# **Technical notes**

# Removing metals from wine using PVI/PVP Background

Metal ions are present in all wines, with sources including vineyard soil and water, fertilisers and agrochemicals, storage vessels and additions during winemaking. Some metal ions, including copper and iron, have major impacts on the flavour, aroma and shelf life of wine, as they play key roles in the oxidation and reduction processes that take place as wine matures (Clark et al. 2018). It is therefore important for winemakers to be able to understand and influence their concentrations.

Polyvinylimidazole/polyvinylpyrrolidone (PVI/PVP) co-polymers can be used to scavenge heavy metals in wine and were approved for use within the Australian wine industry as a processing aid in 2018, after having been used in European wine production for a number of years. PVI/PVP co-polymers have a multitude of cross-industry applications including in processes such as clarification, filtration and decolourising.

Previous research in wine (Mira et al. 2007) has shown that by lowering the concentration of metals such as copper and iron, PVI/PVP co-polymers can mitigate the risk of:

- the loss of varietal thiols
- premature browning
- pinking.

Typical copper concentrations in Australian wines are <0.5 mg/L and typical concentrations of iron are <2 mg/L, with the majority of the iron in wine attributable to vineyard soil. A recent trial at the Australian Wine Research Institute assessed the impact of two commercially available PVI/PVP co-polymer products on the concentration of metal ions in 38 commercially available wines (19 red and 19 white wines). This article summarises the findings from the trial and highlights the key outcomes that have relevance for winemakers.

# **Experimental set-up**

The two cross-linked polymers trialled were Stabyl MET and Claril HM (sourced through Enartis). Stabyl MET is a co-polymer of PVI and PVP, recognised for its high affinity for heavy metals (especially copper) and removal of hydroxycinnamic acids and low molecular weight catechins. Claril HM has similar properties to Stabyl MET; however, as well as a co-polymer of PVI and PVP, it also contains pre-activated chitosan. Chitosan has been shown to aid in the removal of heavy metals from wine and is also used as a stabilisation and clarification agent. The 38 wines in the trial were treated separately with each product. For each wine/product

combination, a 250 mL Schott bottle was purged with nitrogen for one minute and then filled with the wine sample, with the headspace purged with nitrogen post-filling. Additions of the PVI/PVP product were then made at the average of the supplier-recommended dose rate range (0.35 g/L for Stabyl MET and 0.53 g/L for Claril HM). For each wine there was also an untreated control sample. Samples were stirred on a mixing plate for three hours, after which they were filtered using a 0.2  $\mu$ m regenerated cellulose filter. Metal ion analysis was conducted using inductively coupled plasma mass spectrometry on all treated and untreated samples to assess the scavenging efficiency of each product.

# Key findings for copper and iron

Figures 1 and 2 show the percentage change of copper and iron concentrations (compared with untreated control wines) in the white and red wines following treatment with each of the two PVI/PVP products. Treatment with Stabyl MET resulted in copper concentration decreases ranging from 20% to 87% in the white wines, with an average decrease of 50%. The Claril HM product gave a slightly higher average decrease in copper concentration of 59%.

For iron, Stabyl MET treatment of white wines resulted in a decrease of between 13% and 68%, whereas Claril HM caused decreases in iron concentration ranging from 1% to 57%; slightly lower, on average, than Stabyl MET.

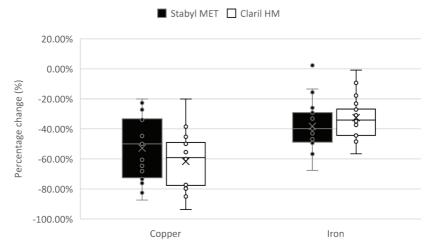
The PVI/PVP products were generally less effective in decreasing copper concentrations in red wines than in white wines. Stabyl MET achieved copper decreases of 0% to 50% and the Claril HM caused changes ranging from a 10% increase to a 60% decrease. Overall, the two products achieved a similar average decrease of copper in red wines. The slight increase in copper noted for one wine was only 0.003 mg/L, which is within the margin of error of the analysis.

For iron in red wines, Stabyl MET achieved decreases ranging from 19% to 63%, while the Claril HM achieved decreases ranging from 23% to 64%.

The data from this trial suggest that when using PVI/PVP, copper is more readily scavenged from white wines and iron is more easily scavenged from red wines. In some cases, the PVI/ PVP products showed no measurable effect on copper or iron. Further research is planned to explore the reasons that the products are less effective in some wines.

#### Effects on other metals

While understanding the impacts of PVI/PVP on copper and iron was the main focus for this study, a broad range of other metal ions were also measured, to understand any additional impacts of the PVI/PVP treatment. Figures 3 and 4 provide a snapshot of the percentage concentration change for metal ions including aluminium, chromium, cobalt, nickel, lead and zinc.



**Figure 1.** Concentration change for copper and iron in 19 white wines, following treatment with two PVI/PVP cross-linked polymer products. For the box and whisker plots, the ends of the box represent the upper and lower quartiles and the horizontal line within the box represents the median value. The whiskers extend to the higher and lowest observations, with outliers marked beyond this range. The 'X' represents the mean of the values for each analyte.

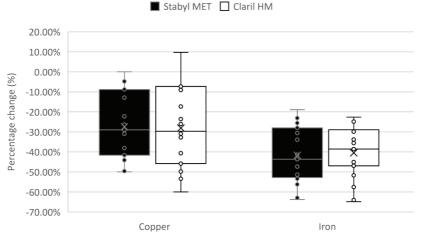


Figure 2. Concentration change for copper and iron in 19 red wines, following treatment with two PVI/PVP cross-linked polymer products

The PVI/PVP copolymers showed a high affinity for aluminium in white wine samples, with concentration reductions greater than 60% achieved with both Stabyl MET and Claril HM, while red wine samples show percentage decreases in the range of 30 to 80% across both products. The two products showed a similar degree of efficacy in scavenging cobalt, nickel and zinc from both white and red wines. There was, however, a significant difference in scavenging efficiency between products for both chromium and lead. Stabyl MET was, on average, more effective at scavenging chromium from both wine styles, while Claril HM was more effective at scavenging lead from white wines. Interestingly, lead concentrations

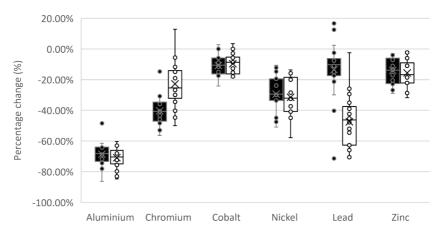


Figure 3. Concentration change for a range of metals in 19 white wines, following treatment with two PVI/PVP cross-linked polymer products

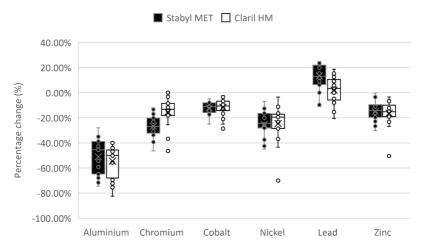


Figure 4. Concentration change for a range of metals in 19 red wines, following treatment with two PVI/PVP cross-linked polymer products

increased following both Stabyl MET and Claril HM treatments on average, for red wines. Further investigation is required to understand this observation.

## **Sensory impacts**

Initial investigations of the sensory impact of the PVI/PVP treatment involved an informal 'bench tasting' with nine expert panellists. This tasting did not highlight any negative wine attributes or characteristics from the PVI/PVP treatment under the conditions specified. Further investigation with a broader range of wine styles is required to better understand any potential varietal and stylistic impacts.

## Conclusions

This study of two commercially available PVI/PVP cross-linked polymers showed that this type of product can be effective in removing copper and iron from both white and red wine, but that the results vary across different wines. These products could provide a practical approach to managing risks of oxidation and reduction in wines, prior to bottling. For winemakers considering using these products, it would be recommended to conduct bench trials on their particular wines to ensure that desired outcomes can be achieved. Understanding the varietal or vintage effects on the efficacy of the cross-linked polymers will be the focus of future studies. This will include a more detailed evaluation of the sensory impact of the treatments and optimising the treatment process in the winery.

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#### References

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> Kieran Hirlam, Project Engineer, *kieran.hirlam@awri.com.au* Neil Scrimgeour, Senior Scientist Eric Wilkes, Group Manager – Commercial Services