxide ions) through a reaction widely known as Fenton [4]. Other components of the wine such as transition metal ions, SO₂ and ascorbic acid are of equal importance in polyphenol oxidation. Sulphur dioxide and ascorbic acid added to wine are able to reduce the *ortho*-quinones, while metal ions can catalyse oxidation reactions [5].

Selenium (Se) can be found naturally present in wines in a concentration range between 2 and 5 µg/L [6]. Several studies have reported that it exerts antioxidant activity by involving different antioxidant mechanisms such as scavenging of reactive oxygen species (ROS), and

increasing the activity of antioxidant enzymes, including glutathione peroxidase and glutathione reductase [7]. Although Se tolerance of wine yeasts has been studied by several researchers, there is a lack of relevant studies focusing on the effect of selenium addition on wine chemical composition and brown color development.

The aim of this study was to study the browning capacity of Assyrtiko (indigenous variety of Greece) white wines after Se addition at two temperatures (35 and 50°C) employing the accelerated browning test. The first temperature resembles wine transportation temperatures in hot Mediterranean countries such as Greece while the second is commonly employed during accelerating browning studies. For this purpose, two concentrations of Se were added at the wine, either alone or with the simultaneous presence of Fe²⁺, and the absorbance at 420 nm was monitored for twelve days.

2 Materials and methods

The white wine, used in this experiment, was made by a native Greek *V. vinifera* sp., Assyrtiko (harvest 2020). The contents of total and free SO₂ were measured with an automatic titrator according to the OIV method [8]. The samples with Fe²⁺ were prepared by addition of two concentrations of FeCl₂·4H₂O to wine (0.1 and 0.25 mM respectively) together with H₂O₂ (0.63 and 1.157 mM respectively) according to Voltea et al. [9]. Se enriched wines were prepared by the direct addition of Se in wine to reach final contents of 1.5 and 3.0 mg/L respectively. Another two wine samples were prepared by the simultaneous addition of the high and low concentrations of Fe²⁺, H₂O₂ and Se according to Vlahou et al. [10].

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The method employed to measure browning development was a modification of that published by Singleton and Kramling [11]. Filtered wine samples (20 mL) were placed in 30 mL screw-cap glass vials. Samples were heated at two temperatures of $50.0 \pm 0.2^\circ\text{C}$ and $35 \pm 0.2^\circ\text{C}$ respectively in a water bath in obscurity. Browning (A_{420}) was measured in triplicate against 12% v/v ethanol during 12 days at 24-h intervals.

All assays were performed in triplicate after 0, 1, 2, 4, 8, and 12 days of heating.

3 Results and Discussion

3.1 Browning development

The reaction rate constants (k) ($A_{420} \times \text{days}^{-1}$) of browning development were calculated from the slope of the regression lines, obtained after plotting A_{420} as a function of time according to Sioumis et al. [12]. Figures 1 and 2 present k -values and percentages of changes in browning (absorbance at 420 nm) at 35 and 50°C respectively. As it is observed, the wines with the lower k values were the control and those that contained Se (both high and low concentration) indicating that these samples would develop browning slower than the rest samples of this study (Fig. 1).

It was of particular interest the observation that when Se was present at 35°C, the color of the wine did not show any change after 12 days of heating while at 50°C, the rate of browning development was similar with that of the control (Fig. 2). However, at both temperatures, the simultaneous presence of Se with Fe^{2+} and H_2O_2 increased the k values. It is thus possible that at lower temperatures Se might protect wine color from oxidation in the absence of oxidant compounds. However, at higher temperatures and in the presence of metals the protecting effect is lost. This could be attributed to the higher contents of reactive oxygen species (ROS) which were formed by the high temperature and were further increased by the addition of Fe^{2+} and H_2O_2 .

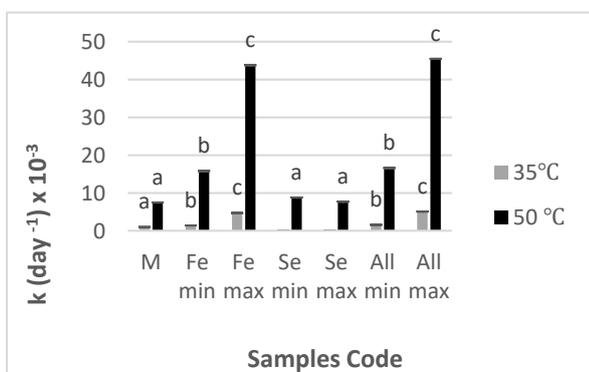


Figure 1. Browning rate constants (k) based on absorbance measurements at 420 nm (A_{420}).

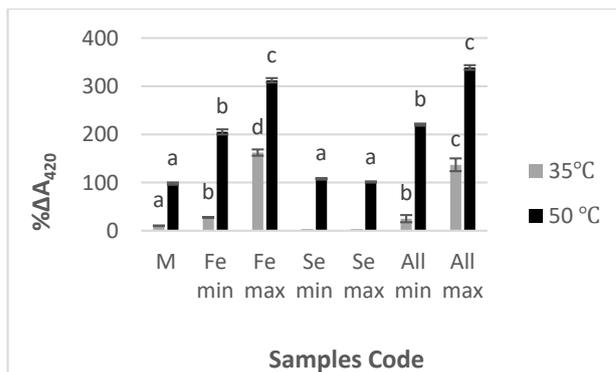


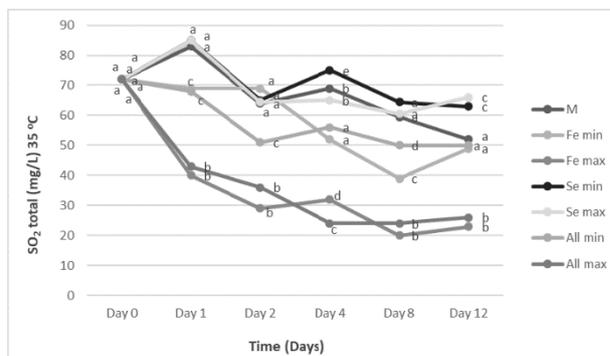
Figure 2. Percentage changes in absorbance at 420 nm (A_{420}).

3.2 Sulphur dioxide

The evolution of the contents of total and free SO_2 for the wine samples studied is presented in Figures 3 and 4. As it can be seen in Figure 3, the addition of Fe^{2+} and H_2O_2 had as result significant lower total SO_2 contents in the wines at both temperatures studied. It is well known that at the simultaneous presence of metal ions, sulfur dioxide is associated with oxygen, and in this way, it offers protection from oxidation reactions and thus of losses of their phenolic and volatile contents [13].

An interesting observation was that the total SO_2 content of the wines was preserved when Se was also present at both concentrations studied (Fig. 3). As far as the authors are aware, this is the first study which shows a possible protective effect of Se on wine color and sulfur dioxide content. The samples with Se contained statistically significantly higher amounts of total SO_2 than the control, at both temperatures tested. However, at the simultaneous presence of Fe^{2+} and H_2O_2 this protective effect was not any longer observed (Figs. 3 a and b).

Regarding free SO_2 content at 35°C, the highest amounts were measured for the control and the wines with Se. However, at higher temperatures (50°C), the wines with the addition of Se contained statistically significant lower contents of SO_2 in comparison with the control (Fig. 4). This observation is in line with the results obtained regarding browning, where at 35°C Se was able to prevent color change. It is possible that Se prevents browning development by preserving the content of SO_2 and by increasing antioxidant activity in wine.



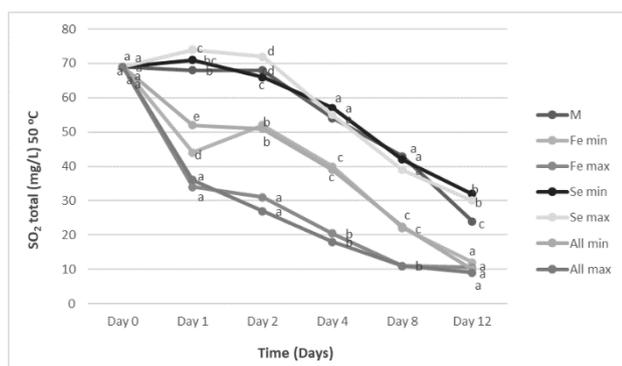


Figure 3. Evolution of total SO₂ of samples during 12 days of heating at 35 (upper) and 50°C (lower).

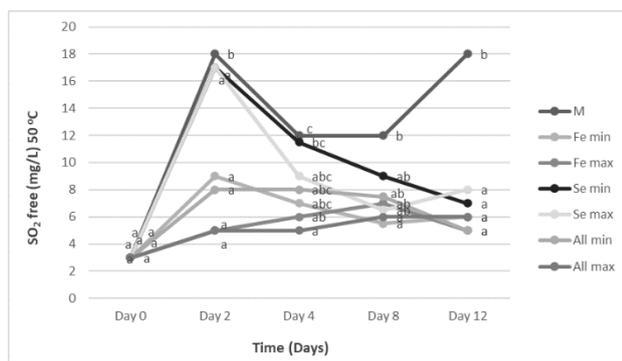
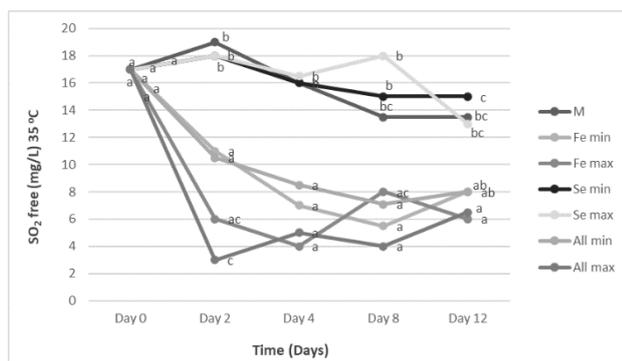


Figure 4. Evolution of free SO₂ of samples during 12 days of heating at 35 (upper) and 50°C (lower).

4 Conclusions

This work demonstrated that the addition of Se in white wines could possibly prevent color change when storage temperature is close to 35°C. However, at higher temperatures such as 50°C Se addition in wine is not adequate to offer similar protection from oxidation and browning.

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