Avoiding Reduction

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DATE 1/21/2020

WEBINAR OVERVIEW

- 40 min presentation
- 15 – 20 min Q&A
- Please leave questions for designated Q&A at end of presentation, avoid using chat box.
- If you are bothered by chat box, you can toggle it closed
- Recorded session!

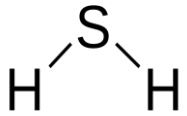
Overview

- Types of Volatile Sulfur Compounds (VSC)
- Some sources of VSC
- Solutions for reductive wines

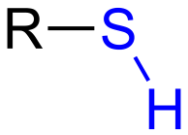
POLL QUESTION #1

What are the Main Volatile Sulfur Compounds (VSC) in wine?

Hydrogen Sulfide



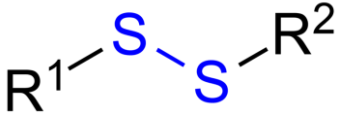
Mercaptans

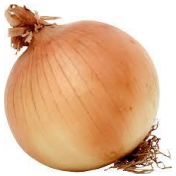


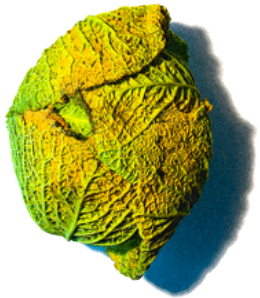
Reductive

Oxidative

Disulfides







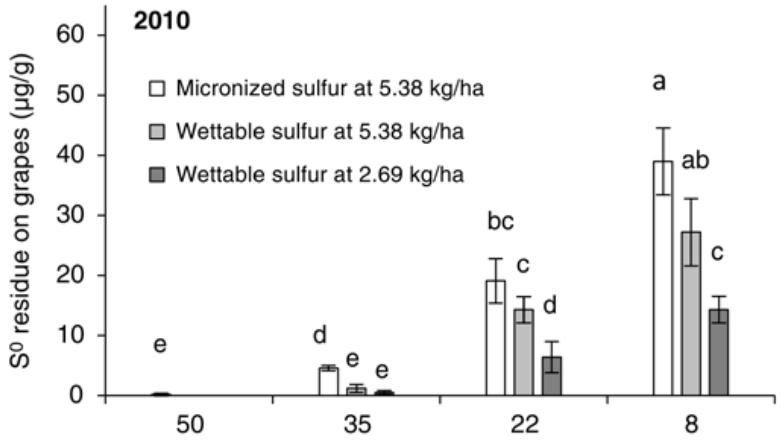
What are the main sources?

Fermentation

- Sulfur sprays – wettable vs. elemental
- Sulfite additions
- Yeast Metabolism/ Nutrition

Elemental vs. Wettable

- Should have < 1 µg/g sulfur on grapes to ensure less H_2S



Sulfur Applied Days before harvest

Adapted from
Am. J. Enol. Vitic. 65:4 (2014)
M. Kwasniewski, G. Sacks, W. Wilcox

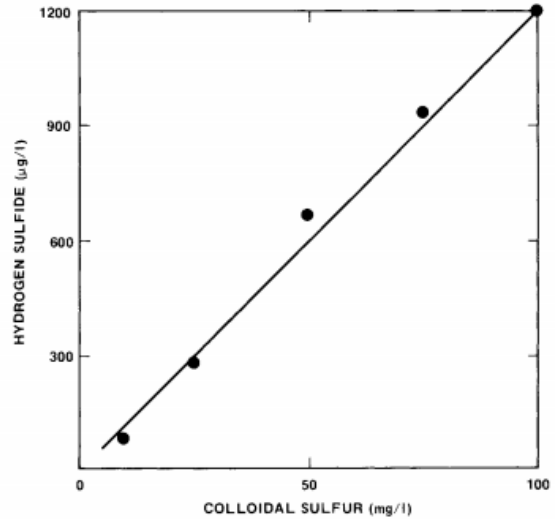


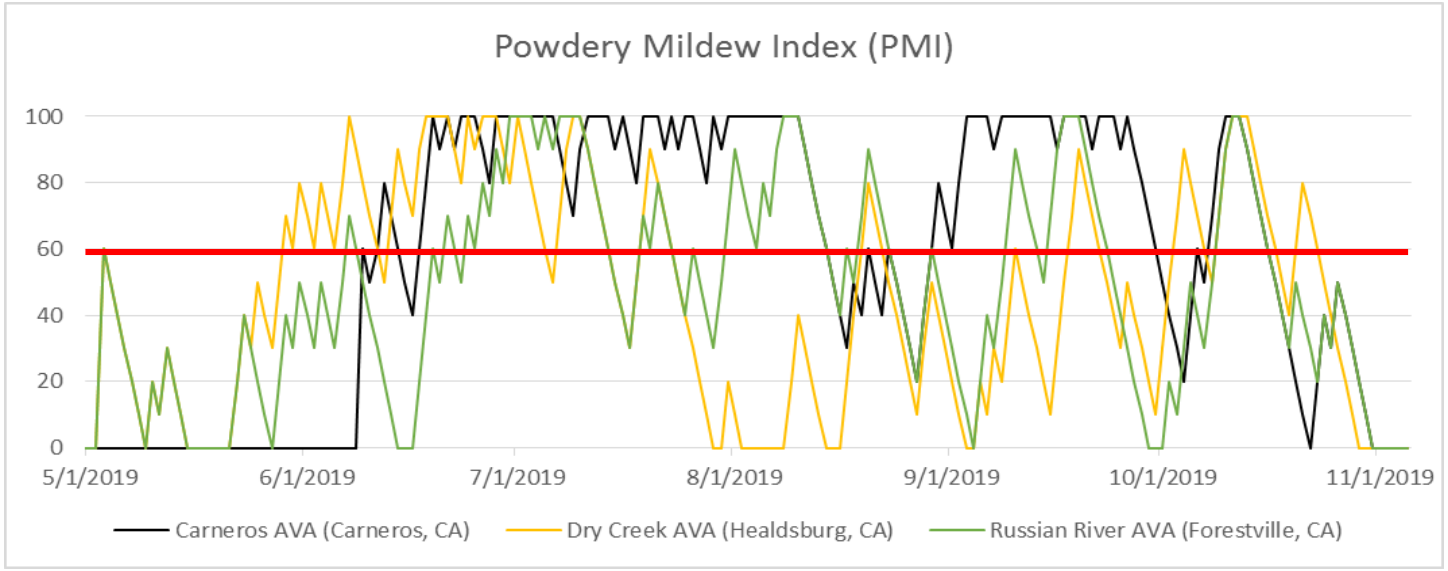
Fig. 4. Dependency of hydrogen sulfide formation during fermentations of grape juice by Montrachet yeast upon the amount of added colloidal sulfur. The fermentation was followed to dryness and the maximum values of hydrogen sulfide are shown.

Am. J. Enol. Vitic., Vol. 28, No. 3, 1977
Michael Schütz and Ralph E. Kunkee

A Bad Year for PM = More Sulfur Sprayed in the Vineyard

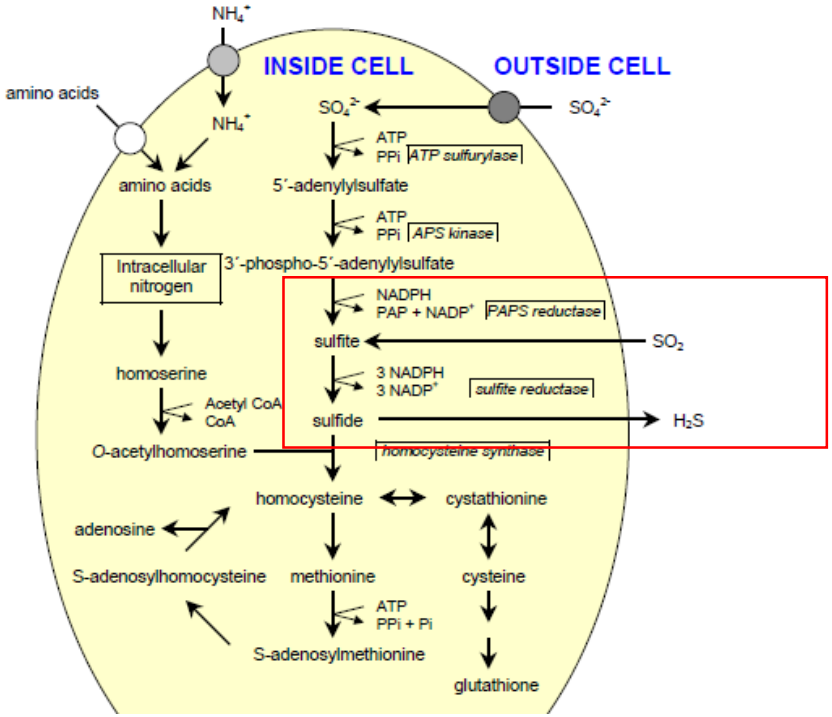
SPRAY INTERVALS BY FUNGICIDE GROUPS BASED ON DISEASE PRESSURE USING THE UC DAVIS POWDERY MILDEW RISK INDEX MODEL

			Suggested spray schedule			
Index	**Disease pressure**	**Pathogen status**	**Biologicals[1] and SARs[2]**	**Sulfur**	**Demethylation-inhibitors (DMI)[3]**	**Strobilurins and Quinolines[4]**
0-30	low	present	7- to 14-day interval	14- to 21-day interval	21-day interval or label interval	21-day interval or label interval
40-50	moderate	reproduces every 15 days	7-day interval	10- to 17-day interval	21-day interval	21-day interval
60 or above	high	reproduces every 5 days	use not recommended	7-day interval	10- to 14-day interval	14-day interval



Data source: *Western Weather Group*, sonoma.westernweathergroup.com; Data interpretation: *UC IPM* www.ipm.ucdavis.edu

Yes yeast can use SO_2 to create H_2S



YAN needs for yeast

- Rule of thumb for adjusting YAN 10 mg/L YAN for every 1 Brix fermented

Table 10. Effect of nitrogen additions to must (25 g/hl) on H_2S development during fermentation.

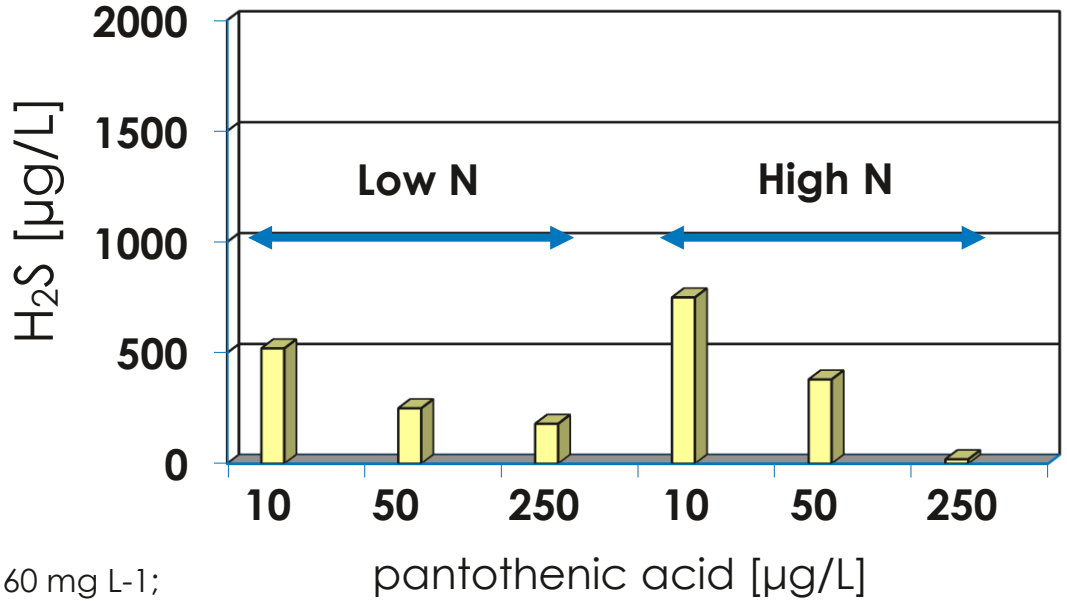
Sample no.	H_2S (μg/l)		% change
	Control sample	Treated sample	
1	536	0	−100
2	675	14	− 98
3	802	56	− 93
4	176	32	− 82
5	660	46	− 93
6	427	0	−100

Table 11. Suppression of H_2S development during fermentation by increasing additions of nitrogen to a must.

Nitrogen addition (g/hl)	H_2S (μg/l)	% change
0	422	0
4	173	− 59
8	127	− 70
12	72	− 83
16	0	−100

P. J. A. Vos and R. S. Gray **Am. J. Enol. Vitic., Vol. 30, No. 3, 1979**

Low pantothenic acid = more H_2S



* Low N 60 mg L-1;
High N 250 mg L-1

NUTRIFERM ENERGY

Yeast rehydration nutrient rich in pantothenic acid

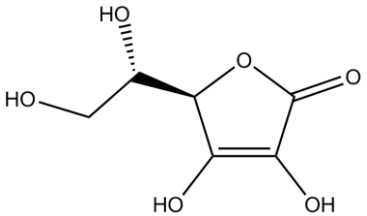
Lit. Wang, Bohlscheid, Edwards 2003, modified

POLL QUESTION #2

What tools are available to winemakers?

- Oxygen – useful during fermentation, does not help much with wine remediation– *Bekker et al 2016 Aust. Jour. Of Grape and Wine Res*.
- Copper Sulfate – H_2S + some mercaptans
- Enological tannins – Mercaptans
- Ascorbic acid + enological tannins/$CuSO_4$ – Disulfides

O_2



Copper Sulfate works well for H_2S, but be careful…

- Copper acts as a catalyst for oxidation

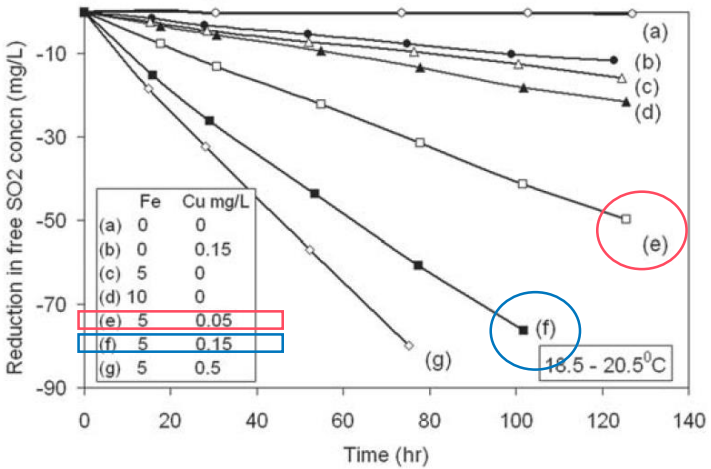


Figure 4 The effect of Fe and Cu concentration on the reaction rate of SO_2 in the presence of 4-MeC (1.2 g/L) in the wine-model system.

Danilewicz

Am. J. Enol. Vitic. 58:1 (2007)

Copper Bound to H2S

Does it precipitate, is it removed by physical filtration?

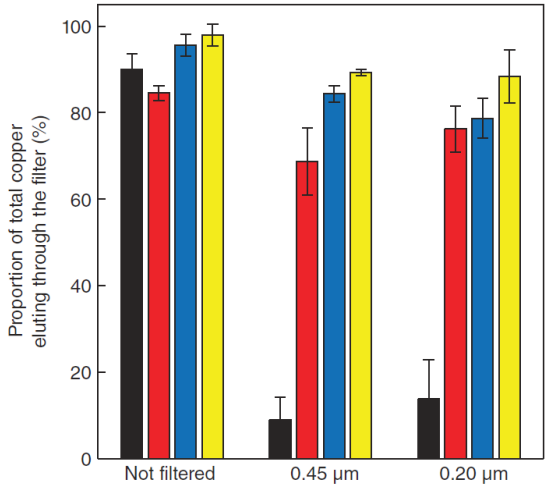


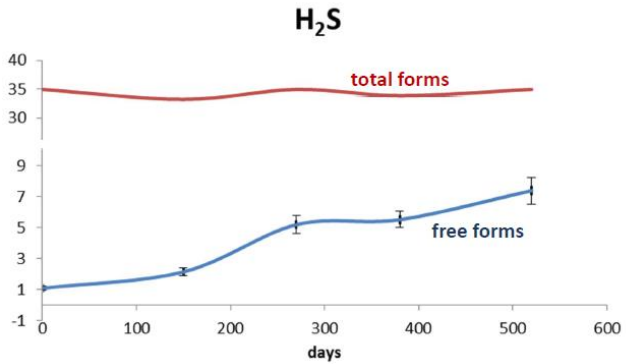
Figure 1. Proportion of total copper (2.0 mg/L), present as sulfide-bound Cu, eluting through the filter (0.45 or 0.2 µm pore size regenerated cellulose membrane filters). The model wine samples contained 0 (■), 1 (■), 5 (■) and 10 (■) % (v/v) white wine. All had sulfide-bound Cu formed in situ with addition of 4.8 mg/L sodium sulfide and 2.0 mg/L copper(II) [mole ratio of 2:1 for hydrogen sulfide to copper(II)].

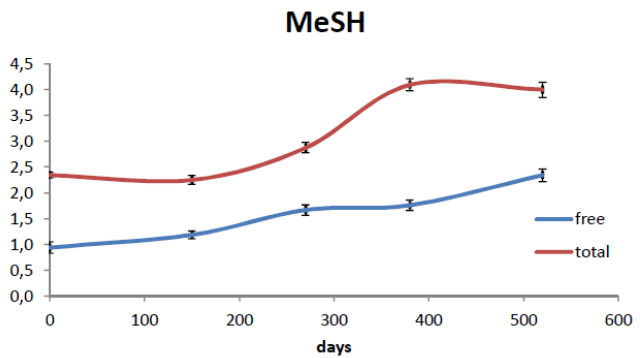
N. KONTOUDAKIS[1,2], A. MIERCZYNSKA-VASILEV[3], A. GUO[4], P.A. SMITH[3], G.R. SCOLLARY[1,5], E.N. WILKES[3] and A.C. CLARK[1,2]

Australian Journal of Grape and Wine Research 25, 53–61, 2019

H_2S and MeSH release from bound forms in anoxic conditions

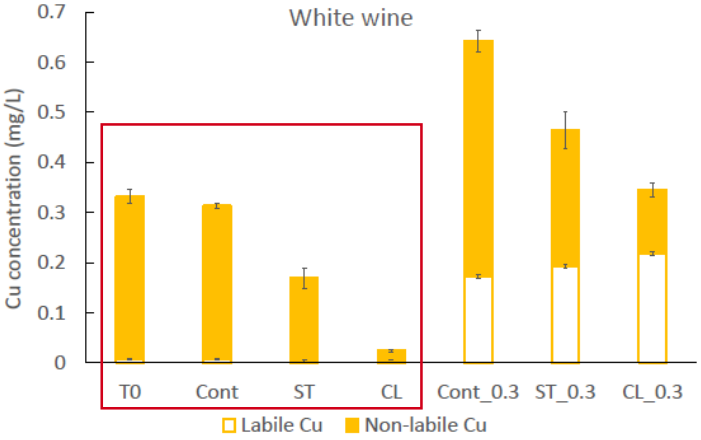
Figure 2: Average contents (µg/L) of total and free forms of H_2S (2a) or of MeSH (2b) of 13 different red wines stored under strict anoxia for 18 months

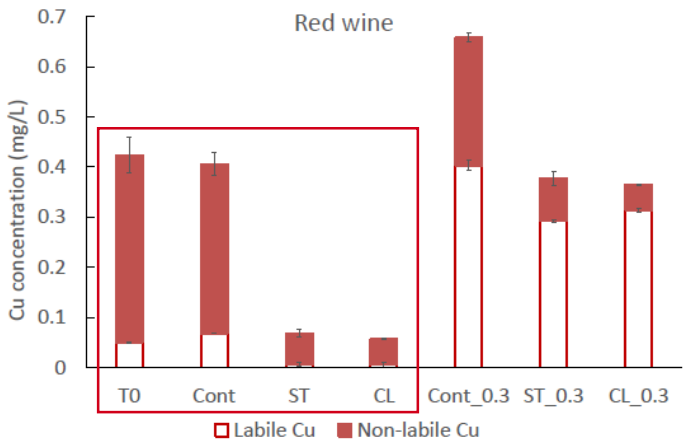




FERREIRA ET AL., UNDERSTANDING AND MANAGING REDUCTION PROBLEMS - INTERNET JOURNAL OF ENOLOGY AND VITICULTURE, 2016, N. 2/1

PVI/PVP can remove copper bound sulfides





Sample key

T0	Cu and H_2S addition
CONT	Cu and H_2S addition, 5 hrs contact time, filtration
ST	Cu, H_2S and CLP1 addition, 5 hrs contact time, filtration
CL	Cu, H_2S and CLP2 addition, 5 hrs contact time, filtration
CONT0.3	Cu and H_2S addition, 5 hrs contact time, filtration, 0.3 mg/L Cu(II) addition
ST0.3	Cu, H_2S and CLP1 addition, 5 hrs contact time, filtration, 0.3 mg/L Cu(II) addition
CL0.3	Cu, H_2S and CLP2 addition, 5 hrs contact time, filtration, 0.3 mg/L Cu(II) addition

Neil Scrimgeour[1], Kieran Hirlam[1], Andrew Clark[2], Nick Kodoudakis[2], Eric N. Wilkes[1]

[1] The Australian Wine Research Institute, PO Box 197, Glen Osmond (Adelaide) SA 5064, Australia, [2] National Wine and Grape Industry Centre, School of Agricultural and Wine Sciences, Charles Sturt University, Wagga Wagga, NSW 2678

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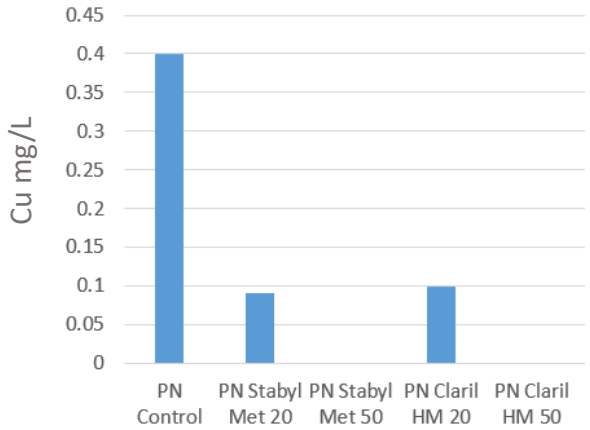
Removing Copper and Copper bound Sulfides



CLARIL HM

Blend of PVI/PVP and pre-activated chitosan

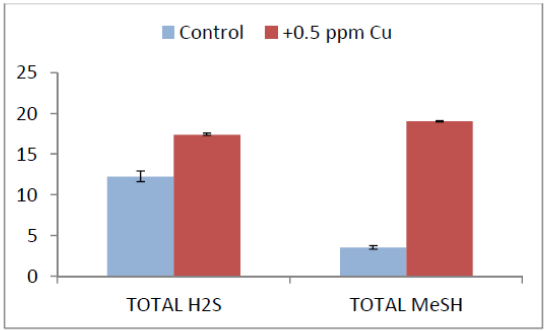
STABYL MET

PVI/PVP and Silica

What are the main sources?

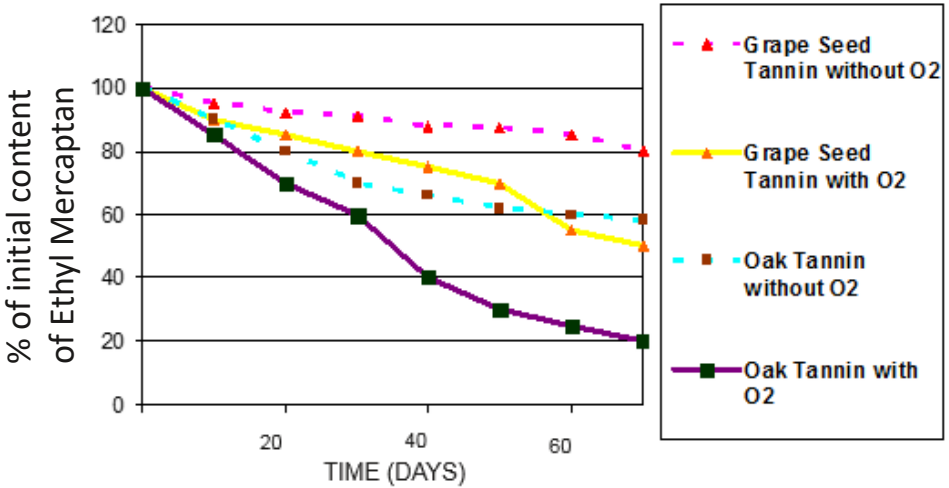
- Yeast metabolism/nutrition
- Copper catalyzed degradation of S-amino acids

Figure 3: Effect of the presence of copper in the total contents of H_2S and MeSH of a synthetic solution containing amino acids and wine phenols and stored in strict anoxia at 50ºC (work carried out by Ricardo López and Sandra González)



INTERNET JOURNAL OF ENOLOGY AND VITICULTURE, 2016, N. 2/1

Mercaptans and Enological Tannin



From Vivas, Revue Oen. N° 98, 2001

Tannins for Mercaptan Based VSCs

Condensed and Ellagic tannin
3-10 g/hL
- Developed for avoiding volatile sulfur compounds in Prosecco winemaking

Ellagic tannin from untoasted oak avoiding high temperature extraction
1-5 g/hL
- Developed for shelf life improvement, works well for reductive compounds

Ellagic tannin from seasoned French oak
1-5 g/hL
- Developed for shelf life improvement, works well for reductive compounds

Sulfide Trials

Control	Copper sulphate 0.2 g/hL	Enartis Tan Elevage 2 g/hL	Ascorbic acid (5 g/hL) + Enartis Tan Elevage (2 g/hL)	Interpretation
Stinky wine	**Off-odour dissappears**	Off-odour is still here	Off-odour is still here	H_2S
	Off-odour disappears	**Off-odour disappe-ars**	Off-odour is still here	Mercaptans
	Off-odour is still here	Off-odour is still here	**Off-odour disappears**	Disulphides

Sulphur compound		Aroma	Threshold
Hydrogen sulphide (H_2S)		Rotten eggs, sewer gas	0,5 ppb
Mercaptans	Methyl mercaptan	Rotten cabbage	1 ppb
	Ethyl mercaptan	Burnt match, earthy	0,02 - ppb
Disulphides	Dimethyl disulphide (DMDS)	Onions, cooked cabbage	15-30 ppb
	Diethyl disulphide (DEDS)	Burnt rubber, garlic	4 ppb

Conclusions

- Dealing with VSCs can be tricky
- Elemental sulfur is a major contributor to H_2S formation in fermentation
- Yeast nutrition is an important factor for limiting H_2S formation
- Copper fining helps with H_2S, but can have some negative consequences for oxidation and potential re-release of H_2S in low redox environments
- Tools like Stabyl Met and Claril HM can help remove excess copper and copper bound sulfides
- Tannins can help reduce levels of mercaptan based volatile sulfur compounds

THANK YOU FOR YOUR PARTICIPATION!

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