Copper, the good, the bad, the ugly

Dr Eric Wilkes
Why do we use copper at all?

Copper has a long history of use in beverage production to remove unpleasant sulfur related smells.

Analysis of 80,000 international wine show entries show ~0.9% of wines rejected for reduction, with no significant difference between closures.
What are these smells

- **H₂S**: 1.1-1.6 µg/L
  - Sulfurous, cheesy, egg

- **MeSH**: 1.8-3.1 µg/L
  - Vegetal, cabbage, intense onion like

- **DMS**: 25 µg/L
  - Blackcurrant, cooked cabbage, asparagus, canned corn

- **DMDS**: 10 µg/L
  - Rotten cabbage, burnt rubber, putrefaction

- **MeSAc**: 40 µg/L
  - Sulfurous, cheesy, egg
The 1950s story.

$\text{H}_2\text{S}$  \[ \text{H}_2\text{S} + \text{Cu}^{2+} \rightarrow \text{CuS} \downarrow \]

**Mercaptans**  \[ \text{CH}_3\text{CH}_2\text{SH} + \text{Cu}^{2+} \rightarrow \text{Cu(CH}_3\text{CH}_2\text{S)}_2 \downarrow \]

 oxidation $\downarrow$ $\uparrow$ reduction

$\text{DMDS}$  \[ \text{CH}_3\text{S-SCH}_3 + \text{Cu}^{2+} \rightarrow \text{unreactive} \]

$\text{DMS}$  \[ \text{CH}_3\text{SCH}_3 + \text{Cu}^{2+} \rightarrow \text{unreactive} \]
But why doesn’t it always work?

- Why don’t the bench trials always reflect what I see in tank?
- Why does my wine go stinky again after it is treated in tank?
Myth 1, the size of copper additions.

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.
Myth 2, filtration does not really work.

So what is this residual copper?

The majority of copper found in commercial wines is in a tightly bound non-labile form.

A study of 52 commercial wines by Nikolaos Kontoudakis and Andrew Clark, Charles Sturt University.

It is the form of copper that is important!

Levels of electrochemically labile copper above 25 µg/L do limit the formation of free H$_2$S.

But most of the copper is in non labile form which does not inhibit the presence of free H$_2$S.
Metals play a crucial role in wine chemistry!
Myth 3, the problem with fining trials

High Oxygen

Low Oxygen
So What?
Increased loss of positive thiols

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

Dr. Mandy Herbst-Johnstone
School of Chemical Sciences
The University of Auckland
More rapid loss of SO$_2$

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!

Increases in sulfides

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

Remember, the threshold for H₂S is about 1 for most people!
What are some of the triggers?
Time in bottle

Shiraz - \( H_2S \)

- Control
- \( Cu \)

Odour Threshold: 1.1 - 1.6 µg/L

Shiraz - MeSH

- Control
- \( Cu \)

Odour Threshold: 1.8 - 3.1 µg/L

oxygen depletion
In this trial from 2014 we looked at the impact on a wine of adding copper immediately after fermentation and just before bottling.

The late copper addition led to significantly higher $\text{H}_2\text{S}$. But more importantly the impact was not apparent until 12 months after bottling.
Increased H₂S correlates with the addition of Cu and SO₂.

These trial were done under the exclusion oxygen.
The impact of pH and copper

As can be seen with this wine pH alone has little impact on the level of H₂S generated.

In the presence of copper however pH has a major role in determining the levels of H₂S generated.

It is not just the copper!

The relationship between Cu/Fe and H$_2$S is shown in the graph. The correlation coefficient $R^2 = 0.9204$ indicates a strong relationship. Cu/Fe ratio is critical to H$_2$S levels. At really high copper levels, other stuff happens. Mn, Zn and Al also seen to have an impact on VSC’s.

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Can’t we manage this with a closure?

MeSH with time

For at least the first 2 years the differences are no greater than impact of metals in other trials.

Average results for 9 different closures.

Pattern typical of what we see as the available O₂ / SO₂ environment changes.
Do we have any alternatives?

Using a commercial “tannin” marketed for its ability to add freshness we see a significant difference in H₂S post 9 months in bottle.

Using a cross linked polymer to reduce Cu and Fe we see a reduction of H₂S after 9 months in bottle.

Have we removed VSC’s with the Cu?
So what can we do?

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

If you have add it later
- Know what sulfur compounds you are treating (copper/cadmium test)
- Look at using copper in bound forms (copper citrate/bentonite)
- Use active yeast to strip the residual copper.
- When available try using cross linked polymers to remove the copper (and possibly the bound sulfides).

Never add on the day of bottling.
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Questions?