A W R I

The Australian Wine Research Institute

Copper, the good, the bad, the ugly

Dr Eric Wilkes

Commercial Services

AWRI
COMMERCIAL SERVICES
More than just a laboratory

Why do we use copper at all?

The Australian Wine Research Institute

- To get rid of the bad smells of course.
- Copper has a long history of use in beverage production to remove unpleasant sulfur related smells.

AWRI COMMERCIAL SERVICES
More than just a laboratory

What are these smells?

The Australian Wine Research Institute

Low MW Sulfur Compound		Odour Descriptor	Aroma Threshold (ug/L)	Detected (ug/L)	
				Literature Review	AWRI
Hydrogen Sulfide	H2S	rotten egg, sewage like	1	nd - 370	nd - 56
Methanethiol	MeSH	rotten cabbage, burnt rubber, putrefacation	1.5	nd - 16	nd - 11
Ethanethiol	EtSH	onion, rubbery, burnt match, sulfidy, earthy	1.5	nd - 50	nd - 3
Dimethyl sulfide	DMS	*blackcurrant* , cooked cabbage, asparagus, canned corn, molasses	25	nd - 474	nd - 980
Carbon disulfide	CS2	*sweet, ethereal, slight green* , rubber, sulfidy, chokingly repulsive	5	nd - 18	nd - 140
Diethyl sulfide	DES	garlic, rubbery	1	nd - 10	nd
Methyl thioacetate	MeSAc	sulfurous, cheesy, egg	40	nd - 115	nd - 53
Dimethyl disulfide	DMDS	vegetal, cabbage, intense onion-like (at high levels)	10	nd - 22	nd - 2
Ethyl thioacetate	EtSAc	sulfurous, garlic, onion	70	nd -180	nd - 32
Diethyl disulfide	DEDS	bad smelling, onion	4	nd - 85	nd - 1.5

CES

It can be very effective.

The Australian Wine Research Institute

H_2S $\quad H_2S + Cu^{2+} \rightarrow CuS \downarrow$

mercaptan $\quad CH_3CH_2SH + Cu^{2+} \rightarrow Cu(CH_3CH_2S)_2 \downarrow$

reduction ↓ ↑ oxidation

DMDS $\quad CH_3S\text{-}SCH_3 + Cu^{2+} \rightarrow$ unreactive

DMS $\quad CH_3SCH_3 + Cu^{2+} \rightarrow$ unreactive

AWRI COMMERCIAL SERVICES
More than just a laboratory

But why doesn't it always work?

The Australian Wine Research Institute

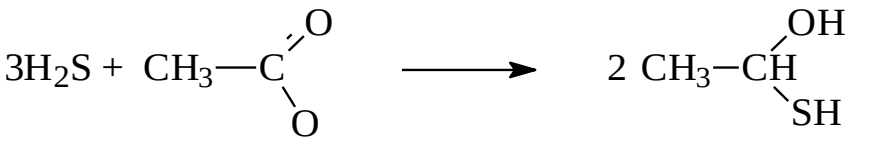
- Why does my wine go stinky again after it is treated in tank?
- Why don't the bench trials always reflect what I see in tank?

It is all a question of *equilibrium!*

AWRI COMMERCIAL SERVICES
More than just a laboratory

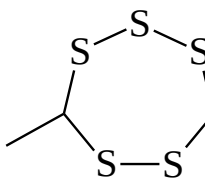
Its not quite as simple as you may think!

The Australian Wine Research Institute

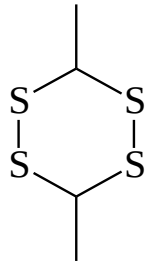


1-hydroxy-ethanethiol

H_2S



Too Hard



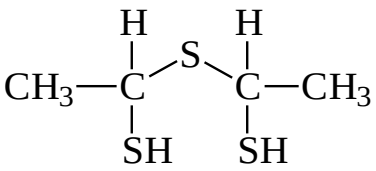
Intense rubbery or sulphury odour

cis/trans-4,7-dimethyl-1,2,3,5,6-pentathiepane
meat like aroma

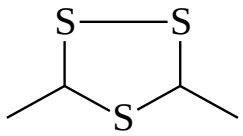
-H_2S

H_2S

cis/trans-3,6-dimethyl-1,2,4,5-tetrathiane
rubbery chemical aroma



[O]

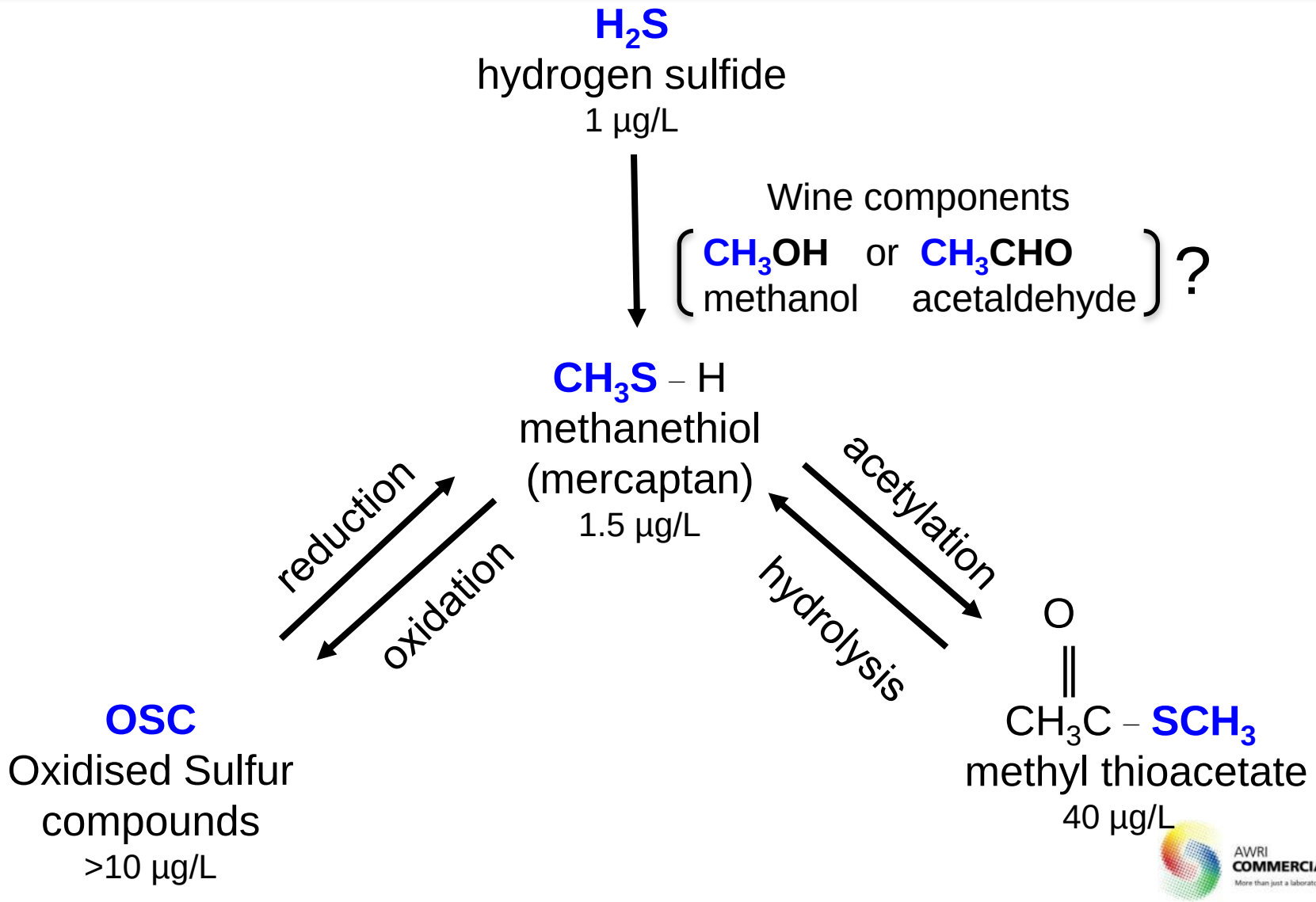


bis(1-mercaptoethyl)sulfide

cis/trans-2,5-dimethyl-1,2,4-trithiolan
spicy meat, meat like or allium arom

If only it was that simple!

The Australian Wine Research Institute



AWRI COMMERCIAL SERVICES
More than just a laboratory

Myth busting!

The Australian Wine Research Institute

All the copper I add drops out as insoluble sulfide!

Sulfide

1-2 µg/l
0.000002 g/l

Copper Sulfate

0.5ppm
0.0005 g/l

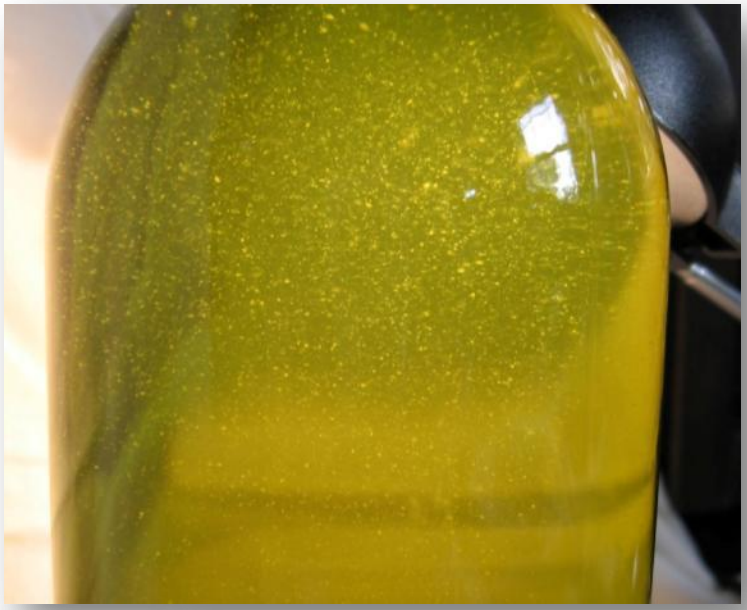
It is not unusual to see copper values increase at exactly the same rate as addition.

AWRI COMMERCIAL SERVICES
More than just a laboratory

Downsides of residual copper

The Australian Wine Research Institute

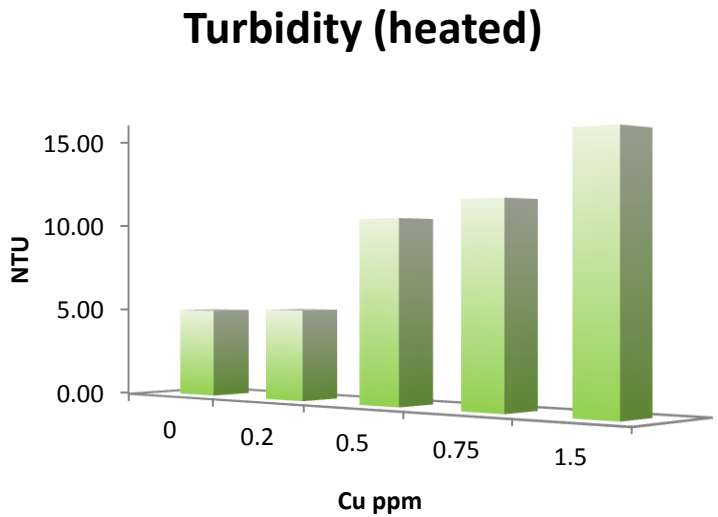
- Hazes
- Increased loss of 3-MH and 3-MHA
- More rapid loss of SO_2
- Increases in sulfides

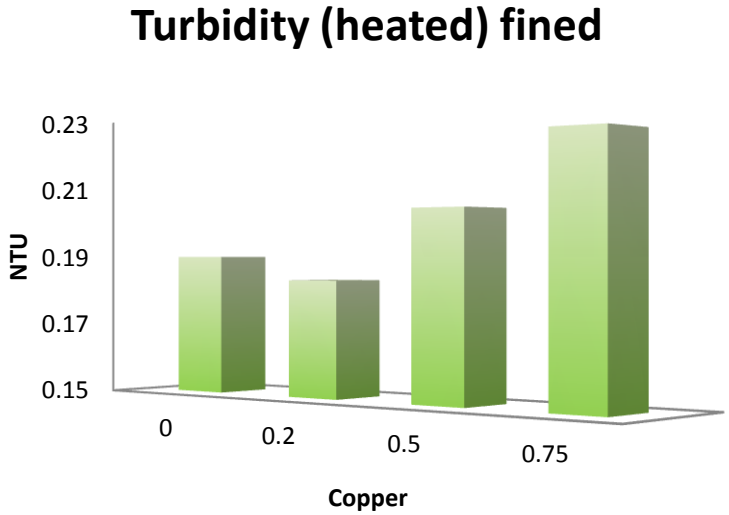


AWRI COMMERCIAL SERVICES
More than just a laboratory

Hazes and protein instability.

The Australian Wine Research Institute





Increased copper levels in bottled wine are well know to increase of protein instability.

Generally recommended to keep levels below 0.5 ppm, but limit depends on the wine.

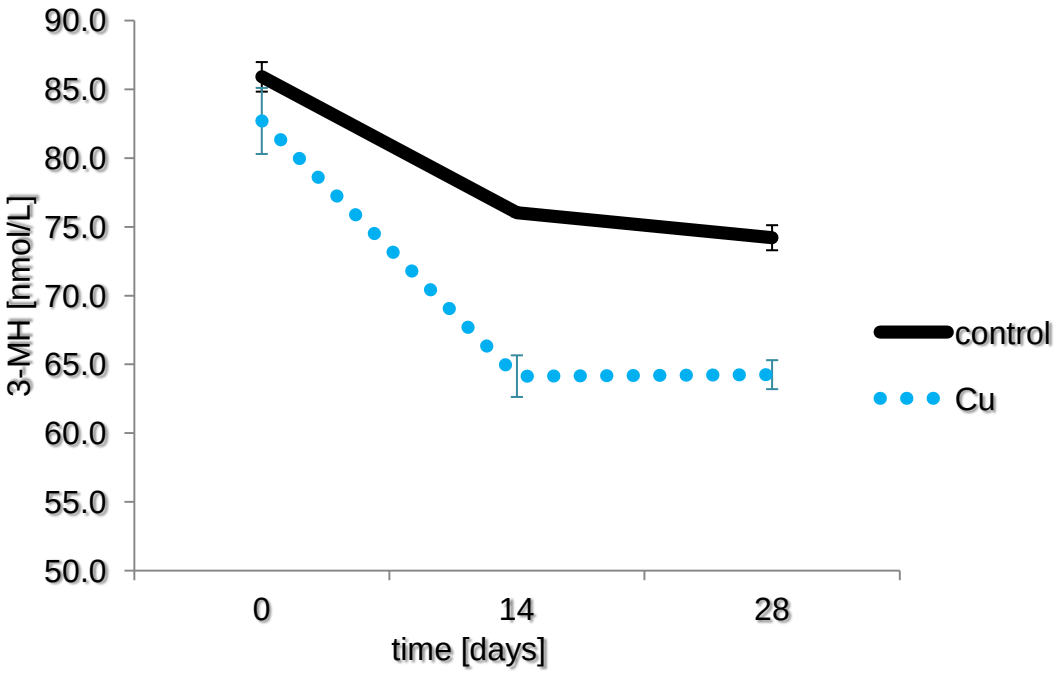
AWRI COMMERCIAL SERVICES
More than just a laboratory

Increased loss of 3-MH and 3-MHA

The Australian Wine Research Institute

3-MH (3-Mercaptohexan-1-ol)

3-MHA (3-Mercaptohexan-1-ol acetate)



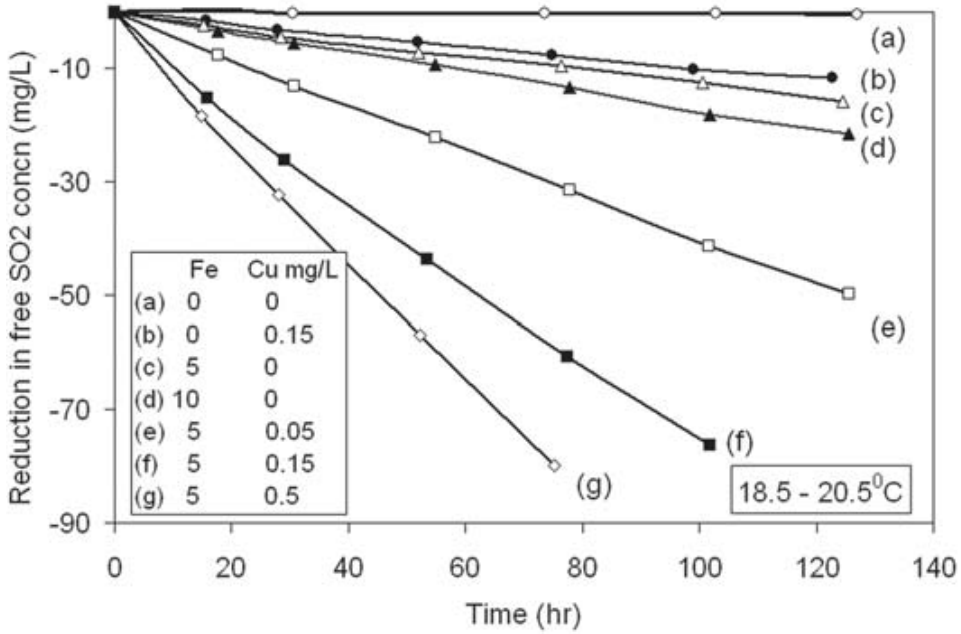
Dr. Mandy Herbst-Johnstone
School of Chemical Sciences
The University of Auckland

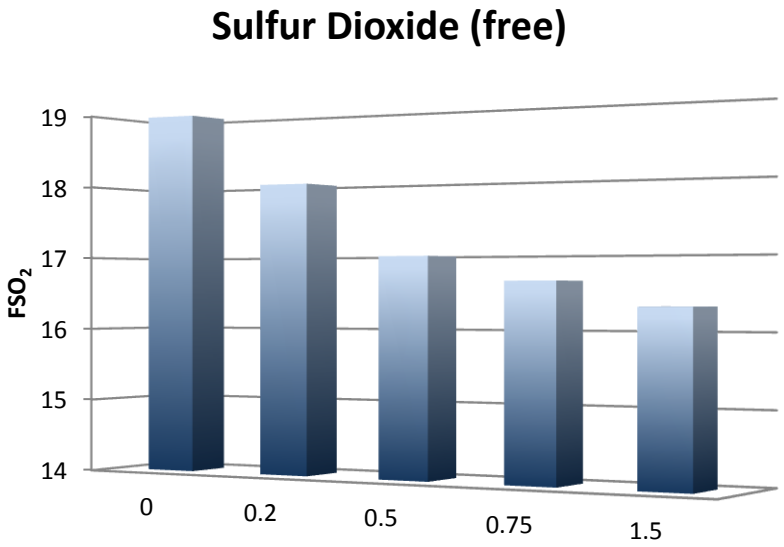
AWRI COMMERCIAL SERVICES
More than just a laboratory

More rapid loss of SO_2

The Australian Wine Research Institute

SO_2 cannot interact with O_2 directly. It requires the presence of metals such as copper and iron.





After just six months in bottle!

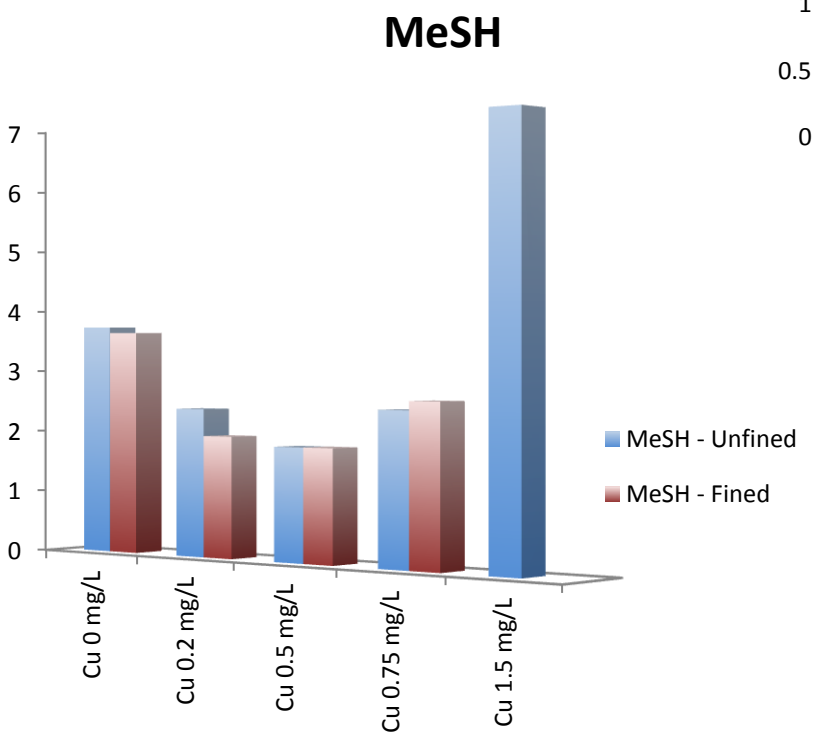
Danilewicz, J. (2007). Interaction of sulfur dioxide, polyphenols, and oxygen in a wine-model system: Central role of iron and copper. *American journal of enology and ….*

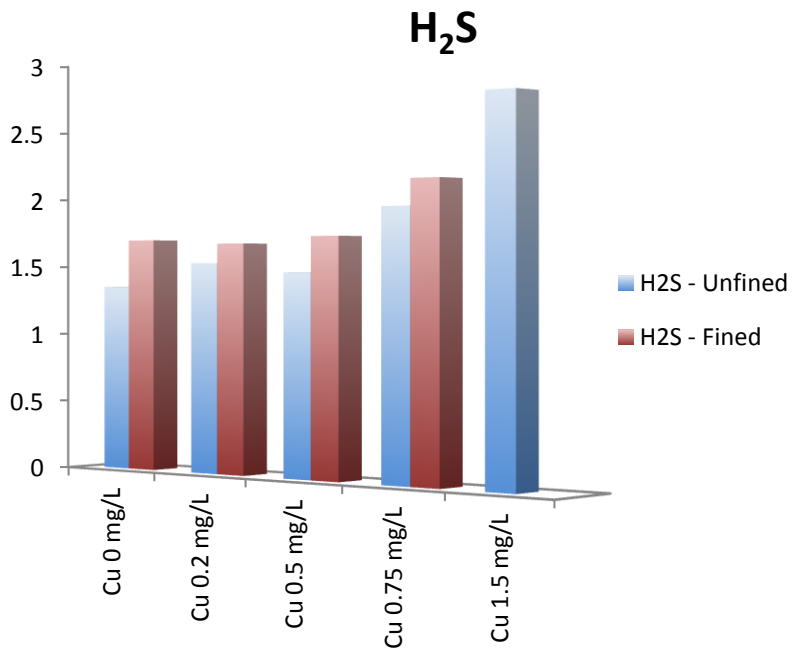
AWRI COMMERCIAL SERVICES
More than just a laboratory

Increases in sulfides

The Australian Wine Research Institute

After just 2 months this chardonnay was already showing the impact of increased copper.



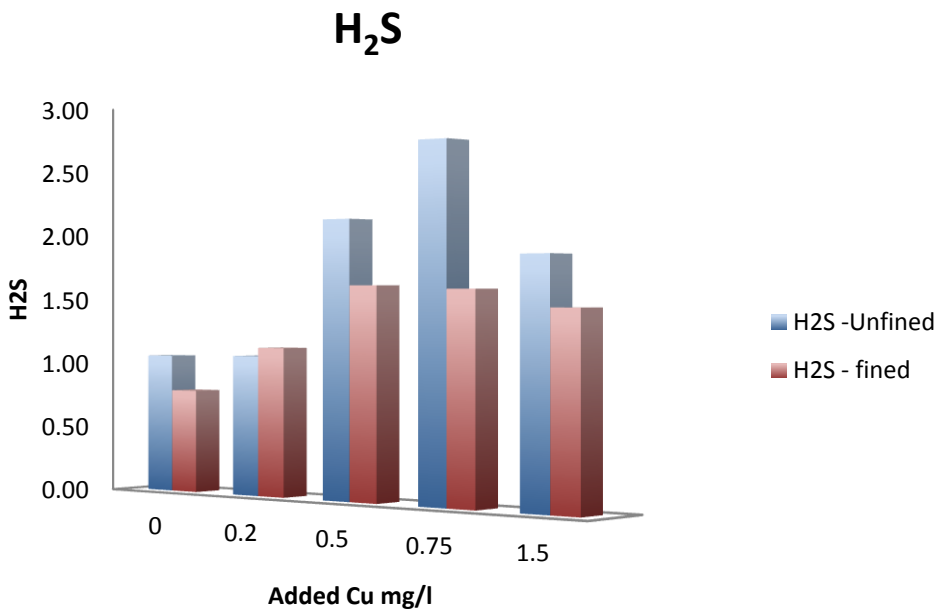


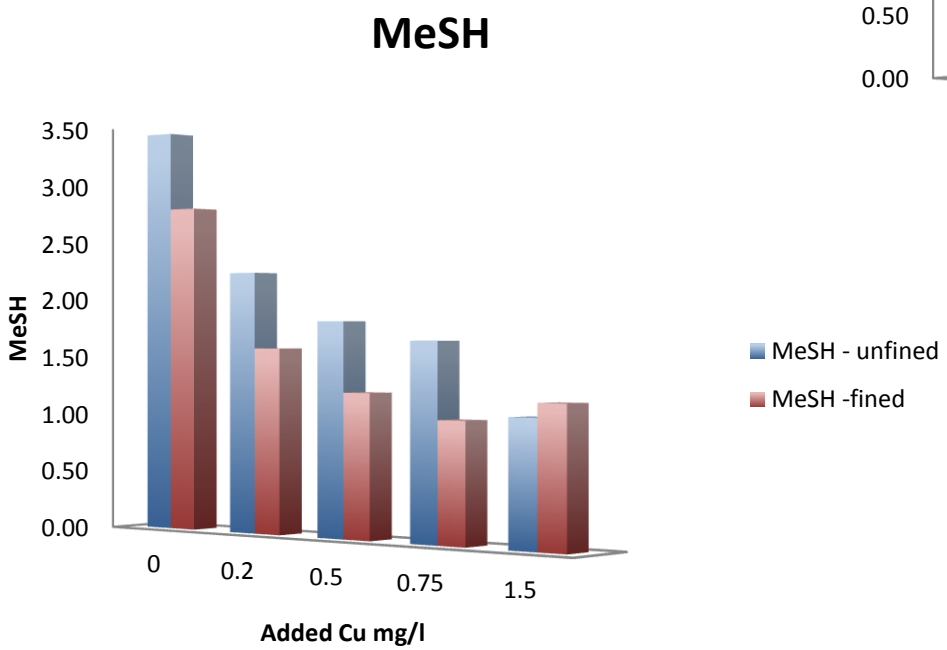
AWRI COMMERCIAL SERVICES
More than just a laboratory

After 6 months.

The Australian Wine Research Institute

While the MeSH has gone down, we don't know where!
The H_2S seems to be maxing at typical copper levels.

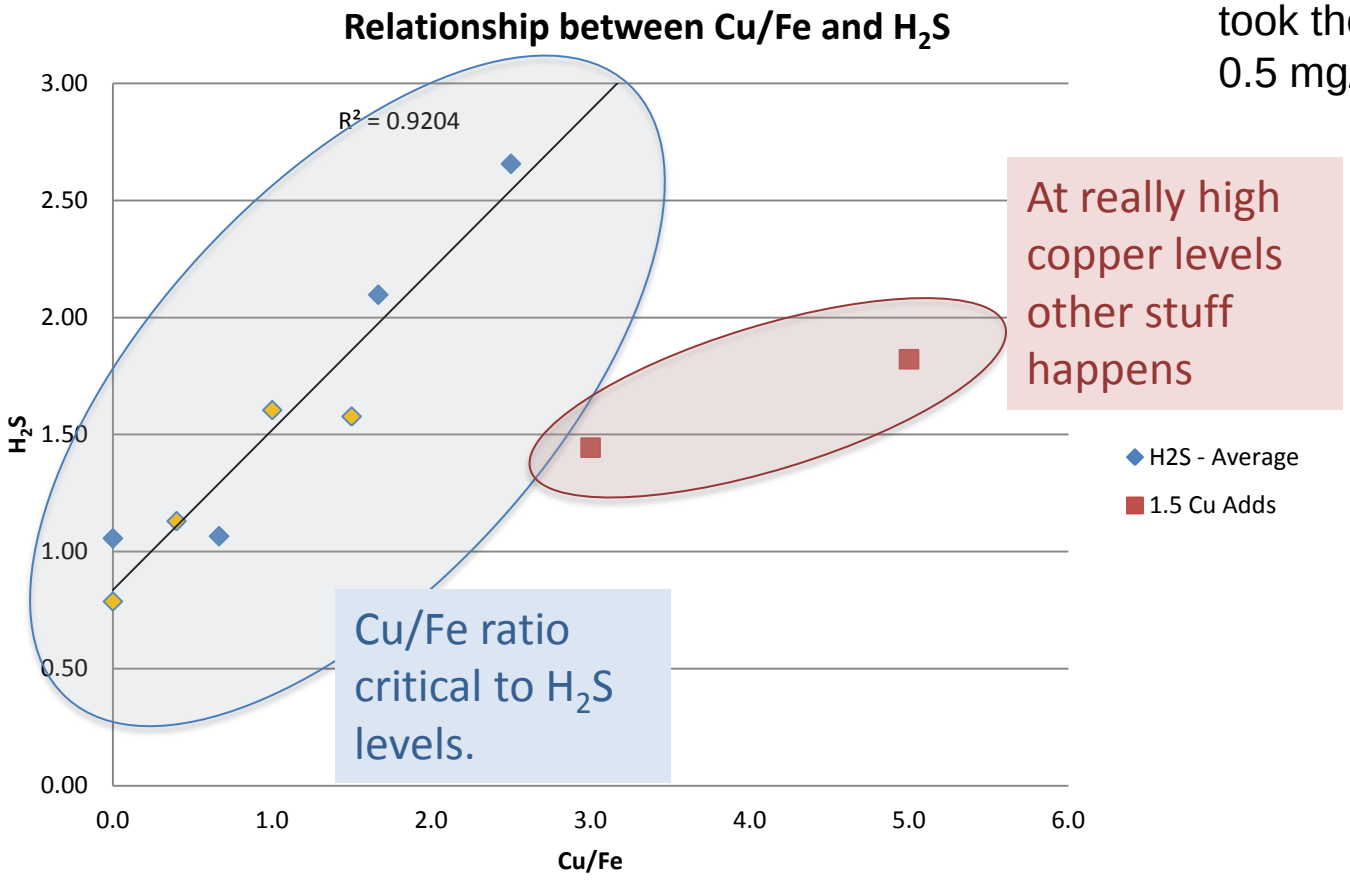




AWRI COMMERCIAL SERVICES
More than just a laboratory

fined / unfined?

The Australian Wine Research Institute

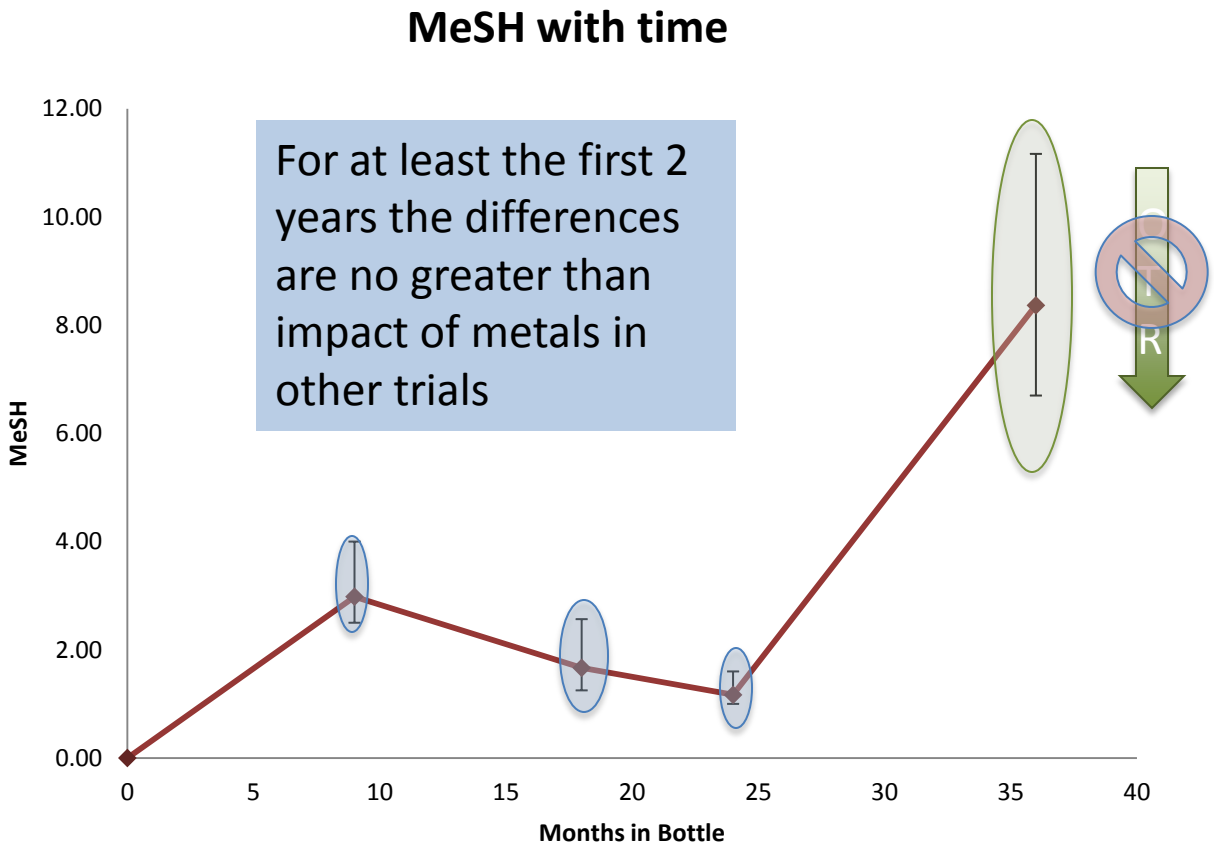


Fining with Bentonite took the wine from 0.2 to 0.5 mg/L of Iron.

AWRI COMMERCIAL SERVICES
More than just a laboratory

Isn't this just driven by the closure?

The Australian Wine Research Institute



Average results for 9 different closures.

Final level does not correlate with closure OTR!

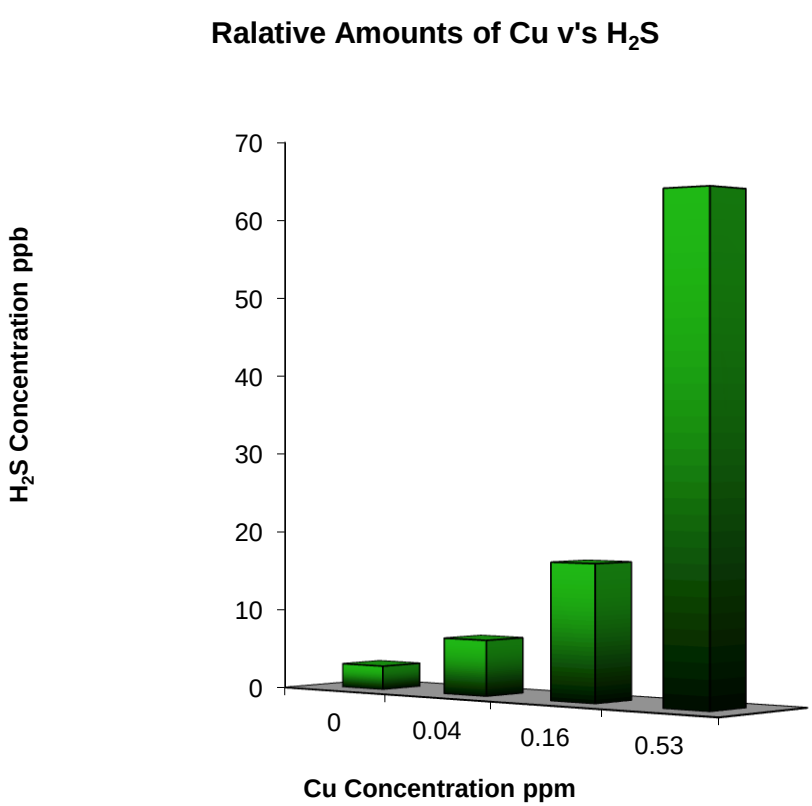
Pattern typical of what we see as the available O_2 / SO_2 environment changes.

AWRI COMMERCIAL SERVICES
More than just a laboratory

How bad could it get?????

The Australian Wine Research Institute

Clare Valley Riesling after 8 months.



Remember, the threshold for is about 1 for most people!

AWRI COMMERCIAL SERVICES
More than just a laboratory

Why the differences between wines?

The Australian Wine Research Institute

- No such thing as free copper in wine.
- It is all interacting in some way with the different species in wine.

- Some of these prevent copper getting involved in the oxidation/ reduction chemistry.

- Others don't!

- Incredibly important to tailor copper additions to the wine in question.

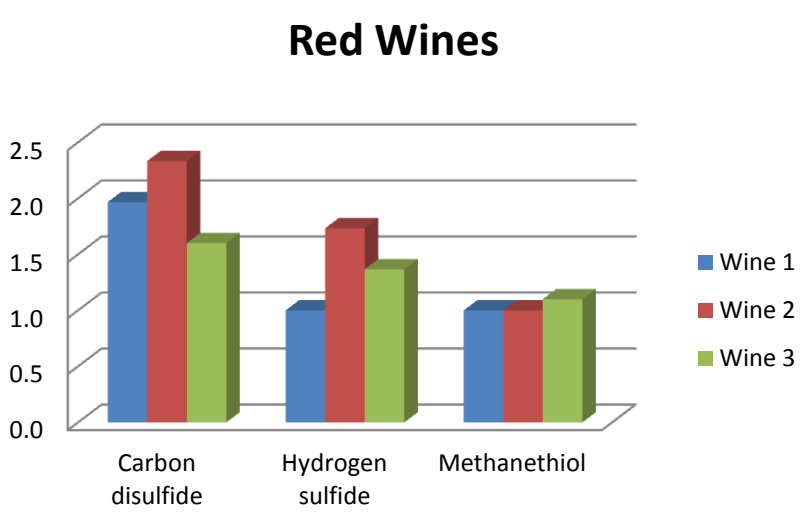
Never just make a standard addition!

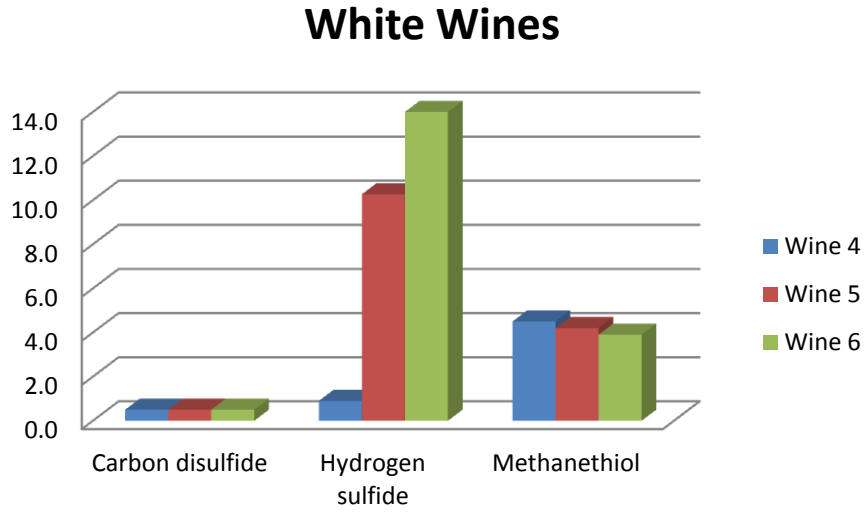
AWRI COMMERCIAL SERVICES
More than just a laboratory

The wines in front of you.

The Australian Wine Research Institute

		Carbon disulfide	Dimethyl sulfide	Hydrogen sulfide	Methanethiol	Methyl thioacetate
Wine 1	Red Control	2.0	73.7	<1	<1	6.4
Wine 2	Red 0.5mg/L Cu	2.3	87.0	1.7	<1	7.4
Wine 3	Red 0.75 mg/L Cu	1.6	65.7	1.4	1.1	6.7
Wine 4	White Control	<0.5	21.0	0.9	4.5	<5
Wine 5	White 0.5mg/L Cu	<0.5	21.7	10	4.2	<5
Wine 6	White 0.75 mg/L Cu	<0.5	21.0	14	3.9	<5





AWRI COMMERCIAL SERVICES
More than just a laboratory

When is it ok to use copper?

The Australian Wine Research Institute

- Best time to add is at the end of fermentation
  - Eliminate the potential precursors as early as possible
  - Use the solids to remove as much of the excess copper as possible

- If you have to do it later
  - Know what sulfur compounds you are treating (copper/cadmium test)
  - Add the minimum amount of copper.
  - Give it time to stabilize before bottling.
  - Test the copper levels before and after addition.

Never add on the day of bottling.

AWRI COMMERCIAL SERVICES
More than just a laboratory

Summary

The Australian Wine Research Institute

- Copper can be incredibly effective in preventing the development of off sulfur characters.
- However if excess is left in the wine it can lead to
  - the development of the same undesirable characters
  - hazes
  - degradation of SO_2 levels and desirable sulfur compounds
- Copper is best added early in the wines life when fermentation solids can help to remove it.
- Later additions can lead to a build up of available copper.
- Not all copper is striped from wine post addition as sulfides.
- Careful trials can lead to successful management of copper levels.

AWRI COMMERCIAL SERVICES
More than just a laboratory

Acknowledgements

The Australian Wine Research Institute

- Paul Smith
- Marlize Viviers
- Mark Smith
- Martin Day
- Mandy Herbst-Johnstone (Uni of Auckland)
- Treasury Wine Estates
- The rest of the AWRI team.

AWRI COMMERCIAL SERVICES
More than just a laboratory

Thankyou

The Australian Wine Research Institute

Questions?

AWRI COMMERCIAL SERVICES
More than just a laboratory