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SULPHIDES IN WINE

Treatment and Prevention
- a practical approach

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SULPHIDES and the screwcap challenge

A VERY common wine fault, especially in screwcap wines:

'…of the bottles with faults, cork taint stayed at an average of 29 percent of the faulty bottles. It was interesting to see that reduction carried the same percentage'

International Wine Challenge data from 2006-2009

'Too many wines showing sulfides under screwcap'

Chief judge's report, Air NZ Wine Awards 2004

'This is the article I never wanted to write about screw caps. It is a major concern. I have never seen widespread reduction issues in a clutch of wines like I did in the NZ wines. Do we need to introduce a Screwcap License system?'

Campbell Mattinson, Winefront Monthly. Mar/Apr 2006

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SULPHIDES – compounds and aromas

From a recent study by the AWRI

Siebert T.E. et al, J. Agric. Food Chem 2010, 58, 9454-9462

Hydrogen sulphide	H2S	Rotten egg, sewage	1.1-1.6μg/L
Methanethiol	MeSH	Rotten cabbage, burnt rubber	1.8-3.1μg/L
Ethanethiol	EtSH	Onion, rubber, burnt match	1.6μg/L
Methyl thioacetate	MeSAc	Sulphurous, cheesy, egg	50μg/L
Ethyl thioacetate	EtSAc	Sulphurous, garlic, onion	10μg/L
Dimethyl sulphide	DMS	Black current at low levels Canned corn/asparagus	25μg/L
Diethyl sulphide	DES	Garlic, rubber	0.9μg/L
Carbon disulphide	CS2	Sweet, green at low levels Rubber	>38μg/L
Dimethyl disulphide	DMDS	Vegetal, cabbage, onion	29μg/L
Diethyl disulphide	DEDS	onion	4.3μg/L

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SULPHIDES - AWRI study, published 2010

From the above AWRI study:

- 68 commercial, bottled wines, 2004-2007, characterised as ‘reductive’ in sensory analysis, analysed for all 10 compounds
- Most important contributors: H2S, methanethiol, DMS, CS2
- H2S in 61 wines - it’s not only a fermentation problem!
- DMS concentrations at higher levels in older wines i.e. delayed accumulation of DMS and re-release of thiols?
- CS2 in 66 wines, contribution to aroma is not well understood, could be positive as well?
- Other 6 compounds may be present - not always, at lower concentrations
- Important to think of the aroma of the wine as an INTERACTION of the different compounds – a sum of the whole, not individual components

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SULPHIDES - tasting

1 control wine (no addition)

2 + methanethiol (MeSH) - 15µg/L

3 + ethanethiol (EtSH) - 10µg/L

4 + dimethyl sulphide (DMS) - 150µg/L

5 + dimethyl disulphide (DMDS) - 90µg/L

6 + MIX of sulphides (MeSH, EtSH, DMS, DMDS)

7 + DMS + CuSO4

8 + DMS + ascorbic acid + CuSO4

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Identifying sulphide problems in your wine

Identify the CORRECT problem in order to treat it correctly

Cadmium sulphate reacts with H2S

- Reduced odour indicates presence of H2S
- Persisting odour indicates presence of thiols/disulphides

Copper sulphate reacts with H2S and thiols (ethanethiol, methanethiol)

- Reduced odour indicates presence of H2S/thiols
- Persisting odour indicates presence of disulphides

Ascorbic acid reduces disulphides back to the simpler thiols.
Ascorbic acid addition, followed by a copper sulphate addition

- Reduction in odour indicates H2S/thiols/disulphides
- Persisting odour indicates something else, NOT SULPHIDES

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SULPHIDES - a redox equilibrium

- Sulphide compounds in wine exist in a redox equilibrium or oxidation/reduction state

- As redox potential of the wine changes, the composition of these compounds will change

- Examples:
  - methanethiol + oxygen → methyl disulphide
    (as oxygen is absorbed)
  - methyl disulphide + reduction → methanethiol
    (the wine returns to its pre-oxidation state)

THESE REACTIONS CAN HAPPEN PRE- AND POST-BOTTLING

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SULPHIDES - reductive environments

Examples of Reductive environments:

- addition of antioxidants, e.g. ascorbic acid, SO2, glutathione
- presence of phenolic compounds
- anaerobic environment post-bottling (especially in screwcap wines)
- presence of yeast lees
- other anaerobic conditions like full stainless steel tanks

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SULPHIDES - some common misconceptions

Misconception:

“adding oxygen to remove reduction”

Adding oxygen:

- may improve the wine TEMPORARILY,
- but it DOES NOT REMOVE the sulphide compound, it only alters it according to the redox equilibrium
- oxidation of thiols (e.g. methanethiol) to disulfides (e.g. methyl disulphide) is easy and requires only a small amount of O2
- a reduction in odour occurs because SENSORY THRESHOLDS SHIFT, and NOT because sulphides have been removed

- even oxidation of H2S to S will still leave a sulfur deposit

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SULPHIDES - some common misconceptions

Misconception:

“it is necessary to do a filtration of the deposited copper sulfides to truly clean a wine after a copper fining”

- winery filtrations are NOT at molecular level, and will not remove these compounds

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SULPHIDES - some common misconceptions

Misconception:

"*copper will solve my SLO problems*"

- Cu may be instrumental in the PRODUCTION of a range of sulfides from H2S to Methanethiol and DMS
- In some instances sulphides would not have occurred if Cu was not present
- COPPER ADDITIONS JUST BEFORE BOTTLING MAY RESULT IN INCREASED SULPHIDE FORMATION
- COPPER DOES NOT REACT WITH ALL SULPHIDES

ADDING COPPER MAY BE A DANGEROUS PRACTICE

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SULPHIDES - some common misconceptions

Misconception:

“free SO2 scavenges O2 and so protects the wine.”

- Oxygen has to wait its turn in the redox-reaction queue
- The reaction rate of O2 combining with SO2 is slow
- This explains bottle shock and why SO2 levels after bottling take some weeks to stabilise

ASCORBIC ACID is able to scavenge O2

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Preventing sulphides in wine

Vineyard issues

If late season fungicides are applied:

- juice settling is advised
- nutrient addition becomes even more important

Other vineyard related issues:

- pesticides
- magnesium, zinc, copper
- diseased or damaged grapes may be depleted of nutrients and vitamins

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Preventing sulphides in wine

Eliminate the incidence of elemental sulfur

- 5mg/L residual sulphur is sufficient to produce sensorily detectable levels of H2S
- In the vineyard: sulphur-containing sprays should not be used 5-6 weeks before harvest
- In the winery: take care when burning sulphur wicks/candles, rather use sulphur boats

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Preventing sulphides in wine

Manage SO2 levels in juice

- Too little SO2: 15-20mg/l SO2 is necessary to inhibit the enzyme polyphenol oxidase which will otherwise scavenge oxygen

- Too much SO2: levels above 80mg/l make organic sulphur available to yeast which the yeast may then convert to H2S

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Preventing sulphides in wine

Yeast nutrition during fermentation

THIS IS VERY VERY VERY IMPORTANT

- measure YAN; add nitrogen according to YAN-calculated dose rates; add nutrients in 3 stages
- too much nitrogen in a fermentation may also cause H2S production – use YAN values
- DAP and ammonium sulphate do not contain amino acids - yeasts need amino acids as well as NH4
- yeasts also need vitamins (e.g. pantothenic acid, thiamine, biotin) and minerals

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Preventing sulphides in wine

Manage fermentation to reduce yeast stress

- rehydrate and prepare yeast according to instructions
- fermentation rate: too high OR too low indicates stress
- fermentation temperatures
  - >15ºC, less H2S is formed
  - >25ºC, causes increased stress
- avoid temperature fluctuations
- presence of other yeast, bacteria may cause stress (competition for nutrients, production of toxins)

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Preventing sulphides in wine

Yeast cells need oxygen during fermentation

- oxygen is an essential nutrient required for yeast growth
- 8-10mg/l is needed for an efficient fermentation
- oxygen in juice is rapidly consumed, fermentation becomes anaerobic and can result in stuck fermentation
- 15-20mg/l SO2 inactivates enzymes which will otherwise scavenge oxygen
- some O2 should be present in the first 30-72 hours of fermentation

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Preventing sulphides in wine

Manage juice turbidity

- Levels higher than 300ntu's:
  - the removal of high density solids along with associated elemental sulphur and any residual metals is important
  - settle, centrifuge or filter before fermentation

- Levels lower than 100 ntu's
  - insufficient nutrients for yeast

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Preventing sulphides in wine

Nitrogen additions and H2S formation during fermentation

- H2S at start of fermentation is usually a nutrient issue

  DO A TRIAL: in a small glass containing the wine, add some DAP, if the H2S goes away after a few hours, it is a nitrogen deficiency and a nitrogen addition will help
- H2S at end fermentation is a more serious problem
- DON'T add nitrogen after mid-fermentation, yeast can't use it
- aerating may help, but may also send redox equilibrium in a dangerous direction! DO TRIALS with cadmium, ascorbic acid and CuSO4 to find the problem so you can treat it in the correct way
- NEVER ADD Cu DURING FERMENTATION

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Preventing sulphides in wine

SO2 additions after fermentation

2 different approaches in the literature:

- Yeast can convert SO2 to H2S – add 30mg/l SO2 right after fermentation and RACK THE NEXT DAY
- Remove the wine from lees before sulphur addition

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Preventing sulphides in wine

Lees management

- yeast lees creates a reductive environment
- remove from heavy lees after fermentation
- remove wine from fine lees if sulphides start to develop
- fine lees can be kept separately and stirred regularly to treat sulphides later through absorption of the sulphide compounds

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Preventing sulphides in wine

The use of glutathione

Results from AWRI closure study:

- at bottling and up to 12 months after bottling:

  - H2S levels higher in glutathione-treated wines compared to non-treated wines even with Cu additions

  - H2S levels were even greater if glutathione-treated wines had added copper before bottling

- after 12 months in bottle:

  - glutathione effect on H2S levels was less noticeable

  - wines with Cu added had higher H2S levels

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Preventing sulphides in wine

Red wine fermentations

- aeration is often used to deal with H2S instead of managing the fermentation
- aeration at first racking will volatilise H2S
- increased H2S if aeration at completion of or soon after alcoholic fermentation (S acts as hydrogen acceptor forming H2S)

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Removal of sulphides from wine

- N2 sparging may also remove desirable components
- Cu additions only react with thiols and H2S; add ascorbic acid to reduce disulphides before Cu addition
- note that Cu additions also remove fruity ‘positive’ thiols - not so important for Shiraz
- add Cu to finished wines ONLY - never during fermentation
- SO2 additions: SO2 induced oxidation of H2S to form S, S can then be removed by filtration after precipitation
- inactivated yeast cells

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Adding CuSO4 before bottling

Suggested protocol for pre-bottling copper additions

(from Geoff Cowey at the Winemaking and Extension Services division at the AWRI)

KNOW THE HISTORY OF YOUR WINE

ONLY USE COPPER ON WINES THAT NEED IT

- do these additions a few weeks before bottling
- first stabilise SO2
- add 2mg/l ASCORBIC acid – wait 12 hours to react
- add another 2mg/l ASCORBIC acid – wait 12 hours to react
- then add CuSO4 – DO TRAILS FIRST
- wait one week
- measure copper levels
- ensure Cu levels lower than 0.3mg/l before bottling

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THANK YOU

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