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Canned Wine: New Information for Preparing Wines for Canning

George Crochiere, Jasha Karasek, Neil Scrimgeour, and Eric Wilkes

DATE 5/21/20

WEBINAR INFO

- Recording in progress..
- If you are experiencing a bad connection, try exiting and re-entering the webinar
- Please use chatbox only for Q&A at the end of the webinar
- Please be respectful of each other if you use the chatbox

SOME QUESTIONS TO BE ADDRESSED IN THIS WEBINAR

- What makes a can a unique form of packaging?
- What factors contribute to reduction appearing in canned wines?
- How can winemakers avoid reduction appearing for canned wines?
- What treatments are available to prepare wines for canning?

AGENDA FOR TODAY

- George Crochiere – Crochiere & Associates
  Packaging perspective

- Neil Scrimgeour – Australian Wine Research Institute
  Understanding and mitigating the development of reductive characters in canned wines

- Eric Wilkes – Australian Wine Research Institute –
  Wine in cans? A tale of two metals with various supporting players!

- Jasha Karasek – Enartis USA
  Analysis and Treatments for Canned Wine

- Q&A – 20 - 30 mins

POLL QUESTION!

GEORGE CROCHIERE – CROCHIERE & ASSOCIATES

- President and Co-Owner of Crochiere and Associates LLC. Since 1977, George has worked polymers, ranging from development of plastics and rubber materials while working for spalding, to working as technical manager of coating & closure systems for W.R. Grace in North America. He has worked most recently with beverage, bottle, closure, and plastics manufacturers providing services and test results that lead to improved shelf-life, performance and consistency in their packaging materials. George is also working currently as the materials development manager for Vibram.

Wine in Cans – Packaging Perspective

George K. Crochiere

Crochiere & Associates

www.beerandwinepackagingperformance.com

Wine in Cans – Packaging Issues

- Oxygen or Lack of it
- Barrier Coatings
- Pack Testing
- Storage & Interaction Issues
- Information & Communication

Oxygen Issues

- While most packages have too much oxygen, cans may not have enough.
- At filling – cans flushed, counterpressure filling, LN2 injection = very low initial oxygen
- EOE double seam = zero ingress
- Cans are one of the lowest oxygen level pacages

Barrier Coatings In Cans

- Internal easy-open-end coating
  - Coil coated before ends are made
  - Typically solvent based
- Internal body coating/liner
  - Spray applied into the formed can
  - Typically water-borne

Barrier Coating Performance Criteria

- Properly Cured
- Proper Application
- Best Chemistry

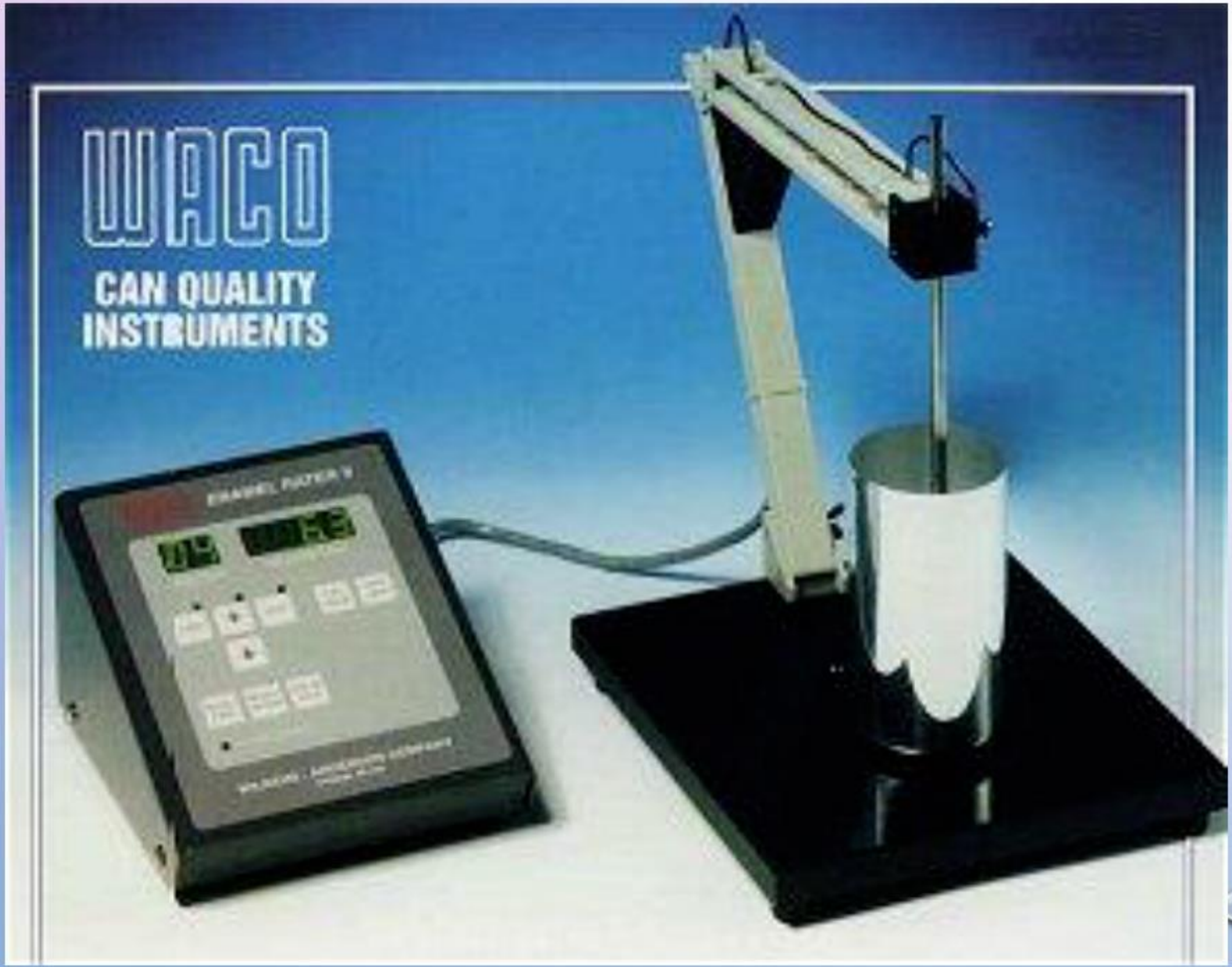
Proper Cure = Optimum Properties

- After application, the solvent/liquid evaporates & chemical cross-linking creates coating properties
- Cure takes place in ovens at specified temperatures for a specified period of time
- Undercured coatings have weak physical and chemical properties
- Overcured coatings can burnt or brittle

Proper Application = Optimum Properties

- Proper film weight/thickness gives the best balance of properties
  - Low film weight saves cost but has poorer barrier properties
  - High film weight increased cost and barrier properties
- Porosity, skips, pinholes create a path for corrosion
- Puddles, drips, blisters can be a sign of too much coating, trapped solvent and poor cure
- Sometimes two coats are needed for the best barrier properties (not common in beverage cans

TESTING COATING BARRIER PROPERTIES



Can Coating Chemistry

- BPA is a monomer in traditional epoxy resins used to make epoxy-acrylic can coatings, the industry standard for decades. Also used in epoxy-amine and epoxy-phenolic food can coatings. High performance, chemical resistance, adhesion, durability.
- BPA-free (NI-BPA, Non-BPA, etc.) coatings include all others
  - Each has different physical, chemical and sensory properties
  - BPF epoxies new to the market, may be closest match to established coatings
  - Polyesters, Acrylics, Vinyls, PET, etc.

Which BPA-Free Coating?

- Coating companies and chemists have been working on alternatives
- Each coating formula or recipe will have different properties, the resin type is just the starting point.
- Lab work and trials start with bench-top testing to predict performance and chemical resistance (soft drinks, beer, wine, etc.)
- Pack tests are the only way to truly evaluate the coating performance
- Accurate records of all materials, conditions, settings used in all aspects of a pack test are needed to identify the strengths and weaknesses of each coating.
- Comparing results of many tests allows the industry to find the best packaging

Ideal Pack Test Data Collection

- Coating manufacture, location, formula number, lot number/date
- Coating application conditions, film weight, line speed, bake conditions
- Can & end maker, location, lot number/date
- Filling conditions, wine chemistry, line speed, purge, headspace flush, can pressure, initial TPO
- Storage conditions, time, temperature
- Evaluation method, chemistry, sensory, can and end teardown and examination
- Not all things are possible, but more is better to build the industry puzzle

BPA-FREE COATING SUPPLIERS

- SHERWIN-WILLIAMS, VALSPAR
  - VALPURE V70, NEW EPOXY RESIN, TETRAMETHYL BISPHENOL F (TMBPF), STARTING IN CALIFORNIA
    - BODY SPRAY – ACRYLIC, EPOXY
    - ENDS – POLYESTER, EPOXY
  - VALPURE V30, V60
    - ENDS – POLYESTER
  - VALPURE V40
    - BODY SPRAY – ACRYLIC
- PPG
  - INNOVEL HPS – ACRYLIC, BODY, ENDS
  - INNOVEL VCL - POLYESTER, BODY
- AKZONOBEL
  - AQUALURE
    - BODY SPRAY - AQUALURE G1 50, BPA-NI (NON-INTENTIONALLY ADDED), ACRYLIC
- DIAWA SEIKAN – LAMINATED PET – BODY & END

Storage & Interaction Issues

- The wine is inside a polymer bag within a can
- There should be no interaction with the aluminum
- There will be interaction with the polymer coating
- Most polymer materials contain a variety of additives and modifiers, each of these can interact with the wine.

Types of Polymer Interactions

- Interactions that effect sensory properties
  - Flavor scalping or absorption - Similar polarity between polymer and flavor molecule = More scalping
  - Polymer additive extraction - Low molecular weight, similar polarity to beverage = More extraction
- Interactions that effect the package
  - Liquid absorption by the polymer - Polymer blush/fogging, swelling, adhesion loss and reduction of barrier properties
  - Chemical reactions – Degradation of coatings, films and metal

Possible Effects in Cans and Beverages

- Sensory changes due to scalping or extraction
- Surface tension changes due to coating surfactants
- Internal coating failure
  - Blush
  - Blisters
  - Peeling
- Can Failure
  - Corrosion
  - Holes
  - Leakage

Storage Condition Issues

- High temperature exposure
  - Greater beverage and polymer interaction
  - Waxes and process aids can melt and migrate, change polymer properties
  - Reduction in barrier properties, higher oxygen ingress
- Cleanliness
  - Negative consumer experience if not cleaned

Final Packaging Selection

- All packaging options are a compromise
- No package is perfect
- Just because one can, bag-in-box, screw cap may have issues, others will be different
- Success and failure are often in the details
- Network, communicate, compare results and conditions with others
- New products like BPA-free will have growing pains

Performance Database

- Crochiere & Associates is setting up a forum and database on our website to share and compare packaging performance
- We ask breweries and wineries to list their canning trail conditions and results both good and bad
- We will sort and tabulate the data into a spreadsheet to be shared on the website.
- www.beerandwinepackagingperformance.com

POLL QUESTION!

NEIL SCRIMGEOUR – AUSTRALIAN WINE RESEARCH INSTITUTE

- Neil works in wine research at the AWRI. He is a Senior Scientist for the commercial services division and manages research for new winemaking technologies, saving the industry money, and improving quality.

Understanding and mitigating the development of reductive characters in canned wines

Neil Scrimgeour

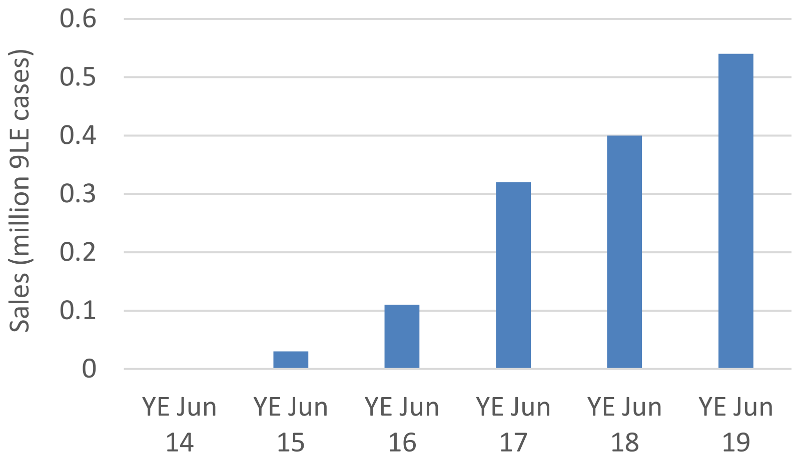
Senior Scientist, Commercial Services

The Australian Wine Research Institute

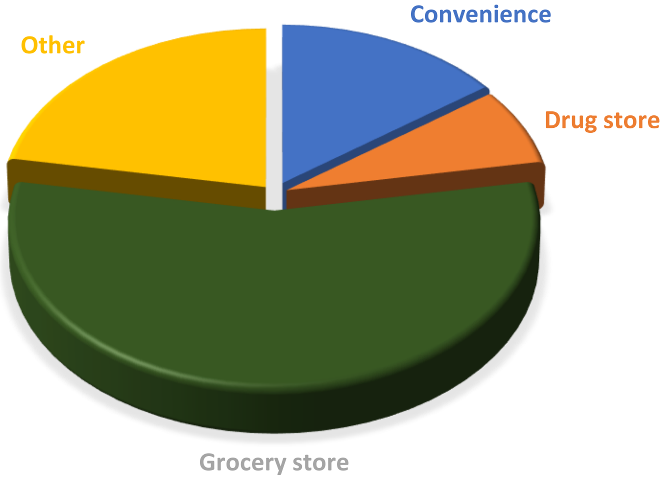
The evolution of canned wine

Canned Wine: Aus vs USA Market Trends

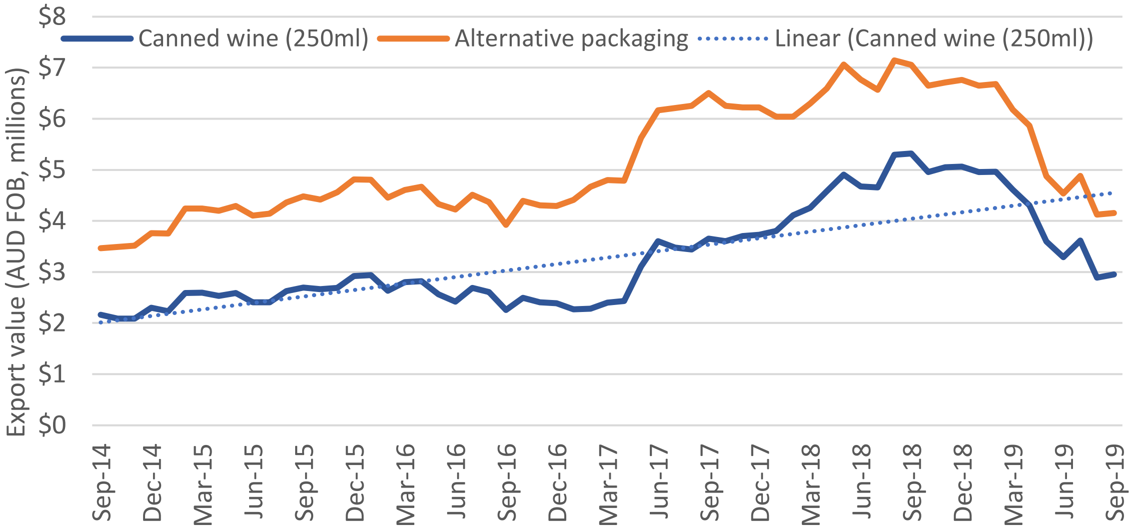
The Australian Wine Research Institute



Total USA off-trade sales of wine in cans



Total USA off-trade sales of wine in cans by channel breakdown (year ending June 2019)



Australian export value of wines packaged in 250ml can containers and alternative packaging

Sources: IRI Worldwide; IRI Market Edge MAT to 30/06/19

Project Summary

The Australian Wine Research Institute

- Canned wines currently have a short shelf-life and are susceptible to formation of volatile (stinky) sulfur compounds
- A better understanding of the chemical pathways involved is required to resolve the issue.
- This will help to identify remediation strategies that can be used to extend wine shelf-life in cans.
- The study is being supported via an industry consortium, including major wine producers and suppliers, both in Australia and in the USA.
- Additional funding is provided through a Food Innovation Australia Ltd (FIAL) grant.

Key Trial Elements

The Australian Wine Research Institute

BENCHMARK

- Understand the extent of the reduction issue (*and some underlying trends*) through analytical monitoring of commercial canned wines, post-packaging.

INVESTIGATE

- Identify the key chemical pathways that support the formation of reductive characters post-packaging and gain a better understanding of the potential role of the can liner in these processes.

MITIGATE

- Trial the use of remediation methods that can be used to mitigate the risk of formation of reductive characters post-packaging.

VALIDATE

- Undertake field trials to validate the performance of commercial wines in achieving extended shelf-life.

Canned wine – risk factors

The Australian Wine Research Institute

Attribute	Upper limit
Free SO_2	<35 mg/L
Copper	<0.2 mg/L
Chloride	<50 mg/L
pH	
CO_2	
Ullage	
Oxygen (TPO)	

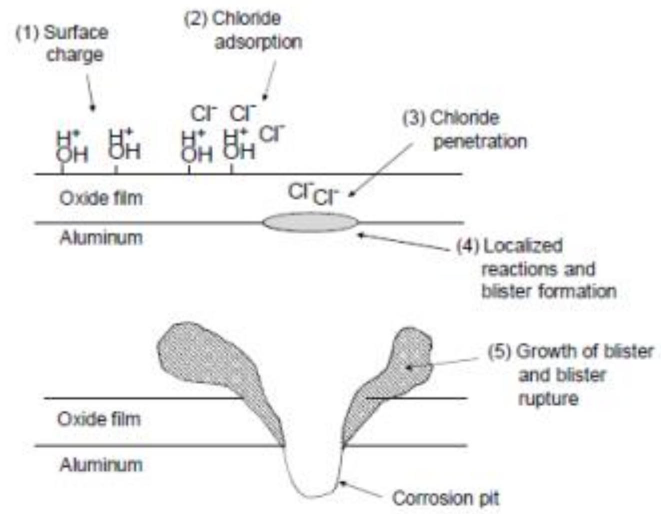


Fig. 10.40 Sequence of steps in the pitting of aluminum [67]

Excerpt from *Introduction to Corrosion Science* [McCafferty, 2010]

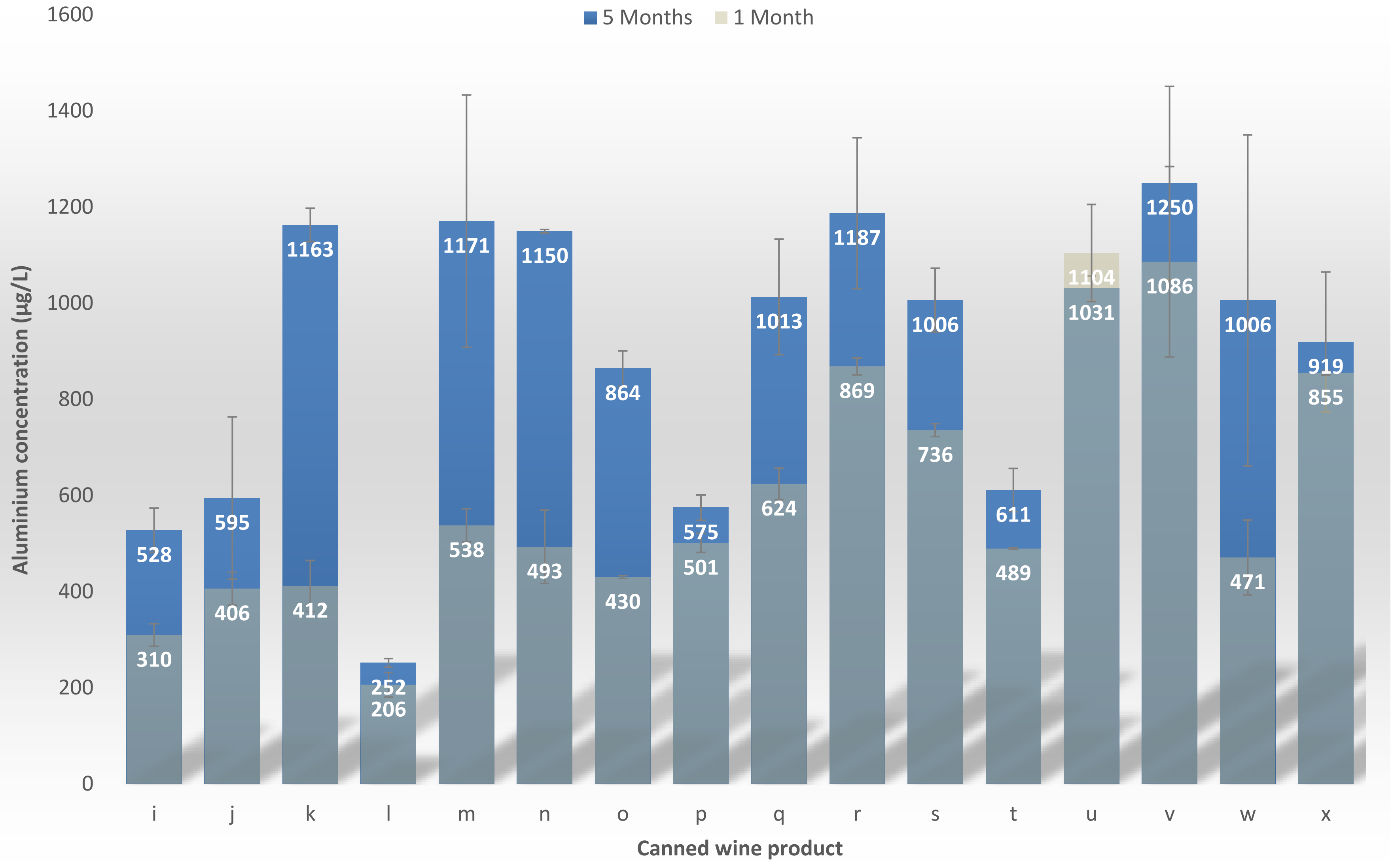
$$Al(s) \rightarrow Al^{3+} + 3\,e^-$$

$$SO_2 + 6\,H^+ + 6\,e^- \rightarrow H_2S + 2\,H_2O$$

$$\mathbf{2\,Al(s) + SO_2 + 6\,H^+ \rightarrow 2\,Al^{3+} + H_2S + 2\,H_2O}$$

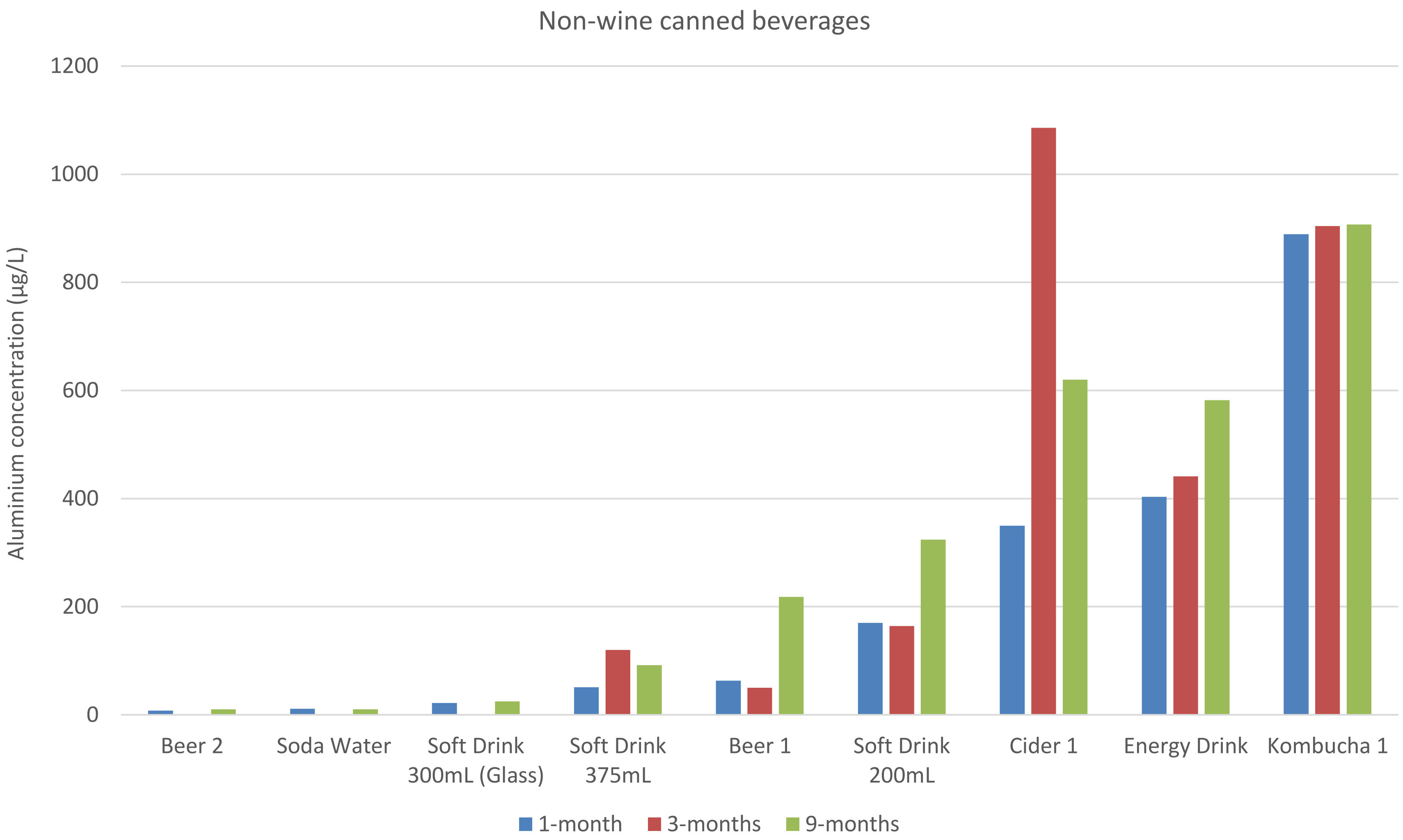
Benchmarking commercial canned wines - Aluminium

The Australian Wine Research Institute



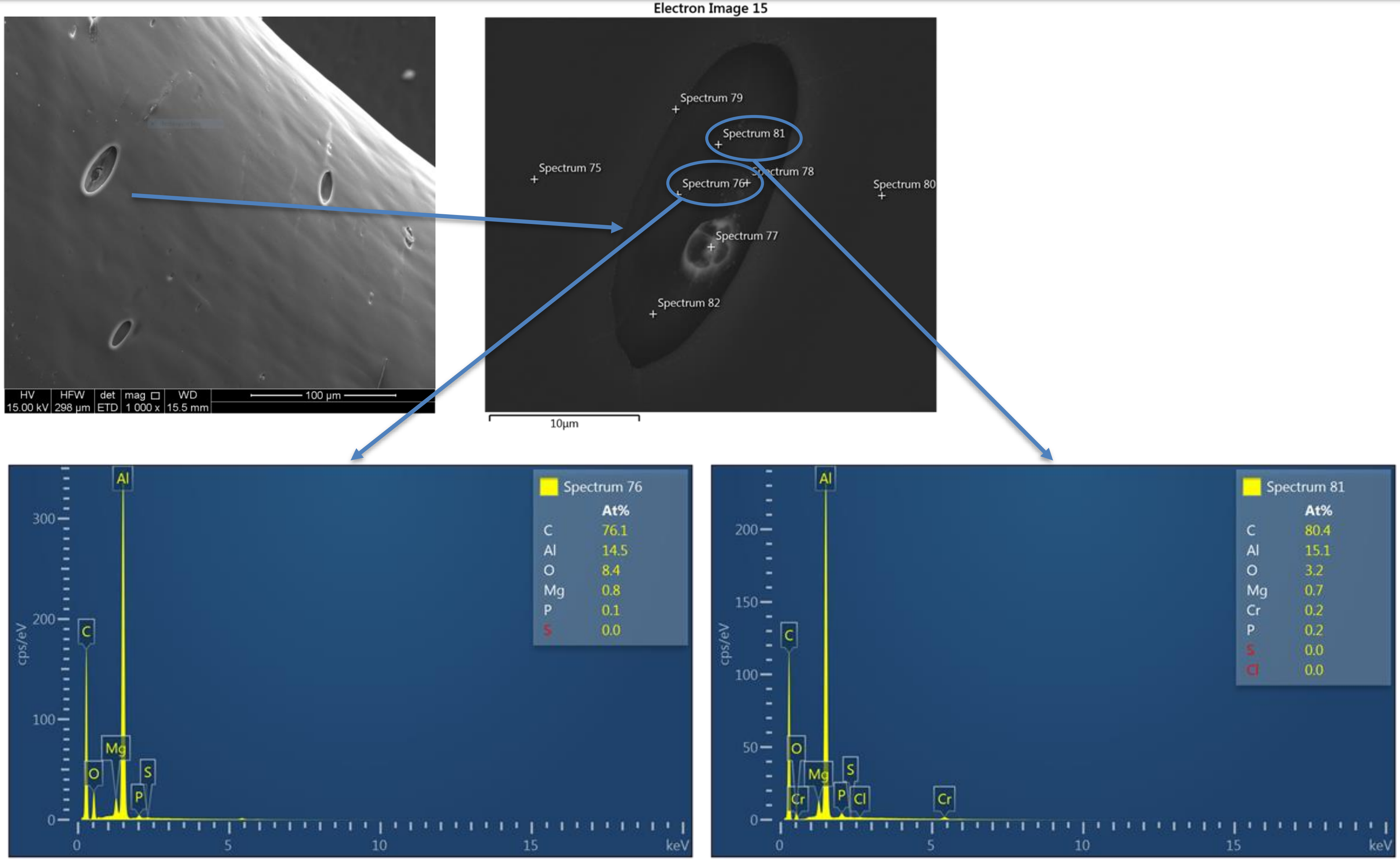
Aluminium transfer in carbonated beverages

The Australian Wine Research Institute

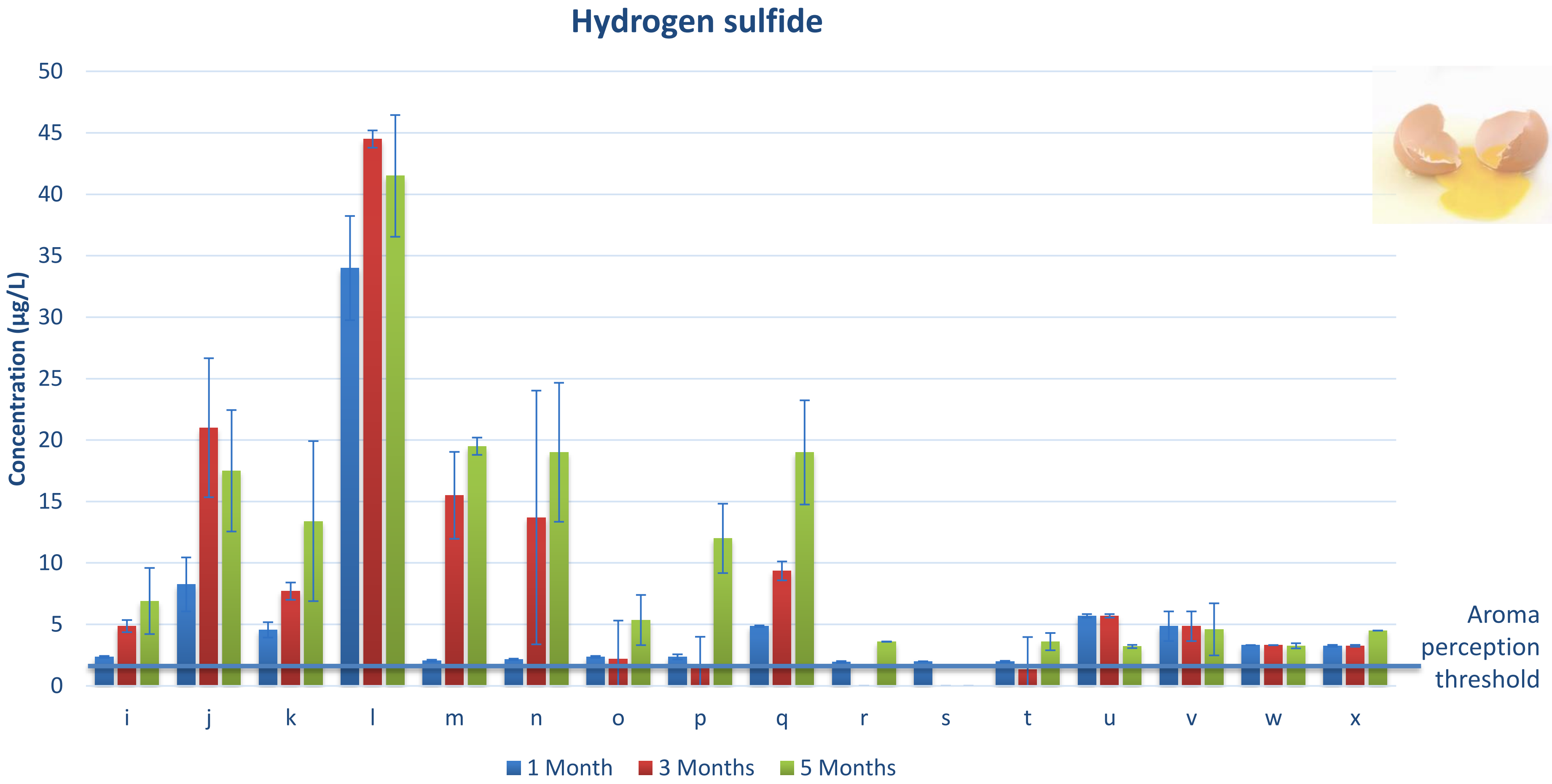


Microscopic analysis of canned wines

The Australian Wine Research Institute

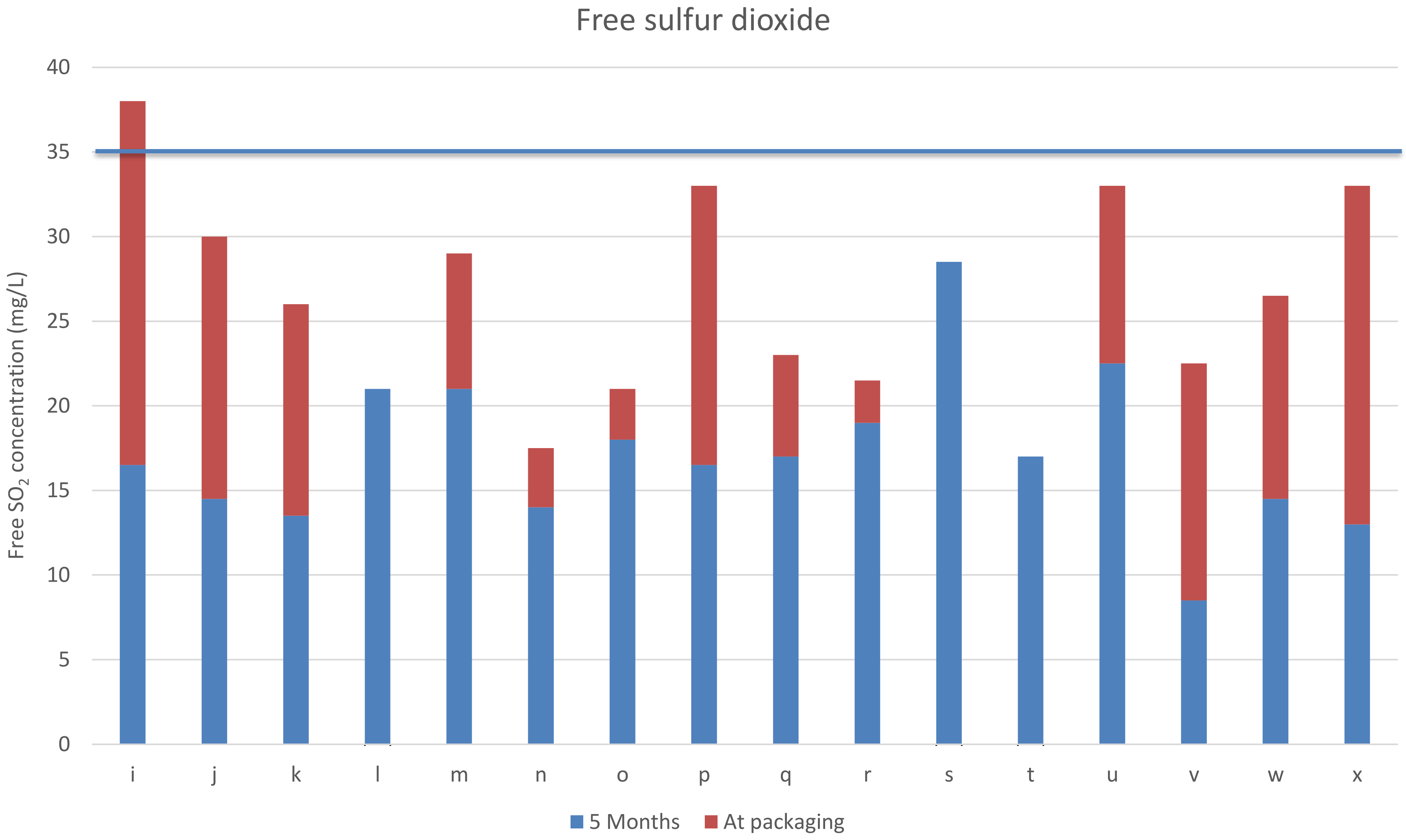


Benchmarking commercial canned wines - sulfides



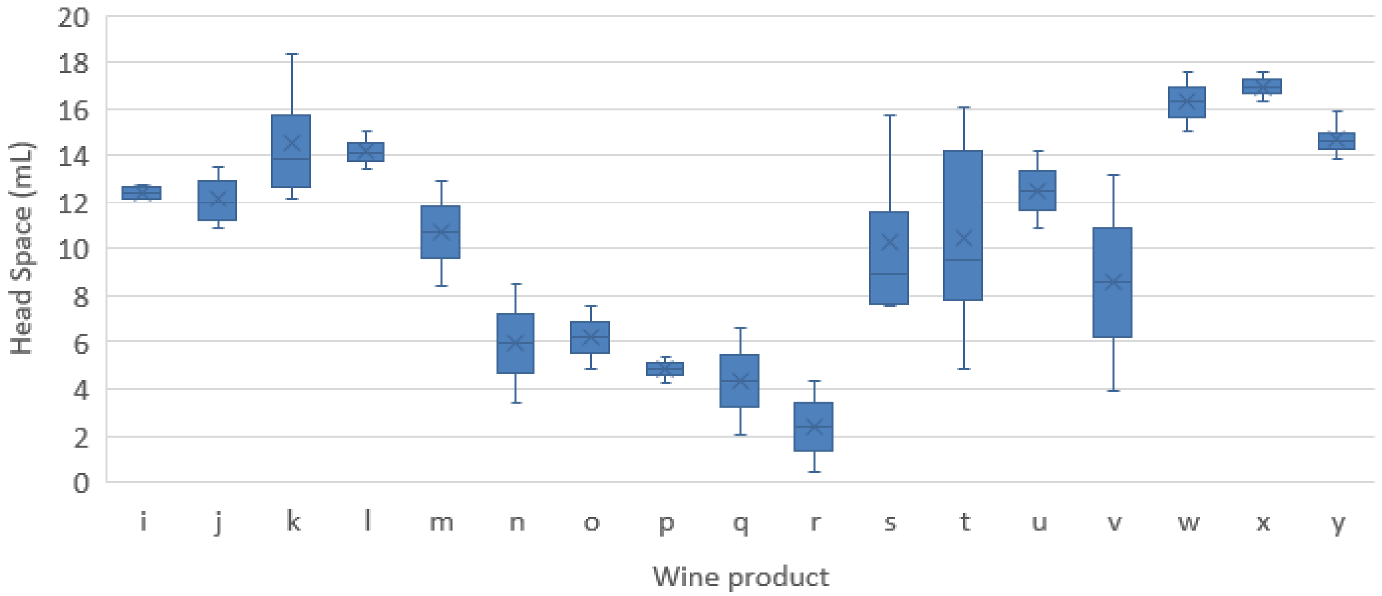
Benchmarking commercial canned wines - SO_2

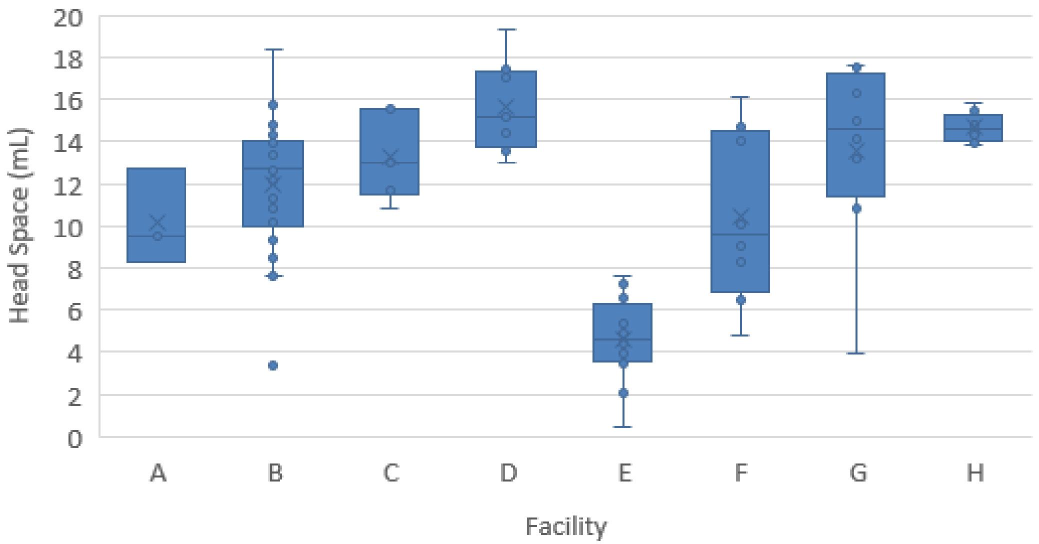
The Australian Wine Research Institute



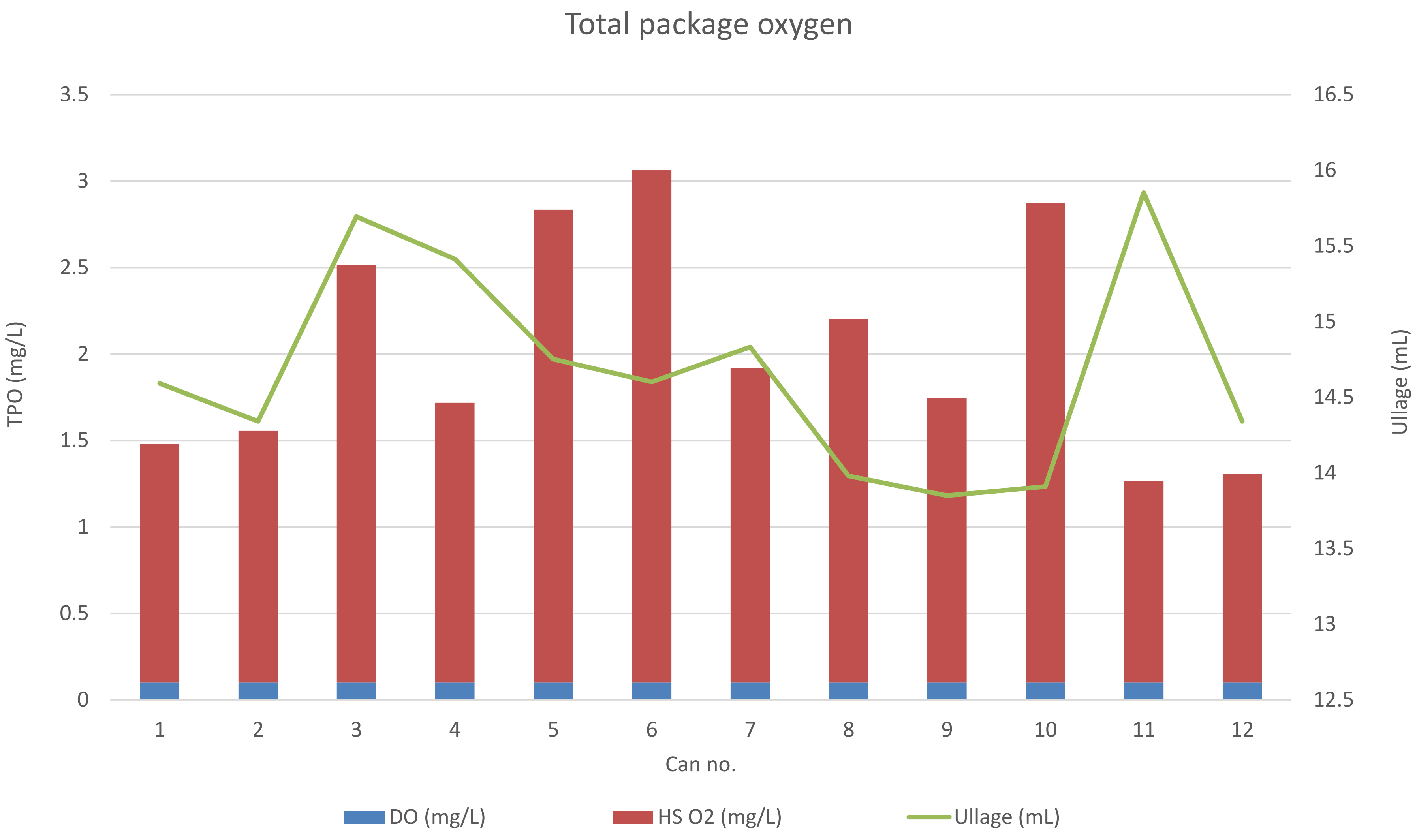
Benchmarking commercial canned wines - Ullage

The Australian Wine Research Institute



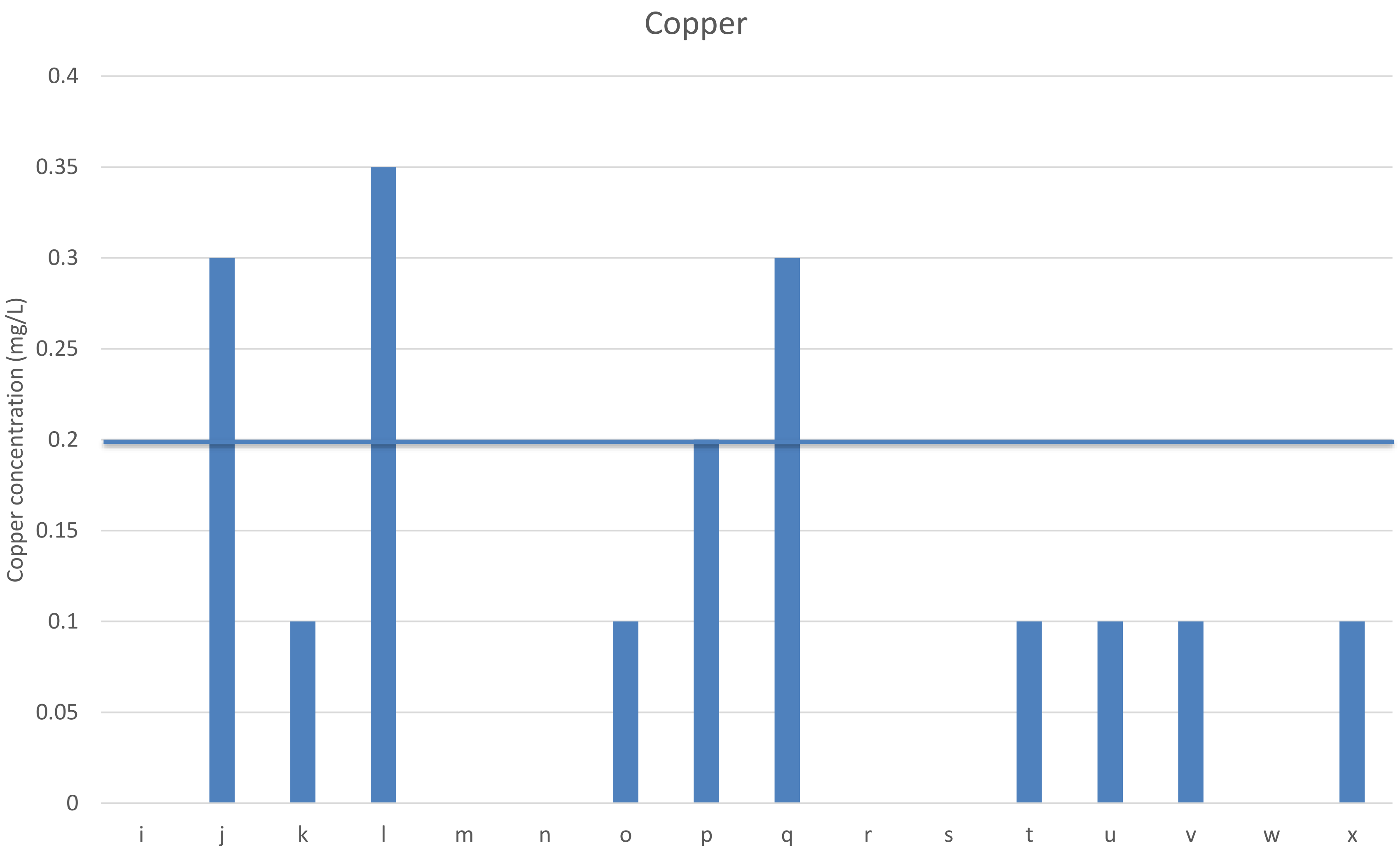


Benchmarking commercial canned wines - TPO



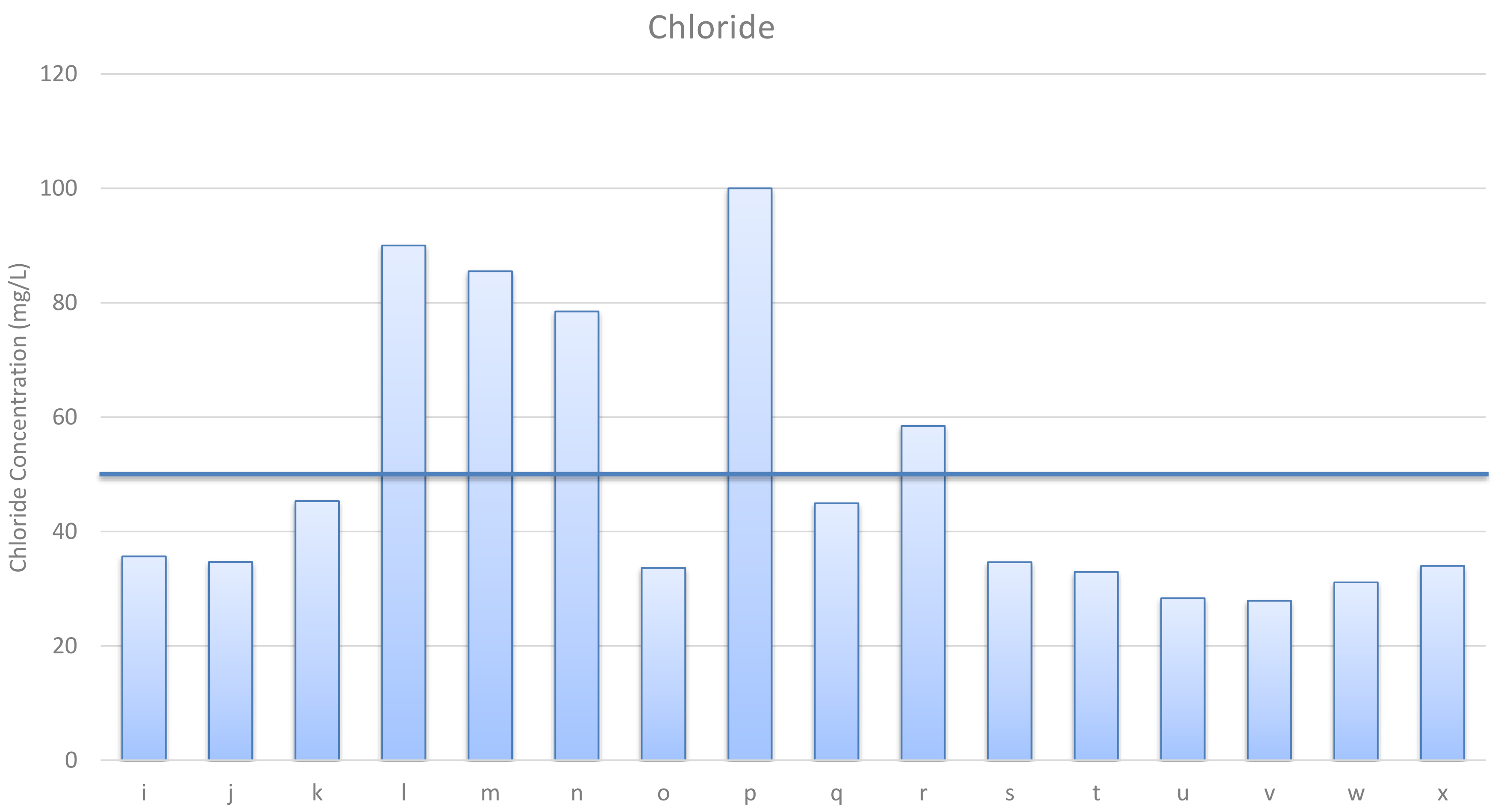
Benchmarking commercial canned wines - Copper

The Australian Wine Research Institute



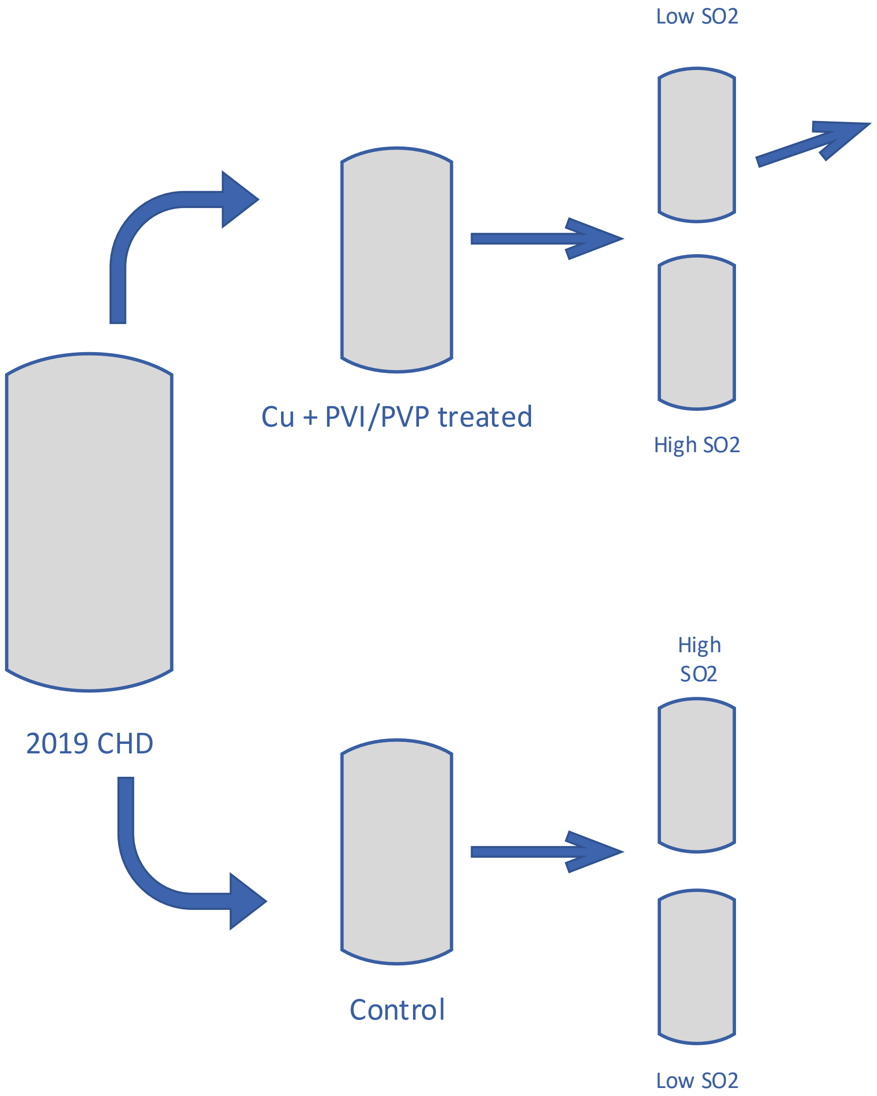
Benchmarking commercial canned wines - Chlorides

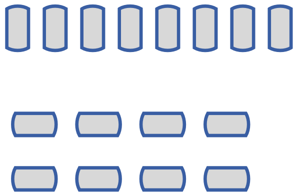
The Australian Wine Research Institute



Small scale canning trial

The Australian Wine Research Institute



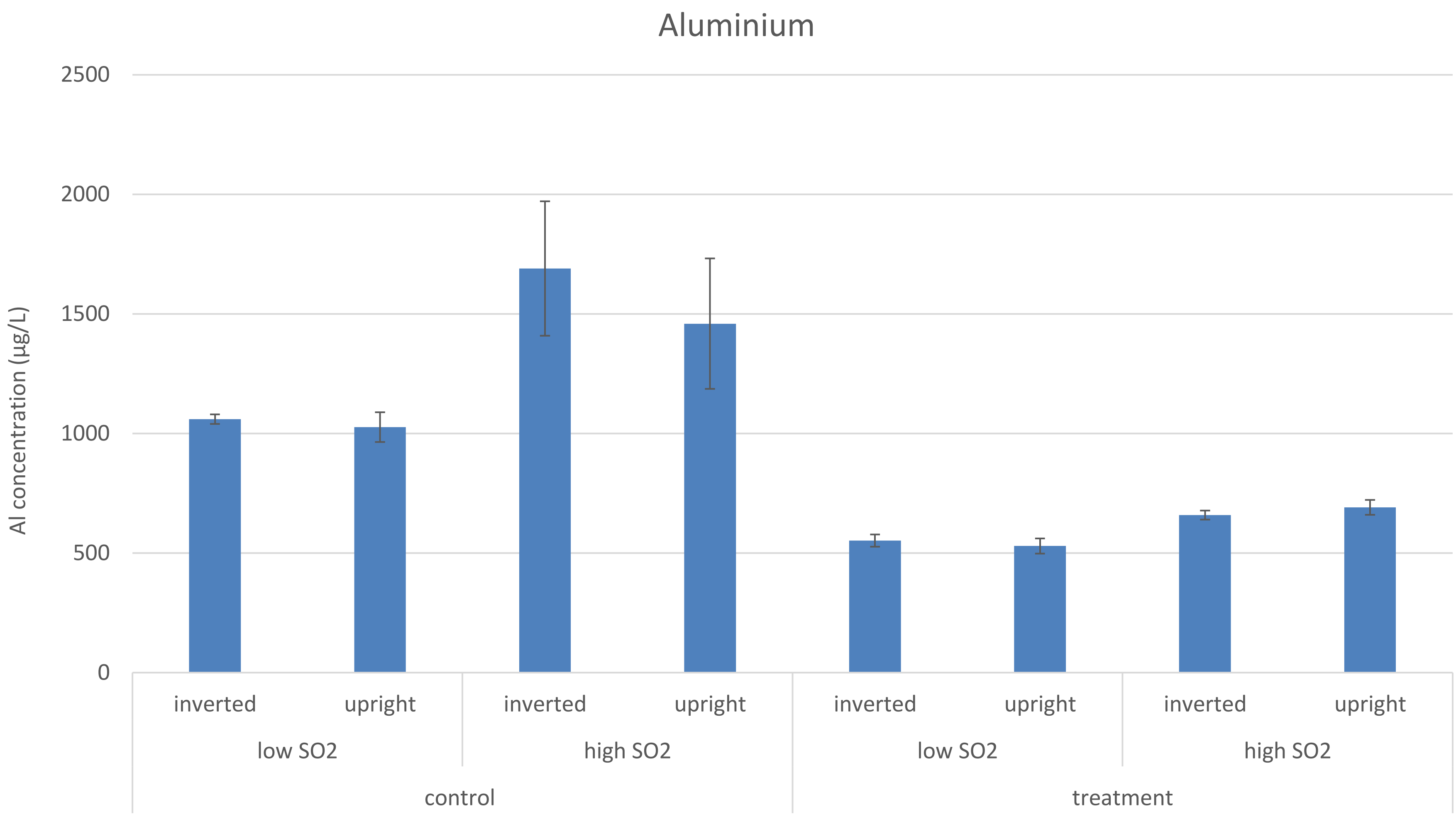


SO_2 mg/L (low)	30-35
mg/L (high)	53-59
Ullage	4-6 mL
CO_2 g/L	1.5-2.2
TPO mg/L	4.5-5.5

Evaluate impact of wine factors on Al concentration and sulfide formation

Small scale canning trial

The Australian Wine Research Institute



Summary

Most commercial canned wines have elevated aluminium levels, due to the corrosive nature of the wine matrix

Most canned wines contain significant concentration levels of hydrogen sulfide (H_2S), even after only 1-month post-packaging

The impact of H_2S formation can be mitigated by removing residual copper prior to packaging

The degree of risk and potential impact of wine reduction (H_2S) is very much wine dependent

ERIC WILKES– AUSTRALIAN WINE RESEARCH INSTITUTE

- Eric Wilkes is the group manager for commercial services at the AWRI. Specialising in technical management, Eric has extensive experience in successfully integrating new technologies and systems into wine production and improving those already in place. He is also a past committee member of the Interwinery Analysis Group, the co-author of a book on wine laboratory analysis and a regular speaker at industry conferences on technical issues around wine analysis and production.

The Australian Wine Research Institute

Wine in cans?
A tale of two metals,

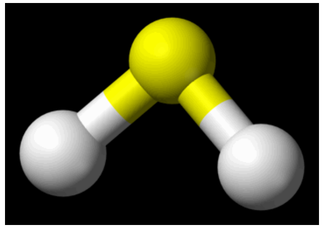
with various supporting players!

Dr Eric Wilkes

AWRI
COMMERCIAL SERVICES
More than just a laboratory

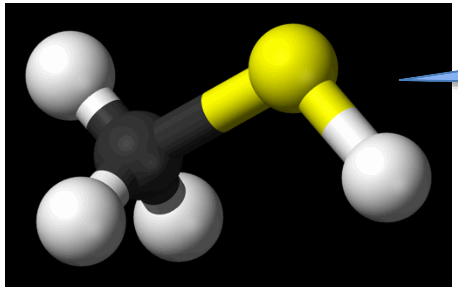
A little bit of background

Before we talk about cans some background on copper and sulfides we have learned from wine in bottles.



H_2S 1.1-1.6µg/L

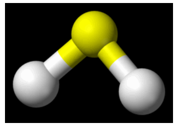
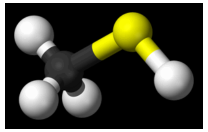
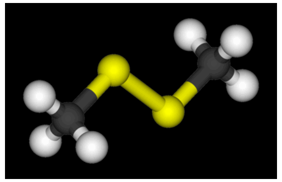
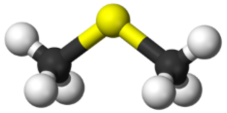
rotten egg, sewage like



MeSH 1.8-3.1µg/L

rotten cabbage, burnt rubber, putrification

The 1950s story.

H_2S	$H_2S + Cu^{2+} \rightarrow CuS\downarrow$	
Mercaptans	$CH_3CH_2SH + Cu^{2+} \rightarrow Cu(CH_3CH_2S)_2\downarrow$	
	oxidation $\downarrow\uparrow$ reduction	
DMDS	$CH_3S\text{-}SCH_3 + Cu^{2+} \rightarrow$ unreactive	
DMS	$CH_3SCH_3 + Cu^{2+} \rightarrow$ unreactive	

Myth 1, the size of copper additions.

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.

Myth 2, filtration does not really work.

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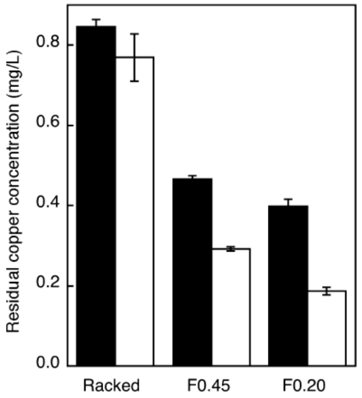
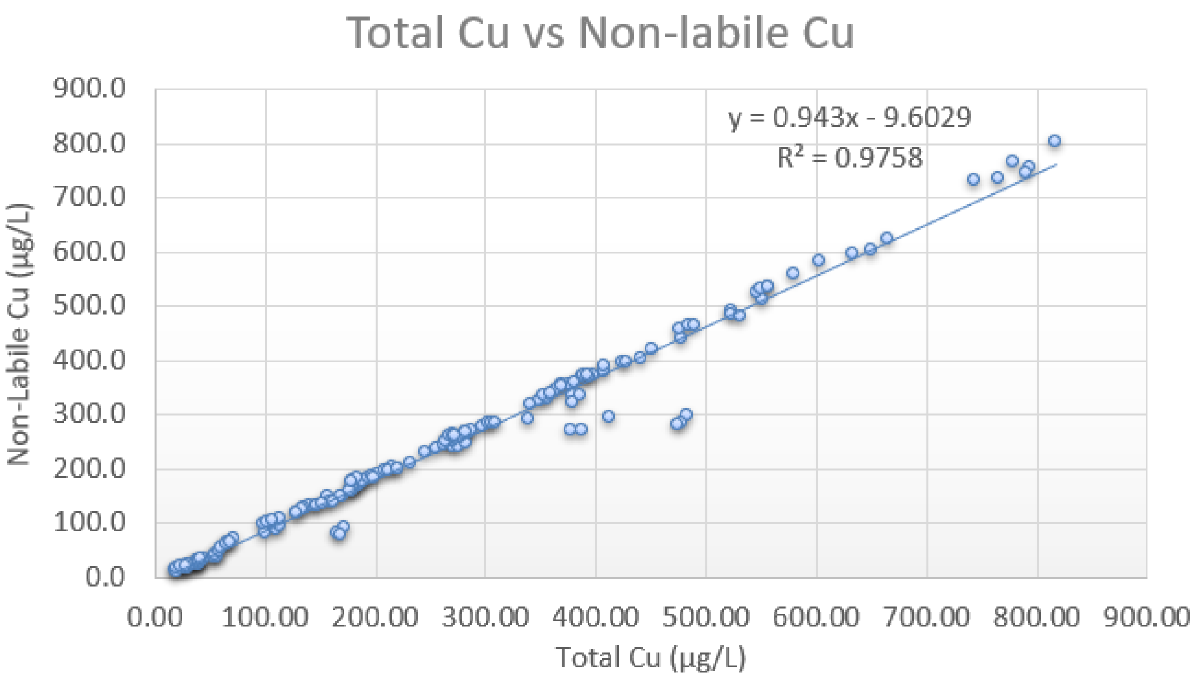


Figure 3. Effect of racking and of filtration through 0.45- and 0.2- µm filters on the concentration of residual copper in tartaric acid-based model wine (■) and in nitrate model wine (□) at 1:1 mole ratio of added hydrogen sulfide and added copper(II). The added concentration of hydrogen sulfide and of copper(II) was 15.7 µmol/L [or 1.0 mg/L for copper(II)]. The error bars represent the standard deviation (n = 3).

Clark, A. C., et al. (2015). "Copper(II) addition to white wines containing hydrogen sulfide: residual copper concentration and activity." Australian Journal of Grape and Wine Research **21**(1): 30-39.

So what is this residual copper?

The Australian Wine Research Institute

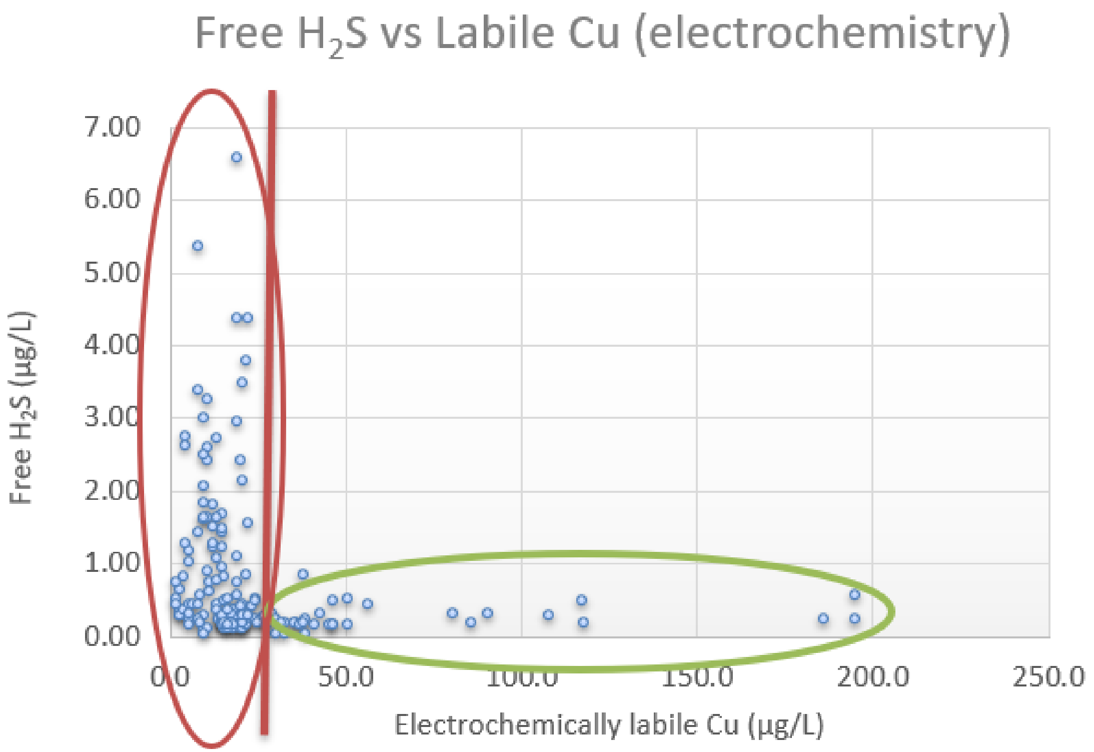


The majority of copper found in commercial wines is in a tightly bound non-labile form.

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

Clark, A.C. et al., 2016. Measurement of labile copper in wine by medium exchange stripping potentiometry utilising screen printed carbon electrodes. Talanta, 154(C), pp.431–437.

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_2S

But most of the copper is in non labile form which does not inhibit the presence of free H_2S

Copper in wine can increases the sulfides over time sulfides

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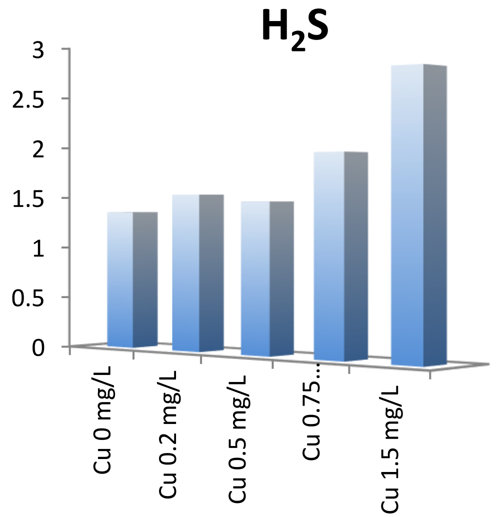
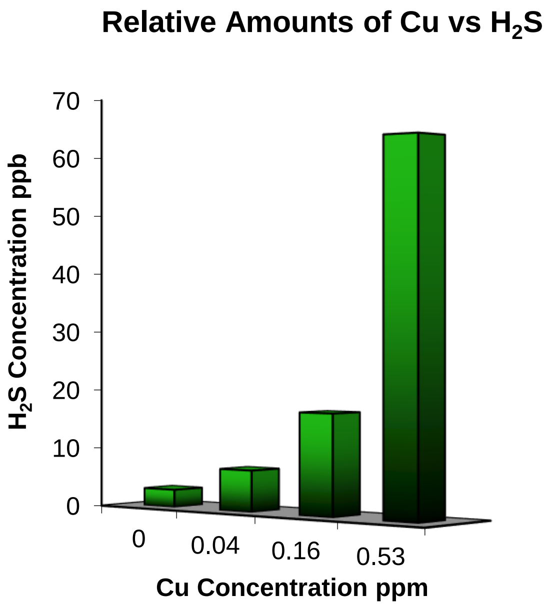


After just 2 months this chardonnay was already showing the impact of increased copper.

Clare Valley Riesling after



Remember, the threshold for H_2S is about 1 for most people!

Important take away!

There are essentially two types of copper.

Non-labile copper
usually bound up with sulfides that cannot really remove H_2S and may act as a source as the wine matrix changes

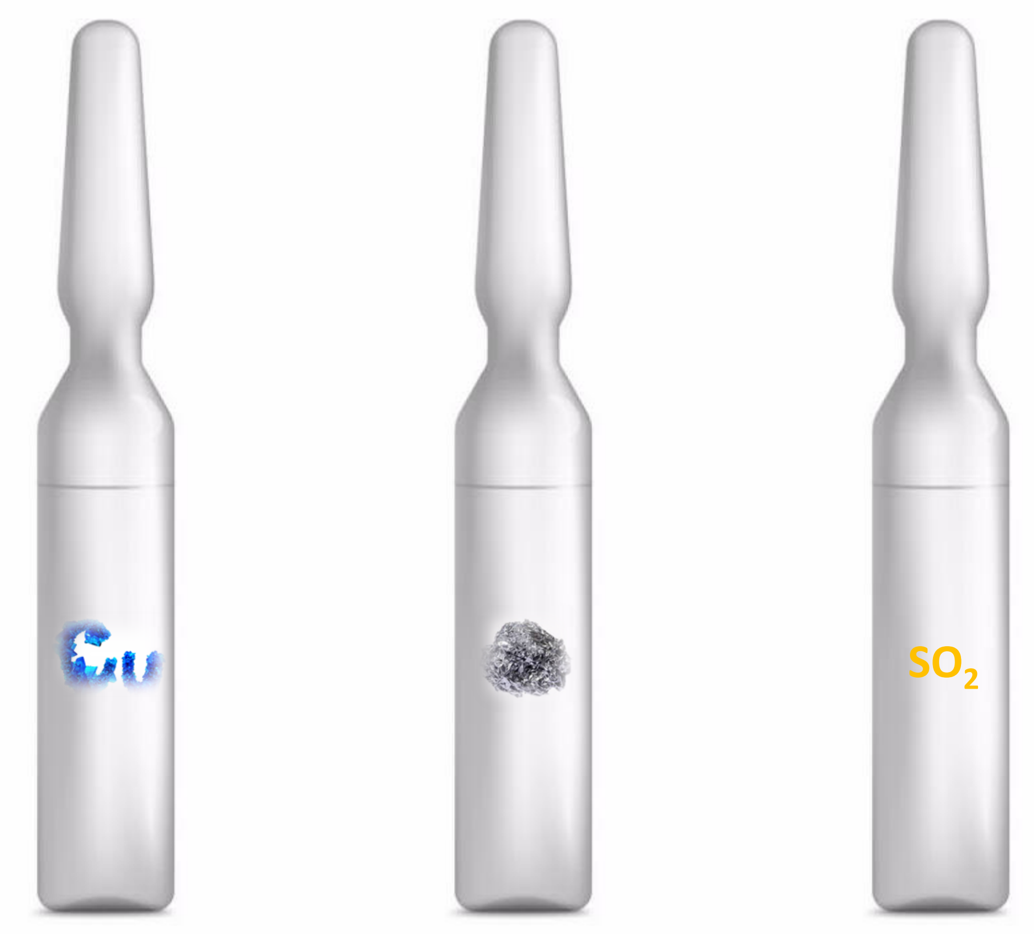
Labile copper
which can scavenge H_2S but also can participate in other reactions

Wine in cans, the ampoule studies

We need to separate out all the components of interactions.

Use glass ampoules as a substitute for the low oxygen environment of a can.

Then add or subtract each factor incrementally.



Contact with Al metal

The Australian Wine Research Institute

- H_2S ↑↑↑
- MeSH ↑

Pros

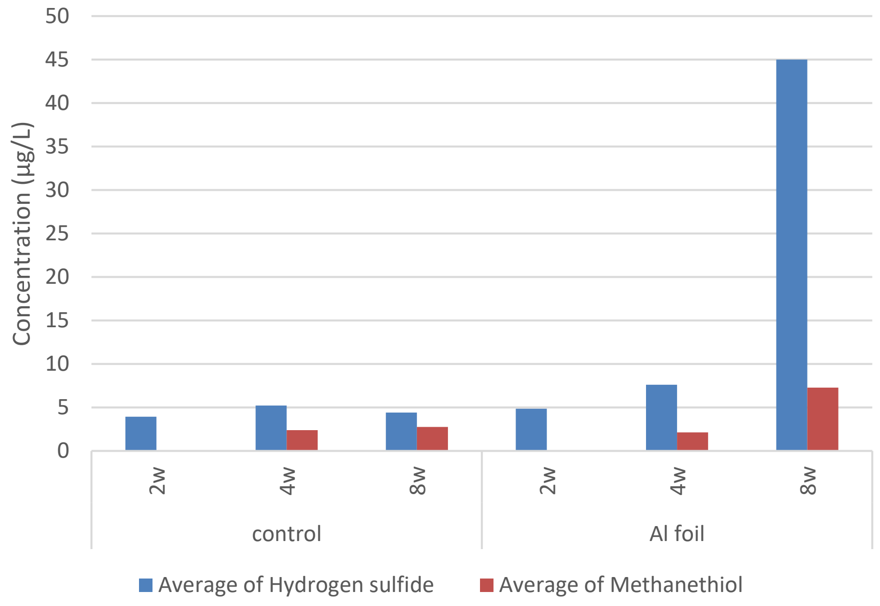
Absolutely none, seems inherent in the current canning systems.

Cons

Massive increases in sulfides, by far the biggest impact of factors tested.

Note

Aluminium salts do not have the same impact, only the interaction between the wine and the metal.



Contact with Al metal + added Cu salts

The Australian Wine Research Institute

- H_2S ↑
- MeSH ↑

Pros

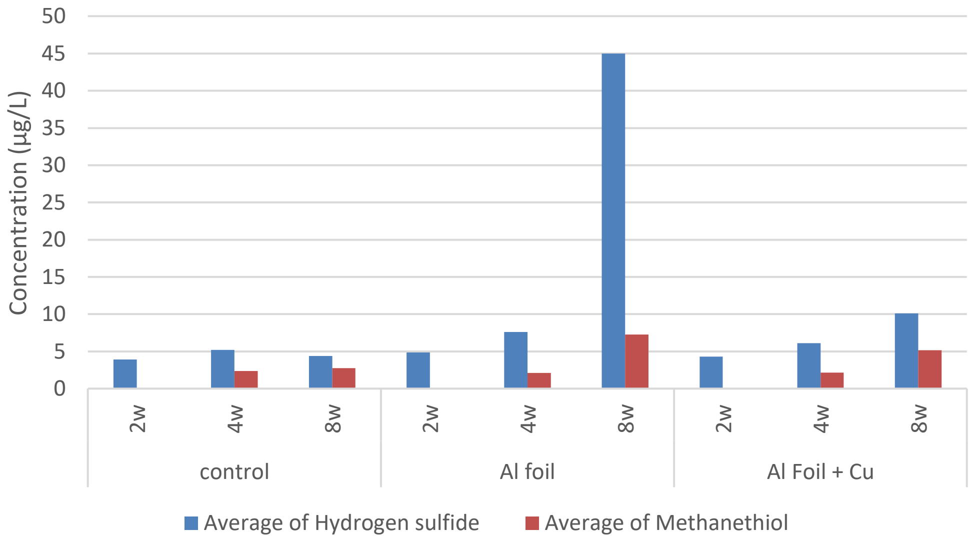
None really, although it does appear to mitigate the impact of the Al

Cons

Increased in sulfides compared to the control, i.e. worse than bottled product.

Note-

The added Cu is most likely in the labile form so it is helping to scavenge out the sulfides formed in the interaction with the Al. May have longer term impacts.



Increasing pH

The Australian Wine Research Institute

- H_2S ↓
- MeSH ↓

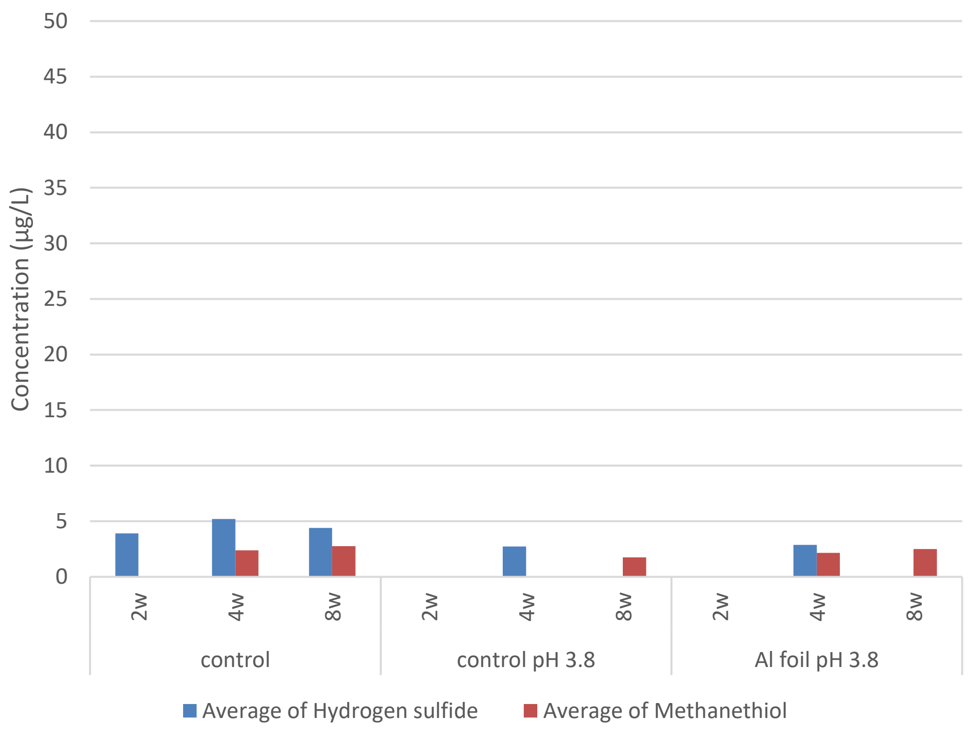
Pros

Has a very strong and obvious impact on stopping sulfide production

Addition of Al at high pH has similar impact to pH alone

Cons

Very difficult to implement while retaining wine flavour profile, essentially impossible in spritz samples



Increasing O_2 (TPO)

The Australian Wine Research Institute

- H_2S ↓
- MeSH ↓

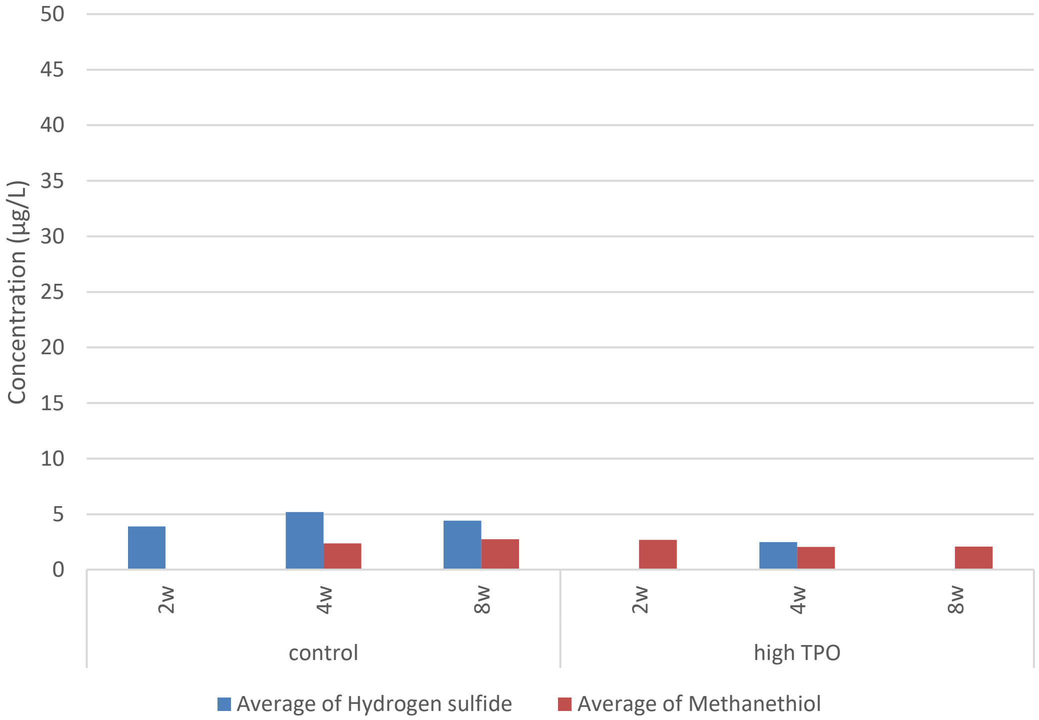
Pros

Has some impact on stopping sulfide production, particularly H_2S

Cons

No indication from this trial on the impact on wine quality.

Note-no Al in this trial



Contact with Al + reduced SO_2 (5-10 mg/L)

The Australian Wine Research Institute

- H_2S ↑
- MeSH ↑

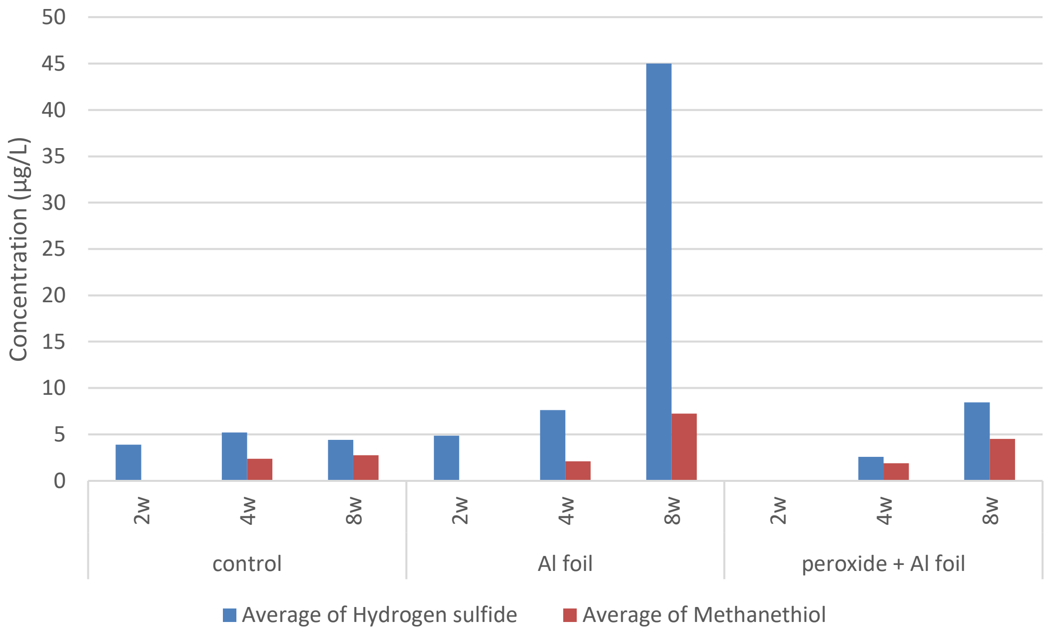
Pros

While increased in relation to control, significantly mitigated compared to Al alone and absolute increase not massive. Could be a ***possible mitigation process***.

Cons

Needs to be put in context with other production concern around oxidation and micro activity.

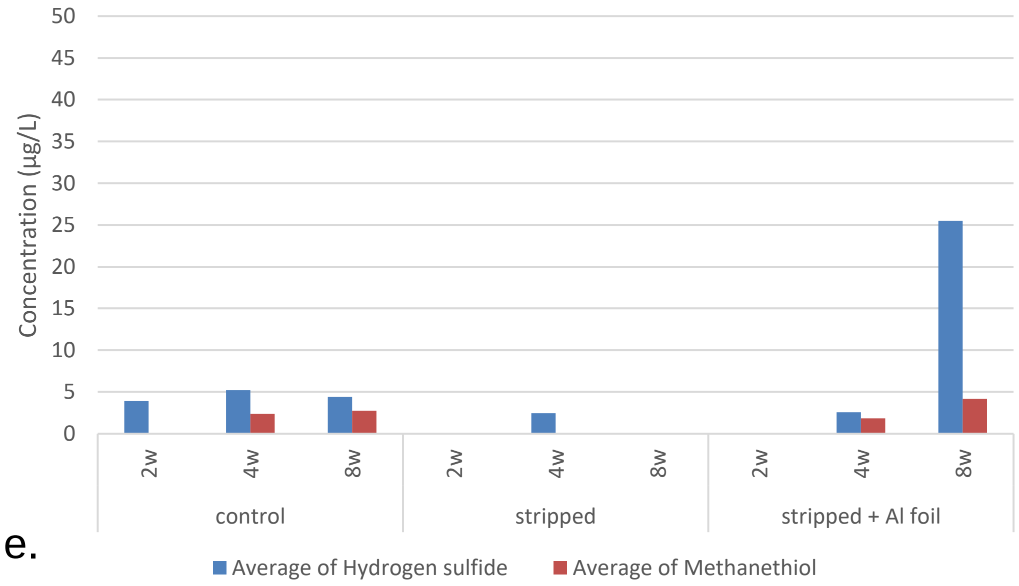
Note- supports the proposed chemistry around Al and SO_2 interactions.



Stripping the original Cu

The Australian Wine Research Institute

- H_2S ↓
- MeSH ↓



Pros

Has a very strong and obvious impact on stopping sulfide production

Cons

Only seems to be truly effective in the absence of Al metal

Note

We are probably stripping non labile Cu, i.e. Cu bound to sulfides that also act as a reservoir of sulfides.

Stripping the original Cu + adding more Cu

The Australian Wine Research Institute

- H_2S ↓ ↓
- MeSH ↓

Pros

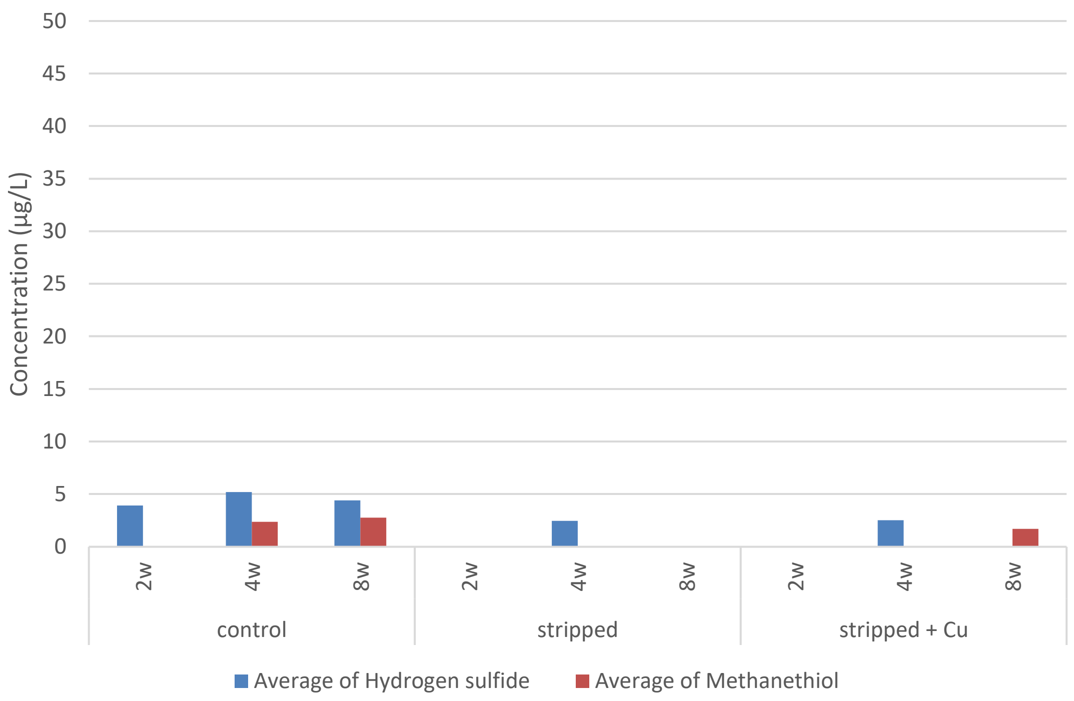
Has a very strong and obvious impact on stopping sulfide production equivalent to pH increase

Cons

This is without Al contact, but if we can *remove or reduce* the Al transfer, then it could be a **significant mitigation process**. Added Cu may have other long term impacts

Note

We are probably stripping non labile Cu, i.e. Cu bound to sulfides that also act as a reservoir of sulfides



Stripping the original Cu + adding more Cu (with Al contact)

The Australian Wine Research Institute

- H_2S -
- MeSH ↑

Pros

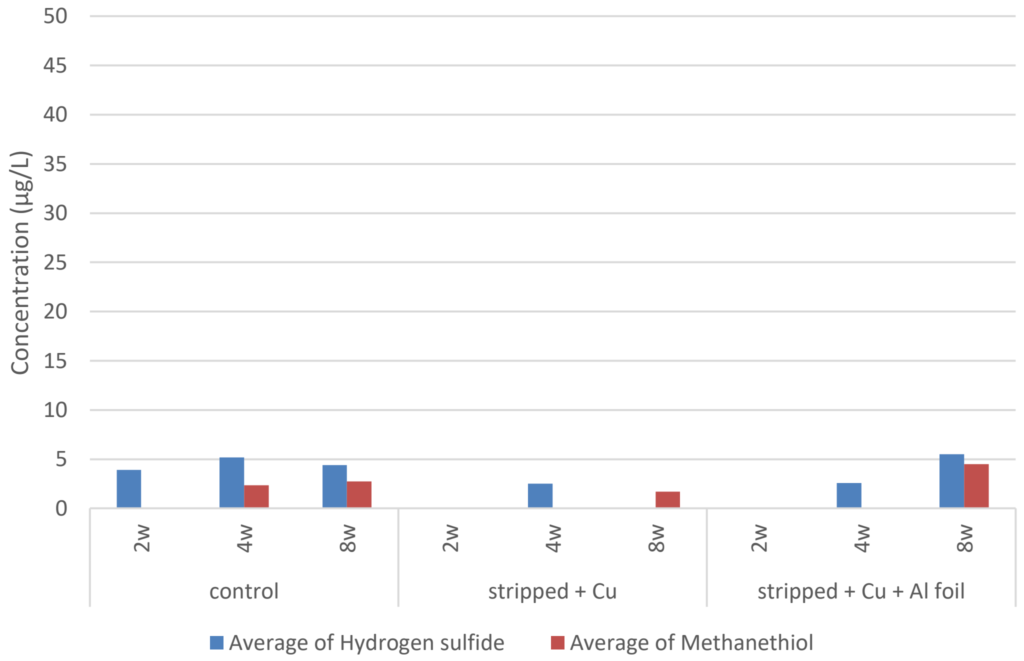
Seems to mitigate sulfide generation to levels similar to control. **Promising mitigation process**, especially with reduced SO_2

Cons

Can added Cu have other long term impacts?

Note

Labile Cu benefits again, combined with reduced SO_2 may be very effective



What can we do?

The Australian Wine Research Institute

Remove the Al source

(not a winery issue)

Strip the non-labile Cu

Reduce the SO_2

Add new protective Cu?

(has risks)

Analysis and Treatments for Canned Wine

Jasha Karasek
Winemaking Specialist, Enartis USA

AGENDA

Overview

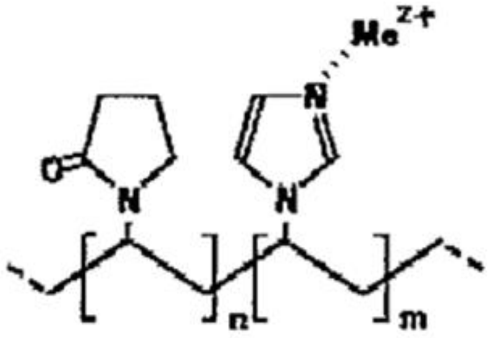
- Analysis and tracking
- Removing metals with Claril HM and Stabyl MET

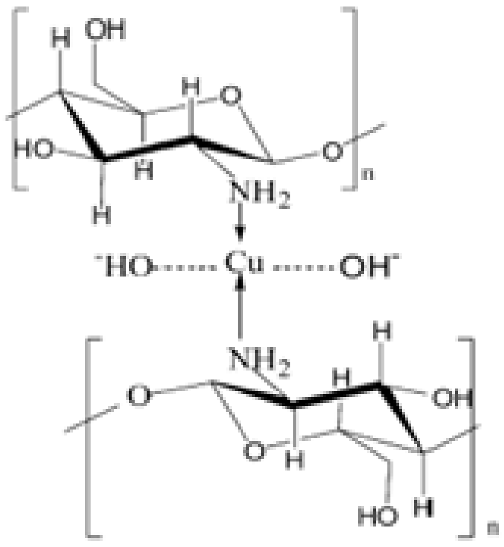
CANNED PACKAGING PANEL by Vinquiry labs

- **ALUMINUM** – Initial and tracking, increases over aging indicate migration of aluminum from the can into the wine
- **pH** – lower = more chances of reduction appearing. Less than 3.5 is problematic. Could be related to molecular SO_2
- **FREE AND TOTAL SO_2**– Lower Free and Total SO_2 will lead to less H_2S formation.
- **COPPER** - < 0.3 mg/L recommended by liner manufacturers
- **IRON** - < 1 mg/L recommended by liner manufacturers
- **CHLORIDES** - < 500 mg/L recommended by liner manufacturers

Triplicate analysis highly recommended! Can be highly variable between cans!

METAL REMOVERS PVI/PVP & CHITOSAN





PVI/PVP

Vinylimidizole vinylpyrollidone

- **Polymer which binds several different metal types.**
- **Also removes smaller phenolics like hydroxycinnamates**

CHITOSAN

- **Different forms available and vary in activities**
- **Processing can improve metal removal capacity**
- **Also removes smaller phenolics like catechins**

METAL REMOVERS: CLARIL HM & STABYL MET

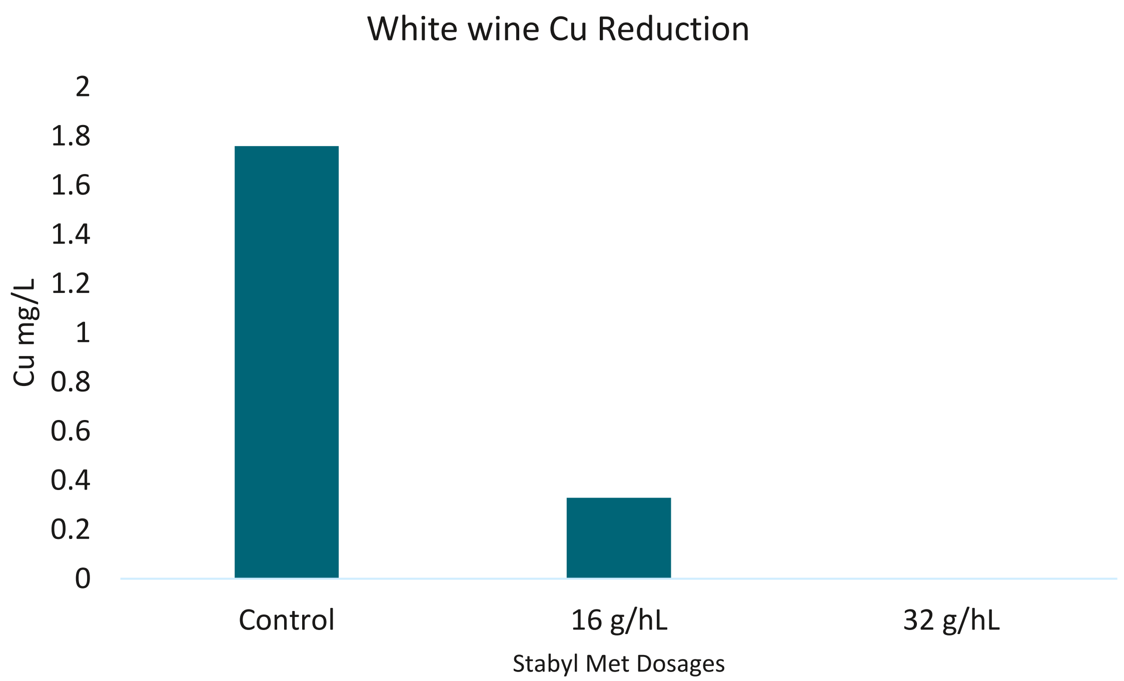
FINING AGENTS
CHIARIFICANTI

CLARIL HM

FINING AGENTS
CHIARIFICANTI

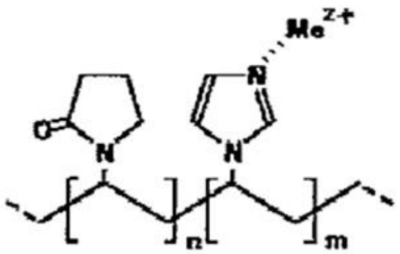
STABYL MET

METAL CHELATORS CLARIL HM & STABYL MET



PVI/PVP
Vinylimidizole vinylpyrollidone

- Binds Cu, Fe, Al, and Copper-bound sulfides
- Dosage 20-50 g/hL
- Trials recommended

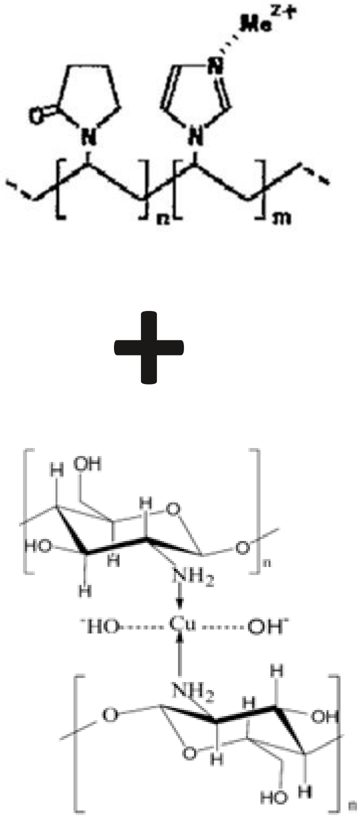


CLARIL HM : COMBINING PVI/PVP & CHITOSAN

enartis

FINING AGENTS
CHIARIFICANTI

CLARIL HM



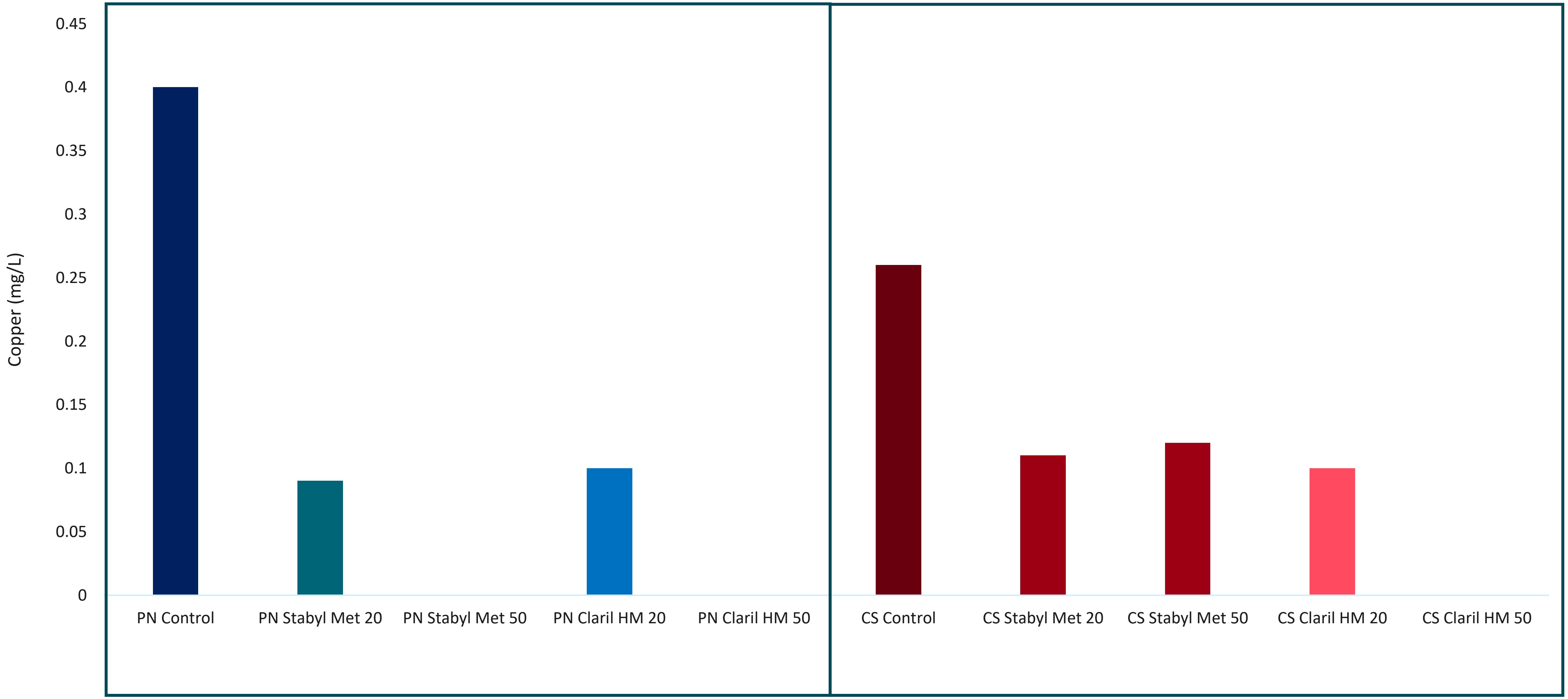
Red wine	Cu ppm	Fe ppm	Al ppm
Control	3,70	6,48	0,98
50 g/hL Claril HM	1,5	3,6	0,6
% removal	59,5	44,4	38,8

White wine	Cu ppm	Fe ppm	Al ppm
Control	3,7	5,8	1,06
50 g/hL Claril HM	1,1	2,1	0,6
% removal	70,3	63,8	43,4

PVI/PVP + Chitosan

- Binds Cu, Fe, Al, and Copper-bound sulfides
- Settles rapidly
- Trials recommended

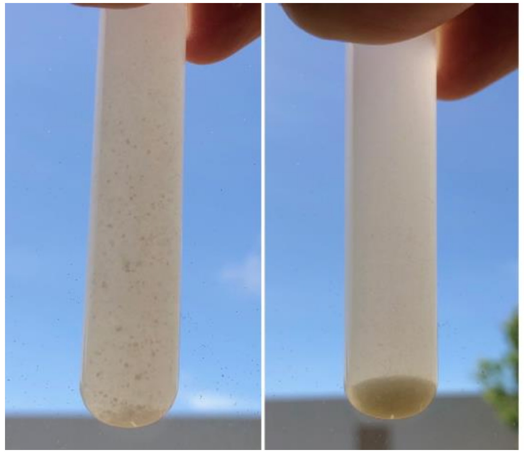
CLARIL HM & STABYL MET COPPER REMOVAL COMPARISON



TIPS FOR TRIALS WITH CLARIL HM AND STABYL MET

- Re-hydration time – 1 hour, 5 - 10% solution recommended
- Settling speed – rapid
- Pipette tips – wide orifice recommended, clogging otherwise possible
- Contact time during trial should be the same as treatment in cellar – 30 mins – 1 hour

T = 0 T = 1 min



CONCLUSIONS

- Analysis via Canning Panel at Vinquiry Labs can be helpful for tracking and monitoring canned wines
- Claril HM and Stabyl MET can both benefit canned products for removing copper and copper-bound sulfides.
- Trials with Claril HM and Stabyl MET can be tricky, consider the provided guidelines if you decide to try either fining agent

CANNED WINE PART 2. MORE ON THE IMPACT OF SO_2

Cornell CALS College of Agriculture and Life Sciences

&

enartis

Inspiring innovation.

June 18th
@ 1 pm pst

THANK YOU!

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