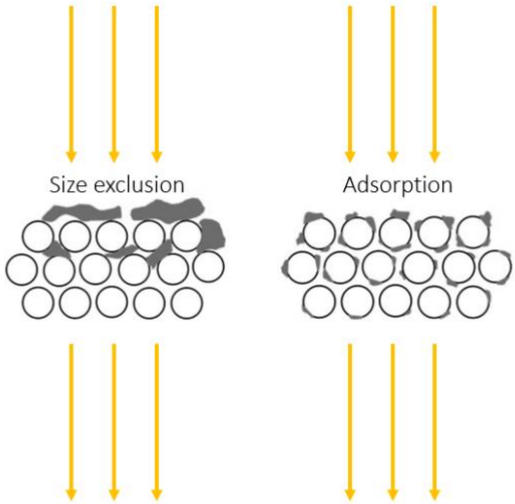
FOCUS ON H_2S: PART 6

REMOVING COPPER-H_2S COMPLEXES USING MEMBRANE FILTRATION



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Basic Wine

30 June 2020

The entire *Focus on H_2S* series has highlighted the **importance of removing the copper-H_2S** complex from wine, especially in cases where copper was added as a remedial treatment for the removal of reductive H_2S off-odours. In Part 5 of this series, the effectivity of a metal-removing fining agent was discussed and **treating wines with PVI/PVP was shown to be an effective method** for the removal of copper and copper-H_2S complexes with minimal sensory impact.

Other mechanisms for the effective removal of copper and copper-bound compounds/complexes are under investigation. A recent study titled, "Removal of sulfide-bound copper from white wine by

membrane filtration[1]" investigated **the filterability of copper-H_2S complexes** using different types of filters as well as how the wine matrix can affect the removal of the complex.

In Part 1 of this *Focus on H_2S* series, the ability to remove copper-H_2S complexes by filtration was reported[2] and results showed that utilising a cellulose-based membrane (often used in depth filters) was inefficient in removing the copper-H_2S complexes from wine. Other filtration media used in wine production include nylon or polyethersulfone (PES) membranes[3] (with pore sizes of 0.45 µm or greater), however, their efficiency for copper-H_2S removal is unknown. In the above-mentioned study, **the filterability of copper-H_2S using five different membranes were determined**. The effect of **different wine components on the filterability of copper-H_2S complexes** was also studied. The main findings of this study will be summarized in this blog post.

MATERIALS AND METHODS

Six different white wines were filtered using five membranes (sourced from Phenomenex). The five membranes tested included:

- Regenerated Cellulose (RC)
- Nylon
- Polyethersulfone (PES)
- Polytetrafluoroethylene (Teflon, PTFE)
- Glass Fibre (GF) (borosilicate)

Apart from the GF membrane, two pore sizes for each membrane were tested: **0.20 and 0.45 µm pore size**. The GF membrane had a pore size of 1.2 µm (the lowest pore size for this type of filter). Samples were prepared in 250 mL volumes and were either left unfiltered (control) or filtered using a syringe fitted with the relevant filter type and size.

RESULTS

TYPE OF FILTER

Of all the filters tested, the **Nylon and PES filters showed the most** potential removing **more than 50%** of the copper from the wine. The RC, PTFE and GF filters all **allowed about 80%** of the copper-H_2S to **pass through the filter**, therefore retaining/removing only a small percentage. The ability to remove the copper-complexes were largely **independent of the pore size** of the filter.

ADSORPTION INSTEAD OF SIZE EXCLUSION

Further investigations[1] showed that the majority of the copper-H_2S particles were below 0.2 µm in size, suggesting that the mechanism involved in the removal of the copper-H_2S is **not via size exclusion** (explaining the insignificant results when comparing the two pore sizes). Instead, it is more likely that the copper-H_2S complexes are **adsorbed** (the collecting of molecules by the external surface by physical and/or chemical mechanisms) onto the filter medium rather than by particle size discrimination.

WINE COMPONENTS CAN PREVENT ADSORPTION

The ability of different wine components to **interfere with the adsorption** of copper-H_2S onto the filter material was investigated[1] to identify components that might decrease the filterability. Results showed that the addition of **polysaccharides and proteins** to a model wine containing copper-H_2S, allowed **100% of the copper-H_2S to pass through** the filter (compared to 4% in the absence of these compounds). Compounds such as polysaccharides and proteins, therefore, **prevent the adsorption** of the copper-H_2S onto the filter, inhibiting the separation of the copper-H_2S complex from the wine. The addition of **phenolic substances** also decreased the adsorption of copper-H_2S and allowed 31% of the copper to pass through the filter.

Likely, these wine components **preferentially adsorb** onto the filter material, decreasing the adsorption sites available to interact with the copper-H_2S.

HIGHER ADSORPTION EFFICIENCY OF DIFFERENT FILTERS

The **high adsorption efficiency** of the nylon and PES filters for copper-H_2S is most likely due to **increased hydrophobic and/or polar activity** of the filters. The back pressure encountered when using

the filters (based on the physical force required to depress the syringe plunger) was in the order of PTFE>Nylon>RC>PES>GF. Therefore, based on this relative back pressure and efficiency to remove copper-H_2S, **PES would appear to have advantages over the other membrane media**.

CONCLUSION

Filtration can be used as a tool to remove copper-H2S complexes from wine. These complexes are not removed by filtration on the basis of their particle size, but instead may be partly removed by **adsorption** onto membrane filters. The use of the **correct type of filter** is, therefore, paramount. The effectivity of the separation is to an extent **impacted by the wine composition** with polysaccharides and proteins significantly decreasing the effectivity of the filtration medium.

Further work is required on a larger scale to provide a **sense of adsorption capacity of a membrane filter for a larger volume of wine**. Depth filters with increased adsorption capability are likely to have increased efficiency in removal of copper-H_2S compared to membrane filters, however, this needs further investigation.

Together with metal-removing fining agents such as PVI/PVP (see Part 5), **the use of a suitable filtration system can remove most if not all of the residual copper after remedial treatment with copper(II)sulphate**, significantly decreasing the risk of latent H_2S release from copper-H_2S complexes.

References

(1) Kontoudakis, N.; Mierczynska-Vasilev, A.; Guo, A.; Smith, P. A.; Scollary, G. R.; Wilkes, E. N.; Clark, A. C. Removal of Sulfide-Bound Copper from White Wine by Membrane Filtration. *Aust. J. Grape Wine Res.* **2018**, No. Ii, 53–61. https://doi.org/10.1111/ajgw.12360.

(2) Clark, A. C.; Grant-Preece, P.; Cleghorn, N.; Scollary, G. R. Copper(II) Addition to White Wines Containing Hydrogen Sulfide: Residual Copper Concentration and Activity. *Aust. J. Grape Wine Res.* **2015**, *21* (1), 30–39. https://doi.org/10.1111/ajgw.12114.

(3) Bowyer, P. K.; Edwards, G. Wine Filtration and Filterability – a Review and What ' s New. **2012**.