Oxidation and Management Of Sulfur Dioxide in Wine

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Oxidation

- Changes associated with oxidation:
- Browning and darkening of color, both in white and red wines
- Decrease in varietal aroma
- Development of ‘nutty’, ‘sherry like’ aroma

In table wines oxidation beyond acceptable limit can impair wine quality

Oxidation occurres in must and also in wine

Phenolic compounds are the main substrates for oxidation

Factors influencing oxidation

Variety, fruit condition, temp, pH, amount of solids, substrate level and air exposure

Example Caftaric acid level

Vinifera < labrusca < V.aestivalis

Oxygen solubility: 8mg/l at saturation (and room temperature)

In must O2 is consumed faster in wine it is slower (about a week)

Must oxidation

- Must oxidation is rapid and catalyzed by enzyme Polyphenoloxidase (PPO)
- Phenolic compounds such as hydroxycinnamates are preferred PPO substrates
- In Botrytis infected grapes another powerful enzyme ‘ Laccase” causes oxidation. Laccase oxidizes a wider range of substrates and is less sensitive to SO2. At SO2 level of 150mg/l only 20% inhibition was observed.

Wine oxidation

At saturation about 8mg/l of oxygen is consumed and the reaction with wine components is slow.

During wine transfer, racking and topping small amount is dissolved. To protect wine from air exposure inert gas is used.

Wine oxidation is not enzymatic and is called auto oxidation.

Reaction:

Phenolic Compound colorless → (No enzyme; oxidation) → Quinone dark colored

oxidation in white wine

Properties of SO2

Colorless non flammable gas with suffocating odor

Molecular weight 64 (32g sulfur reacts with 32 g of oxygen to give 64 g SO2)

Soluble in water depending on temperature:

- 0^oC 228.3 g/l
- 10^0C 162.1g/l
- 20^0C 112.9 g/l
- 30^0C 78.1g/l

SO2 Terms

Useful not so useful

Free	+	Bound	=	Total

Bound SO2

- SO2 is bound to several compounds in wine

Important compounds include:

- Acetaldehyde,
- anthocyanins,
- pyruvic acid,
- alpha Keto- glutaric acid,
- glucose,
- certain phenolic compounds
- and gluconic acid in case of Botrytis infected grapes

Some loosely and some strongly bound

Acetaldehyde-bisulfite complex

- Acetaldehyde is the chief SO2 binding compound in wine
- It almost completely binds SO2 and the complex is stable
- Lactic acid bacteria can degrade this bisulfite complex

and release free SO2 which kill them

- What is the binding capacity of acetaldehyde?
- 44mg of acetaldehyde binds with 64mg of SO2
- 1: 1.45

Ionization of SO_2

- In aqueous SO_2 dissociates according to following equilibrium. All three forms are free SO_2

$$SO_2 \rightleftharpoons HSO_3^- \rightleftharpoons SO_3^{=}$$

Mol.(undissociated) Bisulfite Sulfite

pH dependent equilibrium

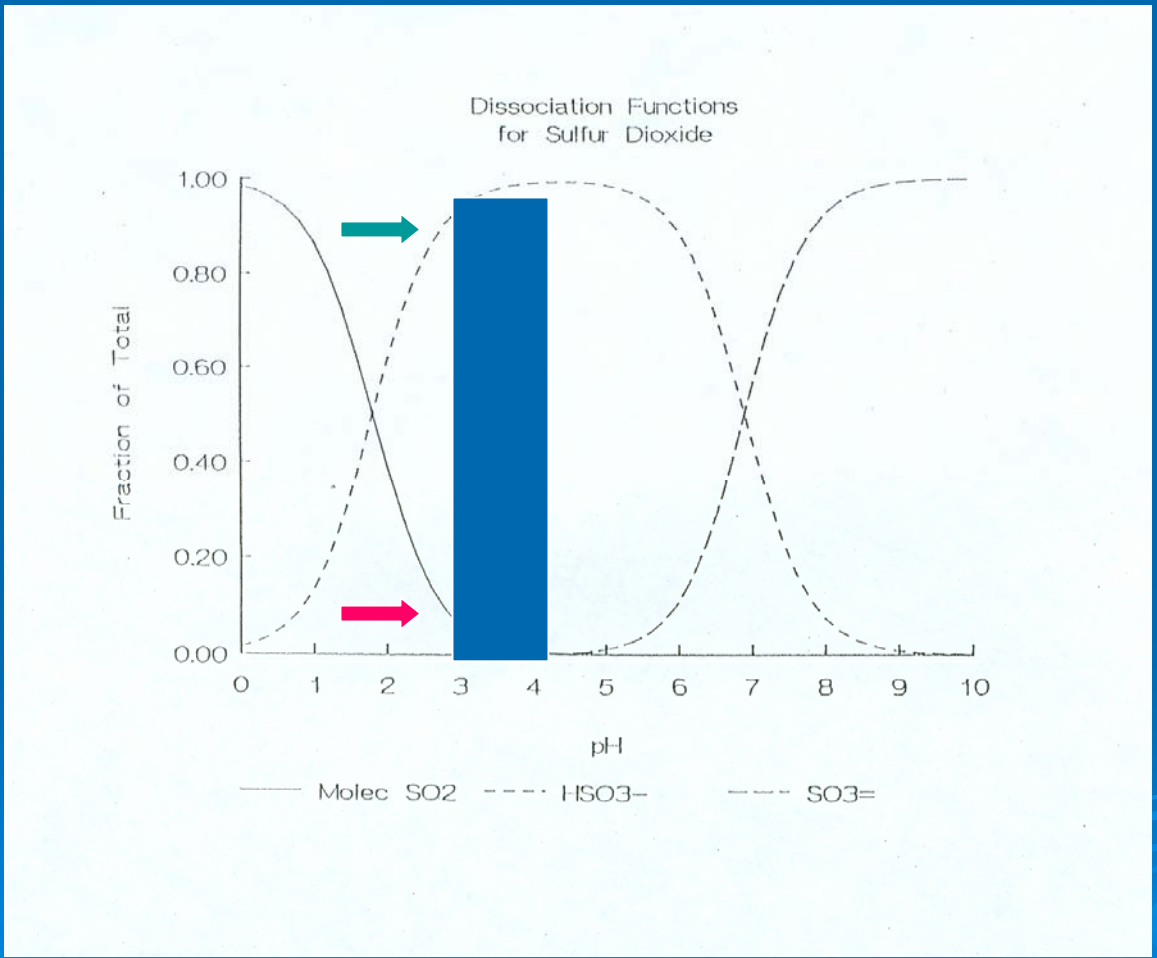
Ionization

- In aqueous SO2 dissociates according to following equilibrium
-
- SO2 gas + H2O SO2. H2O molecular SO2 (volatile) odorous

- SO2. H20 $\xrightarrow{pKa_1\ (1.77)}$ $H^+ + HSO3^-$ bisulfite ion

- $HSO3^-$ $\xrightarrow{pKa_2\ (7.2)}$ $H^+ + SO3^{=}$ Sulfite ion

Dissociation of SO2



Distribution of free SO2 at various pH's

Table 1. Distribution of free SO_2 at various pH's

pH	% SO_2 (m)	% HSO^-_3	% SO^{--}_3	free SO_2 to obtain 0.8 ppm molecular SO_2
2.9	7.5	92.5	.009	11 ppm
3.0	6.1	93.9	.012	13
3.1	4.9	95.1	.015	16
3.2	3.9	96.1	.019	21
3.3	3.1	96.8	.024	26
3.4	2.5	97.5	.030	32
3.5	2.0	98.0	.038	40
3.6	1.6	98.4	.048	50
3.7	1.3	98.7	.061	63
3.8	1.0	98.9	.077	79
3.9	0.8	99.1	.097	99
4.0	0.6	99.2	.122	125

Under normal situations, 0.8 ppm of molecular SO_2 is considered adequate to obtain the required protection.

Molecular SO2

- Most important form due to antimicrobial action, need to maintain 0.8ppm
- It reacts with H_2O_2 form during oxidation of wine
- It is volatile:
- a) contributes to odor and b) is lost as vapor
- At wine pH it's concentration ranges between

6% at pH 3.0 to 0.6% at pH 4.0, a 10 fold difference

Sensory threshold

- Considerable variation among individuals
- Reported thresholds are:
- 10 ppm in air and 15-40 ppm in wine
- Only molecular form is volatile and can be smelled
- pH and temperature both will influence volatility and thus the sensory perception.

Bisulfite form

- Dominant form at wine pH and binds with wine constituents like acetaldehyde, keto acids, glucose, quinones and monomeric anthocyanins

  thus producing BOUND SO2

- Bound SO2 contributes to total but not much help to winemakers

- At wine pH (3-4) it's concentration ranges between 94-99%

Positive aspects :

- Binding with acetaldehyde reduces aldehydic aroma,

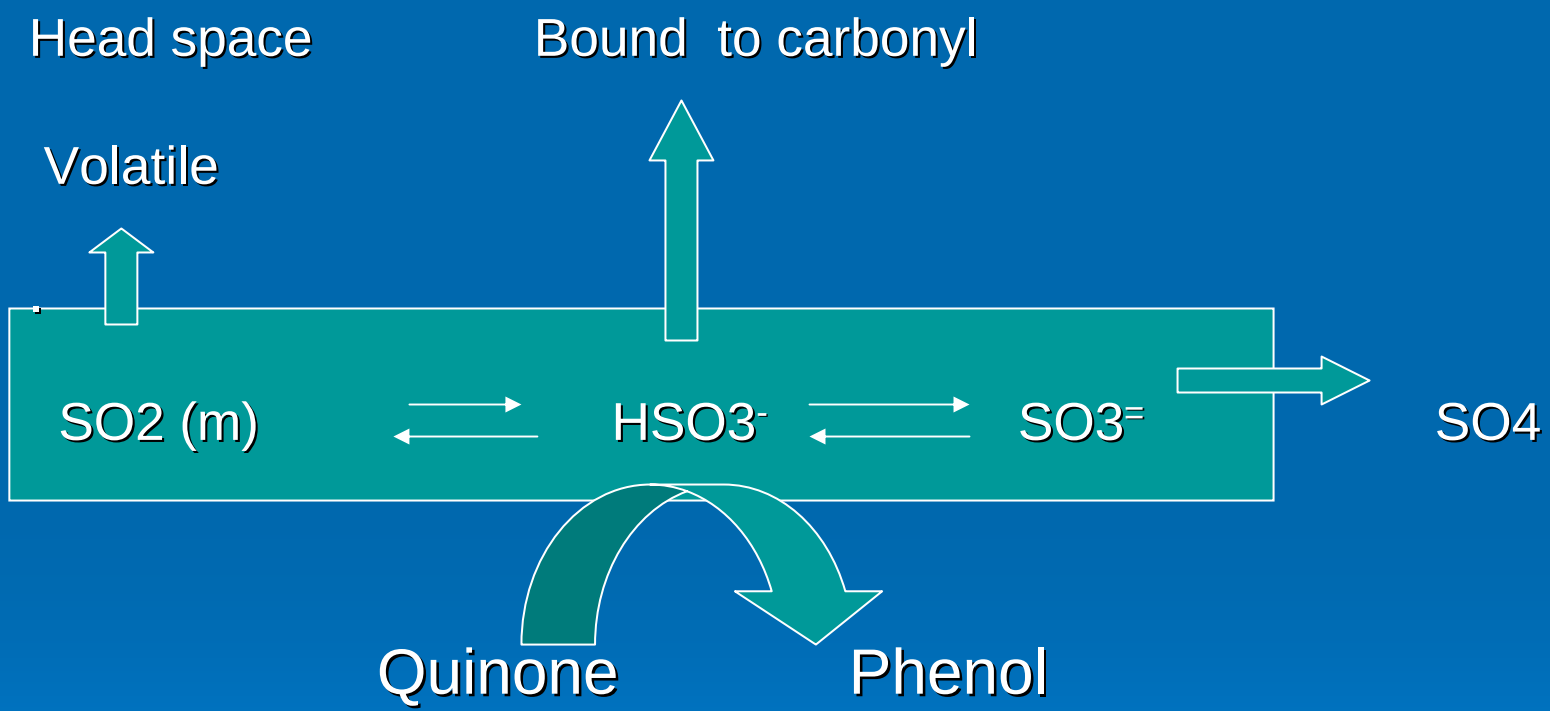
- It prevents both enzymatic and chemical oxidation (converts quinone to phenol or forms complex with quinone)

Sulfite, $SO_3^=$

- It is the antioxidant form but is present in wine at low concentrations

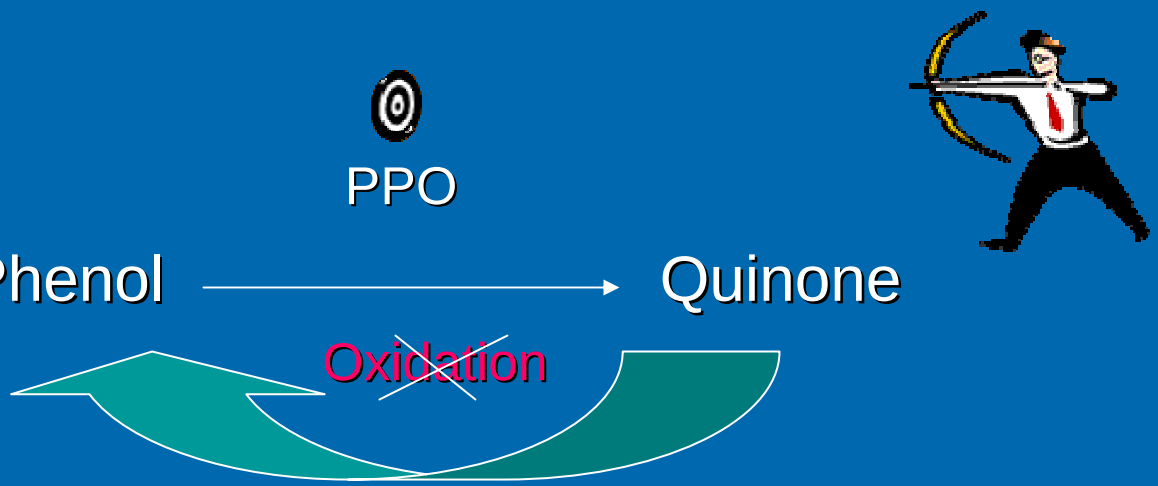
- Its reaction with oxygen in wine is very slow

How SO2 is Lost From Wine?



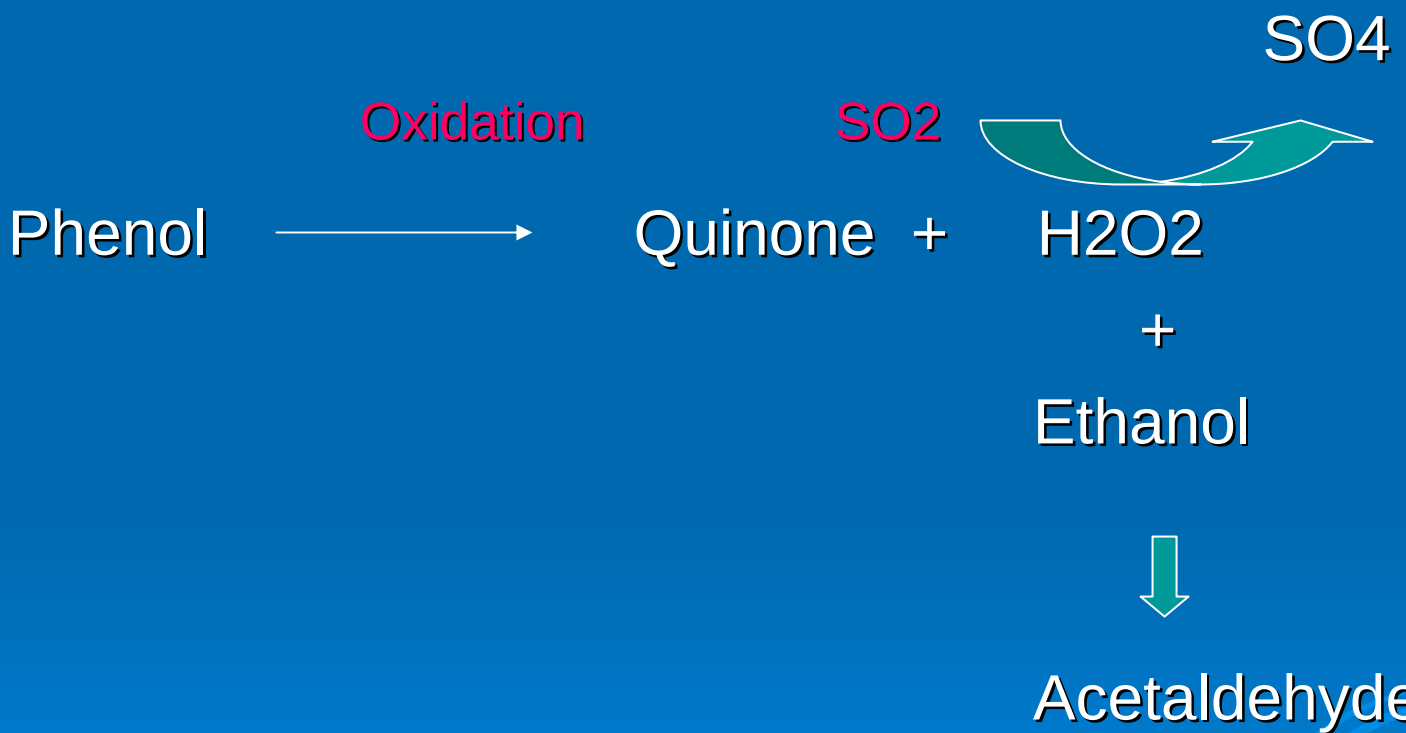
SO2 as antioxidant

- SO2 inhibits enzymatic oxidation (must) SO2



SO2 as Antioxidant

- Auto oxidation



How SO_2 is used?

- Liquefied gas under pressure:
- Potassium meta-bisulfite, which yields about 50% SO_2 when added to must/wine
- Sulfurous acid (H_2SO_3), produced by dissolving SO_2 in Water , 5% solution
- Use hydrometer to measure density and the concentration of SO_2 in solution

SO2 addition as liquid gas

- Liquid SO2 gas available under pressure kept in a cylinder
- Liquid measured in grams (or pounds) can be delivered into wine using sulfitometer where it is admitted as gas. use protective equipment, work in ventilated area
- Amount to be added can be calculated as follows
- Example :
- You need to add 100 ppm SO2 to 2000 liter wine
- Formula
- liquid gas to add = amount to add x $\frac{\text{Volume of wine}}{1000}$
- $100 \times \frac{2000}{1000}$
- = 200 grams

SO_2 addition as KMS powder

- Potassium metabisulfite contains 57% SO_2 by weight but in practice it is assumed to be 50%
- Example: you need to add 50 ppm SO_2 to a 2000 L of wine

Formula

$$\text{Amount of PMS (g)} = \frac{\text{target } SO_2 \text{ ppm}}{0.5} \times \frac{\text{volume of wine (L)}}{1000}$$

$$= \frac{50}{0.5} \times \frac{2000}{1000}$$

$$= 200 \text{ grams}$$

SO_2 application in winemaking
Harvest to Fermenter

- Decide whether to add SO_2. Addition of small amount is recommended

- Consider following factors to determine time and the amount of addition
- Fruit maturity
- Fruit condition (extent of rot)
- Fruit, hand or machine harvested
- Transporting grapes: temperature and distance
- Crushing
- Use of must chiller
- Pressing
- Must treatment fining etc

SO_2 application in winemaking Fermentation

No SO_2 addition

Some times SO_2 is used to stop fermentation, consider other options

- Minimize the formation of sulfite binding compounds during fermentation. Yeast strain, temperature etc

At the end of fermentation no free SO_2 remains in the must

Use of SO_2 during wine storage

Add SO_2 soon after fermentation

Added SO_2 level diminishes over time. Periodic SO_2 analysis and addition is necessary

To reduce the amount of SO_2 needed for protection follow these guidelines

- Operate under most hygienic conditions
- Minimize air exposure during wine transfer
- Keep containers full (no head space)
- Control microbial contamination

Use of SO_2 during bottling

- Do not rely on SO_2 only to achieve biological stability. Consider sterile filtration and sterile bottling
- Add SO_2 based on accurate analysis
- Minimize air exposure, use inert gas for flushing bottles, use vacuum filling and head space sparging
- Add sufficient SO_2 to account for oxygen pick op during bottling
- 1 ppm O_2 will react with 4 ppm SO_2

SO_2 as Sanitizing agent in winery

- Acidified SO_2 solution is used as sanitizer, citric acid is used to make solution acidic. Remember lowering pH increases the % of molecular SO_2 in solution
- Sanitizing hoses, rinsing tanks and general purpose sanitization

SO2 in Barrel sanitizing

- SO2 is applied by burning a wick or sulfur ring in the barrel for storage or prior to filling with wine
- It sanitizes the barrel as well as add SO2 to the wine
- Combustion of 5 grams of sulfur in a 225 liter wooden barrel increases so2 in wine from 10-20 ppm (Chatonnet et ai,1993)

Questions?