Impact of red and white wine macromolecules on the removal of copper(I) sulfide by membrane filtration

N. Kontoudakis[a,b], A. Mierczynska-Vasilev[e], A. Guo[a,c], P.A. Smith[e], G.R. Scollary[b,d], E.N. Wilkes[e] and A.C. Clark[a,b]

nkodoudakis@csu.edu.au

[a] *School of Agricultural and Wine Sciences, Charles Sturt University, Wagga Wagga (Australia).*
[b] *National Wine and Grape Industry Centre, Wagga Wagga (Australia).*
[c] *College of Enology, Northwest A&F University, Yangling (China).*
[d] *The School of Chemistry, The University of Melbourne, Melbourne (Australia).*
[e] *Australian Wine Research Institute, Adelaide (Australia).*

Introduction

Recent work has shown that sulfide appears to interact more strongly with copper (Cu) in wine than other likely copper-complexing species [1-2]. In low oxygen conditions during bottle aging, the total copper concentration in wine has been linked to increases in the hydrogen sulfide concentration, as well as other volatile sulfur compounds, a process contributing to the reductive development of wine [3]. A portion of the hydrogen sulfide that accumulates in wine during reductive aging has been attributed to release sulfide from sulfide-bound Cu in low oxygen conditions although to date, the exact mechanisms of release remain to be established [3-4].

This study investigated removal of sulfide-bound Cu from red and white wines by different membrane filter media and the influence of wine matrix on sulfide-bound Cu filterability.

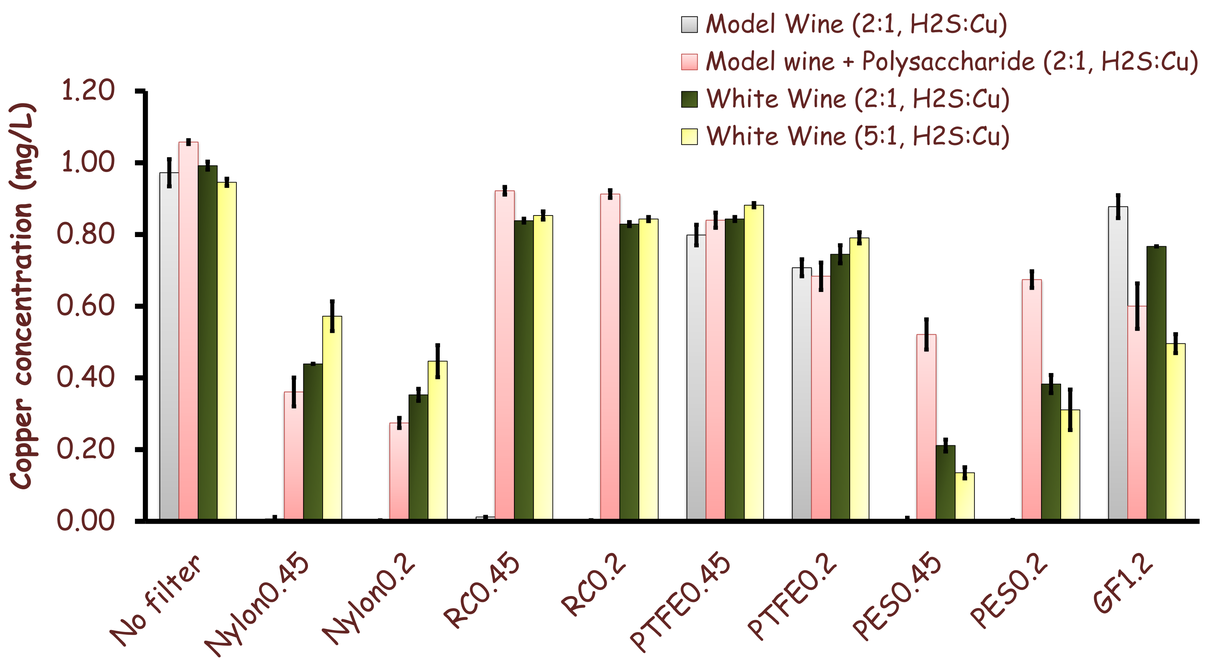

Figure 1. The impact of membrane type on the amount of sulfide-bound Cu eluting through the filter at 1 mg/L copper concentrations of sulfide-bound Cu. The sulfide-bound Cu was prepared at hydrogen sulfide to copper(II) ratios of 2:1 in the model wine, model wine with added polysaccharide and white wine, as well as at 5:1 in the white wine.

Results and discussion

Sulfide-bound Cu formation was conducted *in situ* with copper(II) sulfate and sodium sulfide addition to red, white wine and model wines. The membrane filters used were composed of regenerated cellulose, nylon, polyethersulfone (PES), and polytetrafluoroethylene (Teflon, PTFE) at 0.20 and 0.45 µm pore sizes. A glass fibre membrane filter with pore size 1.2 µm was also used. The amount of copper(I) sulfide retained by membrane filters was determined by flame atomic absorption spectroscopy. The influence of wine components on copper(I) sulfide was conducted by additions to a model wine system. The wine components used had been previously extracted from wine and included white wine protein, polysaccharide and polyphenol.

The results (Figure 1) showed that the regenerated cellulose, nylon and PES membranes could all remove the copper(I) sulfide from the model wine, however, the PTFE and the glass fibre membrane filters had minimal removal capacity. On addition of the white wine polysaccharide or protein to the model wine system, the regenerated cellulose membrane could not retain any sulfide-bound Cu, PES retained 30-40 % of the copper(I) sulfide, while nylon retained the most (~70 %). The white wine polyphenol compounds allowed less sulfide-bound Cu (34 ± 5 %) to pass through the regenerated cellulose membrane filter than the polysaccharide and protein.

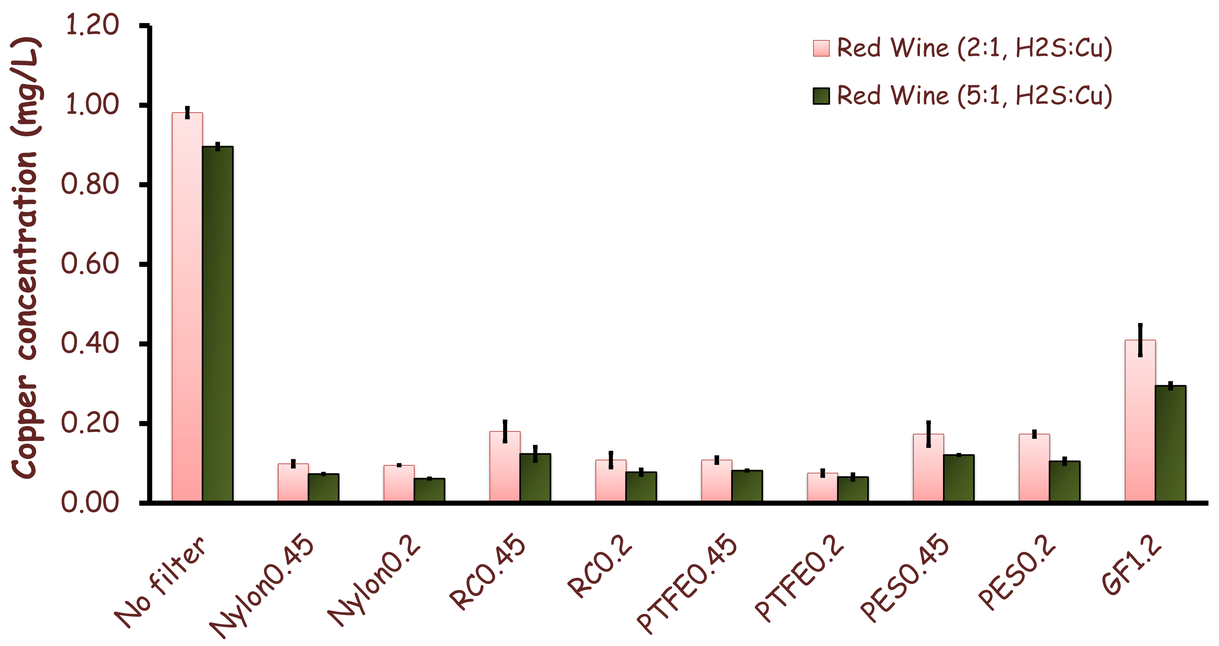

Figure 2. The impact of membrane type on the amount of sulfide-bound Cu eluting through the filter at 1 mg/L copper concentrations of sulfide-bound Cu. The sulfide-bound Cu was prepared at hydrogen sulfide to copper(II) ratios of 2:1 and 5:1 in red wine.

In a white wine, the results were similar to the model wine with polysaccharide and protein added, except for the PES membrane which allowed more sulfide-bound Cu removal in white wine compared to the model wine with added polysaccharide. In contrast to white wine, a red wine (Figure 2), showed that all the different types of filters could remove copper(I) sulfide.

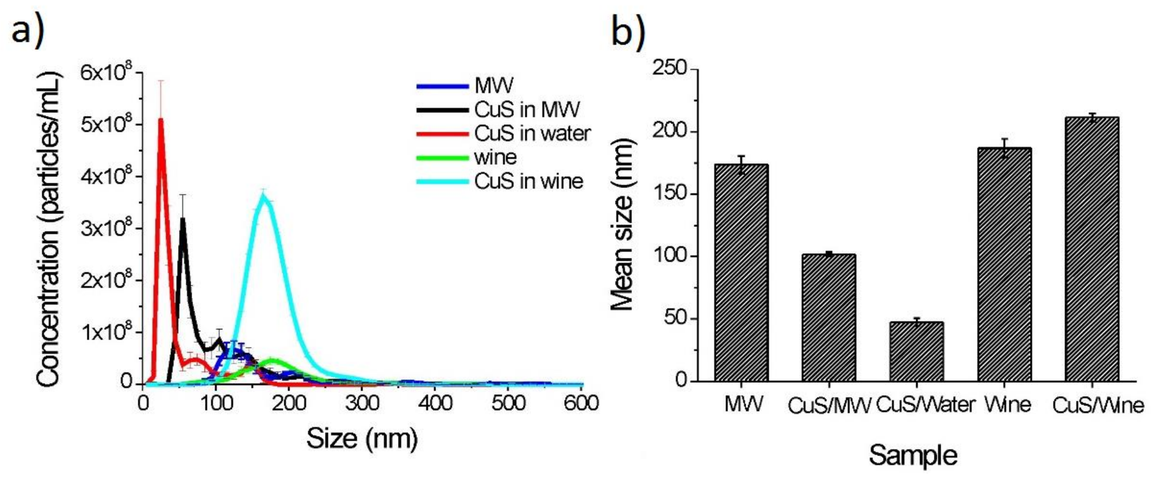

Figure 3. a) The particle size measurements for sulfide-bound Cu prepared by addition of 4.8 mg/L hydrogen sulfide and 2.0 mg/L copper(II) to a Viognier wine, model wine or water, and **b)** the mean sizes of samples mentioned above.

Nanoparticle tracking analysis was utilized to measure sulfide-bound Cu particle size (Fig.3). The sulfide-bound Cu particles formed in the model wine system are smaller than those found in the white wine system, which is the opposite result expected due to previous studies [5]. In all cases the majority of the particle sizes are smaller than 0.2 µm. These results demonstrate that the removal of sulfide-bound Cu from the model wine by the 0.2 µm pore size regenerated cellulose membrane filter was not due to a size-related mechanism. Instead it is more likely that the sulfide-bound Cu particles within the model wine matrix were adsorbed on the filtration medium.

References

[1] Kontoudakis, N., Smith, M., Guo, A., Smith, P.A., Scollary, G.R., Wilkes, E. and Clark, A.C. Food Res Int. 2017, 98, 95-102.
[2] Clark, A.C., Kontoudakis, N., Barril, C., Schmidtke, L. and Scollary, G.R. Talanta 2016, 154, 431-437.
[3] Ferreira, V., Franco-Luesma, E., Vela, E. and López, R. (2017). J. Agric. Food Chem., 2018, 66, 2237-2246.
[4] Smith, M.E., Bekker, M.Z., Smith, P.A., Wilkes, E.N. (2015). Aust. J. Grape Wine Res. 2015. 21, 705-712.
[5] Clark, A.C., Grant-Preece, P., Cleghorn, N. and Scollary, G.R. Aust. J. Grape Wine Res. 2015. 21, 30-39.

Acknowledgments

This work was funded by Wine Australia (project NWG1401) with funds from Australian grape growers and winemakers with matching funds from the Commonwealth of Australia.

The National Wine and Grape Industry Centre (NWGIC) is a research centre within Charles Sturt University in alliance with the Department of Primary Industries NSW and the NSW Wine Industry Association. *www.csu.edu.au/nwgic*