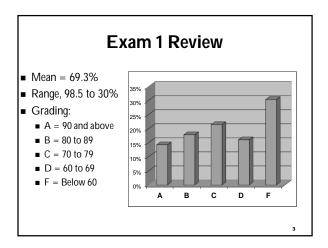
Sulfur Dioxide & Wine Additives

Wine 3 Introduction to Enology

3/4/2014

Tonight's Lecture

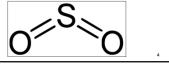
- Exam 1 recap
- The use of sulfur dioxide in wine
 - Chemistry of sulfur dioxide
 - Microbial action sulfur dioxide
 - Forms of sulfur dioxide
 - Adding sulfur dioxide
- Wine additives



Sulfur Dioxide

- Sulfur Dioxide has been used in winemaking since the Romans discovered that if you burn candles made of sulfur inside empty barrels it would prevent them smelling like vinegar.
- 2000 years later sulfur dioxide, or SO₂, remains the most important additive used in

winemaking.



Sulfur Dioxide

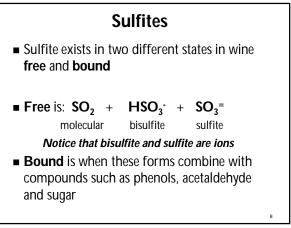
- The terminology of sulfur in wine is often confused. There are three common forms of sulfur in wine.
 - **SULFUR**
 - SULFIDES
 - SULFITES

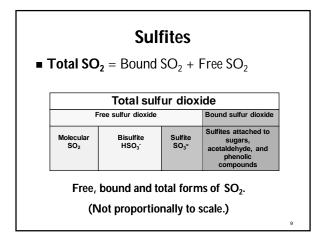
The 3 common forms of Sulfur in wine

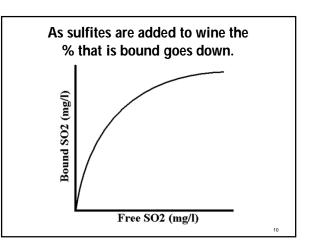
- SULFUR, S Elemental sulfur is present in proteins and used on grapes to prevent rot.
- SULFIDES, H₂S and mercaptans rotten egg and skunk smell produced when yeast and bacteria reduce S to H₂S. This is an example of a reduced sulfur.
- SULFITES, Sulfur dioxide (SO₂) and all its forms, this is an example of an oxidized sulfur.

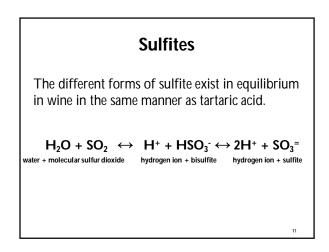
There are also 3 forms of Sulfites in wine

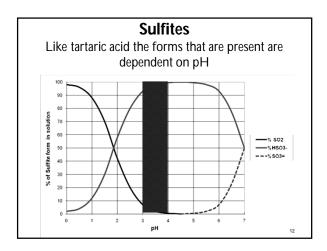
- **SULFITES -** Sulfur dioxide and its products.
 - Molecular sulfur dioxide SO₂
 - Bisulfite HSO₃-
 - Sulfite SO₃=

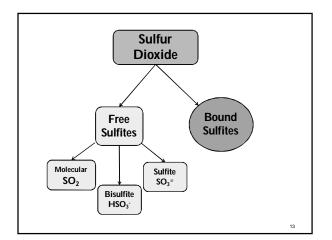






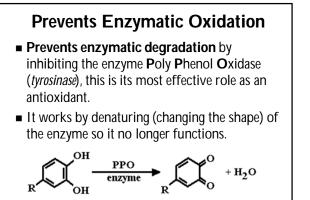


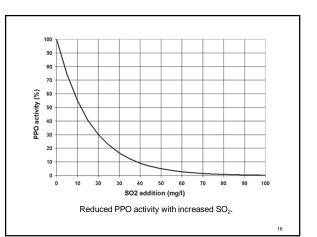


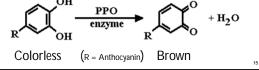


Functions of adding sulfur dioxide

- Antioxidant absorbs O₂ in wine.
 - $SO_3^{=} + O_2 + H_2O \rightarrow H_2SO_4$ (sulfuric acid)
- There is very little sulfite (SO₃=) present at wine pH, so SO₂ is not a strong antioxidant and very little sulfuric acid is produced.
- Note: that this results in Sulfate (SO₄) not Sulfite (SO3).





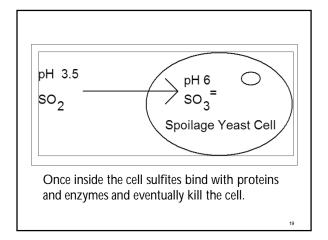


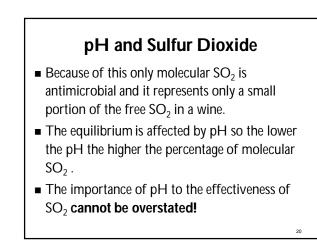


- Laccase is a very powerful polyphenol oxidase enzyme produced by mold and found in moldy grapes.
- It is highly resistant to sulfur dioxide so late harvest wines or white wines made from grapes with rot or mold are often darker/more yellow in color.
- In can be treated with enzymes before fermentation.

Functions of adding sulfur dioxide

- Anti-microbial activity Effective against bacteria and non-Saccharomyces yeast.
- The cell membrane will not allow charged molecules (ions) through, but molecular SO₂ can pass. Inside the cell the pH is much higher (pH 6) so the SO₂ disassociates and more molecular SO₂ get through.





A Word About PPM

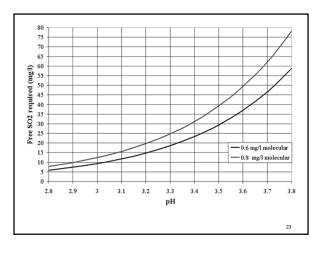
- PPM is an abbreviation for **P**arts **P**er **M**illion.
- It is equivalent to milligrams/Liter (mg/L)
 - There is 1/1000 of a gram in a milligram

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- There is 1000 grams of water in a liter
- So 1,000 x 1,000 = 1,000,000

Effective Level of Molecular SO₂

- S. cerevisiae is inhibited at 0.8 PPM Molecular SO₂. Bacteria, wild yeast and Brett. inhibited at 0.4 PPM Molecular SO₂
- Bisulfite has a weak effect on ML bacteria but is eclipsed by the effect of molecular SO₂.



How much SO₂ to add?

- There is a legal maximum of 350 PPM Total SO₂ (TSO₂) but this is irrelevant because of sensory considerations. Late harvest wines are the only time you may approach the legal limit.
- Sensory, Try to keep total SO₂ < 100 PPM, above that bound SO₂ can give a chemical taste that covers up fruitiness. Molecular SO₂ > 0.7 to 1.0 PPM has a burnt match smell.

How much SO₂ to add?

- Ideally molecular SO₂ should be 0.6 PPM or less (not more than 0.8) *At time of consumption*.
- Molecular SO₂ is a volatile substance that, irritates throat and makes eyes sting. A small percentage of asthmatics react to this, not ingested SO₂.
- Contrary to popular myth SO₂ does not cause headaches.
 More about this in the Wine & Heath lecture.

Degradation of SO₂

- Molecular SO₂ levels fall over time so wine bottled at 0.8 PPM or more should age long enough for sulfur level to fall to 0.6 PPM or less.
- In white wines you lose about 20 to 50% of free SO₂ in the first year after bottling.
- The amount that is lost depends on the composition of the wine and how the bottle is sealed.

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Adding SO₂ to Wine

- Sulfur dioxide is a gas is volatile and harmful to breathe so it is not convenient to work with, so SO₂ is usually added in other forms.
- Gas phase SO₂ comes in pressurized tanks and is very useful for preserving barrels.
- There are new regulations regarding how SO₂ gas is used in empty barrels that we will discuss in the barrel lecture.

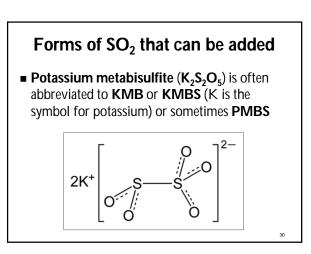
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Adding SO₂ to Wine

 The original method for producing SO₂ is by burning elemental sulfur with sulfur wicks however, be careful that no un-burned sulfur remains in the barrel because it will reduce to

H₂S.





Potassium Metabisulfite

- This is a stable powder that contains SO₂ and potassium, the percentage of available SO₂ is 57.6%.
- Note that PMBS & KMB are abbreviations NOT chemical formulas.



Potassium Metabisulfite

- This is a safe way to add because PMBS is stable and relatively non-volatile and it can easily be measured out by weight.
- Respirators and eye protection should still be used when working with PMBS for safety & comfort.

Adding PMBS

To determine how much PMBS to add to raise a given amount PPM of SO_2 in the wine we need wine we need to know the following:

There are 3.785 liters in a gallon 1 PPM = 1 milligram/ liter There are 1000 milligrams (mg) in a gram PMBS is 57.6% (0.576) SO₂ by weight

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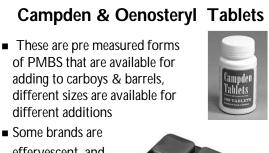
Adding PMBS

Formula for calculating PMBS addition:

(gallons of wine) x (3.785) x (ppm of addition) = grams PMBS (1000) x (0.576)

3.785 is the conversion from gallons to liters 1000 converts mg/L (ppm) to g/L 0.576 is the % of SO₂ in PMBS

This formula can be simplified to: (gallons of wine) x (ppm of addition) x (0.0066) = grams PMBS



 Some brands are effervescent and dissolve without mixing.



- Sodium metabisulfite is also available and is good for sanitation because it is less expensive and dissolves better, but sodium is not healthful so it is not used as often for addition to wine.
- Sodium metabisulfite in 67.4 % sulfite by weight

Aqueous SO₂ (5% to 10%)

- Aqueous sulfur dioxide is made by bubbling SO₂ gas through water (in which it easily dissolves).
- Since % by weight = °Brix you can check by using a hydrometer.
- It can also be made by dissolving PMBS in water. Useful for measuring out if you do not have a scale.

Aqueous SO₂ (5% to 10%)

- Reacts with O₂ so it is not stable over long periods of time.
- Formula for adding aqueous SO₂

(PPM to add) (3.785) (gallons) mL SO₂ = ——————————

(% sol) (10)

When Adding SO₂

- Only total SO₂ is raised by the full amount added, some of the addition is bound and some is free (only a portion of free SO₂ is molecular).
- WARNING: This is where things start to get complicated.

When Adding SO₂

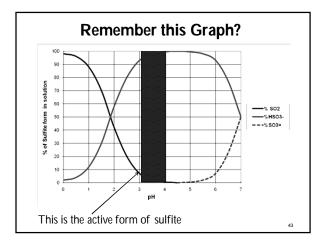
- The ratio of the free/total sulfur depends on:
 - ∎pH
 - Amount of free and bound SO₂ already present
 - Amount of SO₂ binding compounds not already bound
- Basically, how clean and dry is the wine?

When Adding SO₂

- Amount of free SO₂ usually ranges from about 1/3 to 2/3 of the total SO₂ added. The lower the pH the higher the ratio of free to total, wines fermented without SO₂ have a higher ratio of free to total.
- Example: If I add 50 PPM SO₂ to a wine I can expect between 16 & 34 PPM free SO₂.

When Adding SO₂

- Because of this uncertainty there is always a certain amount of estimation (guesswork) involved in making SO₂ additions.
- Now we will run through a couple of examples.



For example:

1000 gallons of red wine just finished malolactic fermentation and needs to be adjusted before being racked from a stainless steel tank to barrels.

Using potassium metabisulfite (PMBS) you want to adjust it to 0.5 PPM molecular SO_2 to protect it from spoilage during the time it will be in BBLs ageing.

Current analysis:

8 PPM Free SO_2 22 PPM Total SO_2 This would be expressed as F/T $SO_2 = 8/22$ pH = 3.45

By looking at the SO₂ chart in the handout you can see to get to 0.5 PPM molecular at 3.45 pH you will need a free SO₂ of 23 PPM.

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If approximately $\frac{1}{2}$ (0.5) of the amount of SO₂ added goes to free SO₂ how much PMBS will you need to add?

23 PPM (desired SO₂) – 8 PPM (current SO₂) = 15 PPM

15 PPM / 0.5 = 30 PPM to be added

(1000 Gal.) (30 PPM) (0.0066) = **198 gm PMBS**

Second Example:

- Make up some numbers:
 - Wine
 - Gallons
 - Stage of production (grapes to bottle)
 - Target SO₂
 - Current analysis (pH, F/T SO₂)

Homework

Question:

If you have 7000 gallons of **dry**, **sterile filtered** Chardonnay that is ready to bottle and it will be 10 months before it is consumed.

You want to adjust it to 0.8 PPM molecular SO_2 to protect its freshness during aging. How much PMBS do you want to add?

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Homework

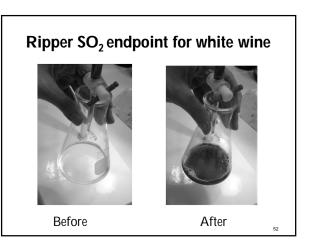
- Current analysis:
 15 PPM Free SO₂ by Ripper
 30 PPM Total SO₂ by Ripper
 pH 3.30
- Answer next week

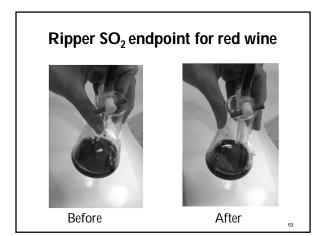
7 Steps to adding SO₂

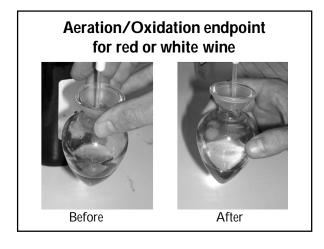
- 1. Wine analysis
- 2. Molecular SO₂ level needed
- 3. pH
- 4. Determine target free SO₂ level
- 5. Estimate the amount of SO₂ that will be bound
- 6. Calculate addition
- 7. Add to wine

When Adding SO₂

- Roughly estimate the amount that will remain free, do the addition, wait overnight for it to equilibrate, then check your results (if you can wait that long).
- SO₂ is measured usually by the Ripper or Aeration/Oxidation method. The Ripper titration has a blue endpoint so it is difficult to use for red wines, AO usually reads free SO₂ a little lower than Ripper.







General recommendations on quality

- Pay attention to pH and add for molecular SO₂ and keep it as low as possible for the desired wine style. Reds done with ML don't need as much.
- Better to add fewer, larger additions than many small ones (shocks the bacteria better and you get a better ^{free}/_{total} ratio).

When to add SO₂, Before or after fermentation?

In whites, post fermentation SO₂ method allows for less SO₂ at bottling. At first, the juice tends to oxidize and the must turns very brown, but this color drops out after fermentation. The choice really depends on style.

No SO₂ Before Fermentation

- Less Phenols
- More color stable
- Less acetaldehyde
- More conducive for ML fermentation
- SO₂ Added Before Fermentation
 - More fruity (more aromas)
 - More phenols
 - No malolactic
 - Less chance for spoilage

When to add SO₂ cont.

- If the wine is being sur lie aged, the yeast help to protect the wine from oxidation.
- With red wines you generally don't add SO₂ until after ML fermentation is done unless you want to protect against *Lactobacillus* spoilage (which I recommend) then you can add about 30-40 PPM total before fermentation.

When to add SO₂ cont.

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When adding SO₂ to white wines before fermentation add at the press sump or juice tank, if added at the crusher or in press it extracts phenols from the skins and you get a poor F/T SO₂ ratio.

Excess SO₂

- Excess SO₂ can be removed by adding hydrogen peroxide (H₂O₂). Will oxidize SO₂ to H₂SO₄ (raising the acidity slightly) this is illegal, but it works and can remove up to several hundred PPM.
- However, H₂O₂ is a powerful oxidant and trials should first be done, and great care must be taken.

Excess SO₂

- $\blacksquare \text{ Reaction}, \quad H_2O_2 + SO_2 \rightarrow H_2SO_4$
- 0.5304 g of 3% hydrogen peroxide removes 1 gram of SO₂
- 0.7 ml of 3% H₂O₂ per gallon will remove 10 PPM of SO₂
- There has to be significant molecular SO₂ present for this to work, and take into account the % solution of H₂O₂. Don't try to go below 20 PPM and add slowly while mixing.

Excess SO₂

 Large amounts of nitrogen gas can be sparged through the tank to blow off SO₂, but this process strips the wine of aromas.

Rough estimate of what stages during a wine's processing to add SO ₂	
At Harvest	20 to 60 PPM depending on condition of the fruit, none if doing "post ferm SO_2 "
At Dryness (or when stopping sweet) or when ML is completed	Bring to 0.8 PPM molecular (whites) 0.5 PPM (reds) About 50 to 70 PPM TSO ₂ , Same for "post ferm SO_2 "
Before first summer If not bottling sooner	If pH 3.5 or below, bring to 0.6 to 0.8 PPM molecular (whites) or 0.5 to 0.6 (reds) If pH is > 3.5 lower pH or add SO ₂ based on tendency to spoil. Try to keep total <80

Rough estimate of what stages during a wine's processing to add SO ₂	
At Bottling	If pH is < 3.5, bring to 0.8 PPM (whites) or 0.5 (reds) if pH is > than 3.5 add on basis of tendency to oxidize or spoil but keep total < 100 PPM if possible
When Consumed	When consumed the molecular should be about 0.6 or less, in no case should it be >0.8

Organic Wines

- Organic wines must be made from organically grown grapes *and* have no added SO₂.
- There is also a small amount of SO₂ formed by yeast in all wines, usually less then 10 PPM.
- Adding SO₂ to organic wines is legal in Europe.
- If a wine has more than 10 PPM sulfur dioxide it must be labeled "contains sulfites"

Organic Wines • It is very difficult to make a commercially acceptable wine without adding SO₂ (especially a white wine) due to decreased shelf life.

Wine Additives

Wine 3 Introduction to Enology

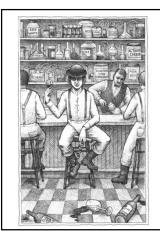
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Wine Additives

- Wine additives are usually used to adjust the flavor, the chemistry or the stability of a wine.
- Historically they are not regulated heavily because they are often already present in the wine to some degree.
- A rule to live by when making wine additions is you can always add more, but you can't add less after it is in the wine.

Wine Additives

- Many wine additives are considered GRAS compounds (GRAS - An acronym for "Generally Recognized As Safe)
- Wine additives are regulated by the TTB and information on their use is found at the TTB website. There is a link at the class website.



By discussing a particular additive I am not necessarily advocating its use!

Wine Additive Labeling

- While US wines have not been required to label ingredients but this is likely to change soon.
 - Ingredient/treatment labeling
 - Allergen labeling
 - Nutritional labeling

Sugar & Acid additions

- Sugar and acid additions were covered in the previous lecture.
- We will review acid addition calculations again.
- Remember: the amount of pH shift you get per gm/L varies but a good approximation is:
- 1 gm/L tartaric addition lowers pH by about 0.1

Adding Acid

- Very easy using the metric system,
 1 gm/L addition Tartaric acid raises TA 1 gm/L
- To raise the TA 1 gm/L of 100 Gal. wine
- (1 gm/L) (3.785 L/Gal.) (100 Gal.) = 378.5 gm
- In English (American) units: Approximately 8.3 #/1000 Gal. = 1 gm/L

Example

- Acid addition, 3,800 gallons of Cabernet Sauvignon wine is has a pH of 3.9 and you want to lower it to 3.5, how much tartaric acid do you add?
 - 4 grams/Liter will lower pH by about .4 (3,800 gal)(3.78 L/Gal) = 14,383 Liters (14,383 L)(4 grams/L) = 57,532 grams 57,532 grams = 57.532 kilograms

Example

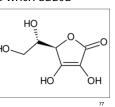
How do we convert this to pounds?
 Addition= 57.532 kilograms of tartaric acid
 1 Kilogram (Kg) = 2.2 pounds (#)
 57.532 Kg x 2.2 Kg/# = 126.8#

Homework 2

- Acid addition, 10,000 gallons of Sauvignon Blanc juice is has a pH of 3.6 and you want to lower it to 3.4, how much tartaric acid do you add?
- How much in grams?
- How much in pounds?
- Answer next week

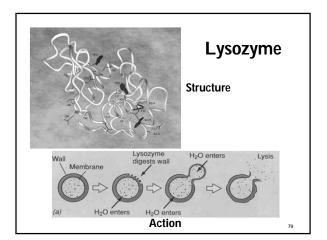
Ascorbic Acid, (Vitamin C)

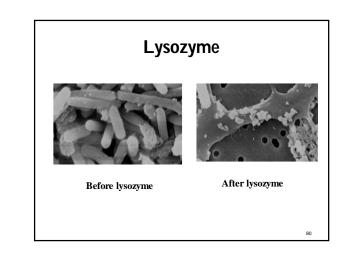
- Added as an antioxidant
- 0.05 to 0.15 g/L (5 to 1.5 #/1000 Gal) works a little better than SO₂.
- Works well for white wines when added before bottling.
- For Ascorbic to work properly you must have significant Free SO₂





- *Lactobacillus, Oenococcus* and *Pediococcus* in wine. It works by breaking down the cell wall of Gram positive bacteria but it does not affect yeast.
- Good for adding to stuck, high pH wines that have the potential for *Lactobacillus* spoilage but SO₂ is ineffective because the pH is too high.





Lysozyme

- Works better at high pH, expensive. 200 to 400 PPM (20-40 g/hL) (hL = hectoliter = 100 Liters)
- One manufacture said it takes 400 lbs of egg whites to get one pound of Lysozyme.
- It costs about \$135/pound!

Enzymes

- As we discussed in the lecture on white crush there are a number of enzymes that are used prior to fermentation to clarify juice and improve yield.
- The major types are pectinases, hemicellulases, and glucanases.
- They act by breaking down the structural components of grape pulp.

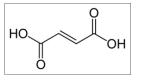
Enzymes

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- Those added to crushed fruit the help to release juice and improve yield.
- Added to juice they breakdown protective colloids (gums that prevent particles from settling) to aid in clarify the juice and improve settling.

Fumaric Acid

- Added to inhibit the growth of ML bacteria works best along with other practices (SO₂, low pH, etc.) Added to 0.03% to 0.05%, very difficult to dissolve.
- Filtering is more effective so fumaric is usually only added if you cannot sterile filter.

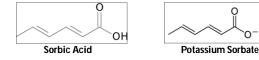


Sorbic Acid ~ Potassium Sorbate

- Preservative, prevents yeast growth but doesn't kill them. About 100 PPM is effective depending on alcohol. Good for home winemakers making sweet wine who cannot filter.
- Used in many food and beverage products as well as non-alcoholic wine.

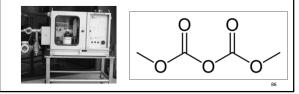
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Dimethyl Dicarbonate (DMDC)

- Sold in the US under the trade name Velcorin, it a powerful and toxic antimicrobial agent.
- It can be added to wine up to 200 PPM and kills microbes including Brett. eliminating the need for filtration.



Dimethyl Dicarbonate (DMDC)

- After it is added to wine it quickly breaks down to harmless amounts of methanol & CO₂. It can only be added with a dosing machine that costs about \$60k or the machines can be rented.
- Randal Gram called his the Deathstar Machine.
- It is used primarily for low alcohol wines as well as bottled fruit juice, soda pop, and sweet teas.

Alcohol

- Must be added in the form of grape brandy for fortified desert or table wines. Legal with permits & tax documents.
- For home winemakers 1 to 2 % aged brandy gives wines made from second crop more mouth feel and oak character, (old Burgundy trick).
- Alcohol effects the body and taste, as well as the perceived aroma of a wine.

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Water

- Legal to add in under prescribed limits for additions of yeast, acids, fining agents etc.
- Water can be added to lower the sugar of musts that are too sweet to ferment dry.
- Used to be semi-legal, but in 2002 California Food & Drug interpreted adding enough water to insure yeast can ferment to dryness on dehydrated grapes is allowable.

Water • A taste test was done with Zinfandel. Zins can dehydrate at harvest and sugar up very suddenly. So essentially, they were replacing the water that had been lost to dehydration. Best {Taste} Worst 25 Brix \rightarrow 28 to 25 \rightarrow 28 Brix \rightarrow Adjusted as is adjusted not adjusted as wine

Water

- Rule of thumb, get harvest Brix right to begin with, and if you don't, keep the adjustment as low as you can.
- Commercial winemakers often ferment high Brix must and then de-alcoholize, this method concentrates flavor instead of diluting it.



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Water

- Raisins present in Zinfandel must can raise the sugar in the tank 1 to 5 °Brix after soaking.
- Remember to add acid to compensate for the lack of acid in the water.
- It is very difficult to get an accurate Brix reading off of a tank of red must on skins so let it soak and mix well before measuring Brix.

Water

• The formula is similar adding sweet and dry wines together.

To get 1000 gallons from 26 to 25 degrees °B

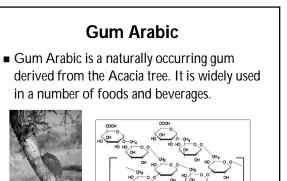
- Let X = Gallons water
 - $(1,000 + X) 25\% = \{(1,000)(26\%)\} + X(0)$ 25,000 + 25X = 26,000 + 0 25X = 1,000X = 40 gal

Saignée

- When you add water you may dilute flavor.
- Before adding water it is best to drain off some off the juice so you end up with the same liquid to skins ratio as you had before the water addition.
- The term for this is saignée from the French word for bleeding.
- Saignée makes an excellent rosé wine.

Enological Tannins

- There are many types of tannins that can be added to wine that are isolated from oak or grape skins and seeds.
- They are used to affect a wines body, flavor, and to stabilize color.
- Enological tannins offer exciting possibilities but taste bench trials first!



Gum Arabic

- Acting as a protective colloid it stabilizes the color of young red wines and improves body/mouthfeel and makes a wine "softer".
- It should only be added to clarified wines.
- Taste trials should be done before use, addition rate is about 10 to 20 grams/hL.

Color concentrates

- Mega-purple & Mega-red, Grape juice concentrates derived from Rubired (a hybrid variety grape bred for color).
- Sweet 68°Brix and expensive (\$130/Gallon)
- Addition rate of about 0.1 to 0.3%.
- Affects flavor and aroma as well as color.



Improving low-end wines

- Tannins, gum Arabic and color concentrates are widely used in inexpensive wines to improve quality and make multiple bottlings more uniform.
- They have a huge affect on wines that are not very good on their own.
- They have much less to offer to well-made wines from quality growing regions.

Should you use wine additives?

- Well..... It depends
 - Do they make your wine taste better?
 - What are the long term and short term effects of their use?
 - How do I feel about using them?
 - Think of them as specialized tools in your winemaking tool box that you may never need.

Fining Agents

- There are many different types of fining agents, they are not technically additives because they do not stay in solution and remain in the wine.
- Since the affect the chemistry of the wine and settle out they are considered a wine treatment instead of an additive.
- We will cover fining agents in a later lecture.

In Conclusion

- There are more additives that are less common than the ones we went over tonight.
- When using additives remember to:
 - Do lab trials before additions
 - Trial the levels recommended by the manufacturer against a control.
 - Taste your trials blind

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In Conclusion

• The best wines always seem to have the least intervention.....

But that might be because they *need* the least intervention.

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Reading Assignment

- There is a link to an in-depth article on Sulfur dioxide I wrote for *Practical Winery Magazine* at our class website.
- There is also a link to excellent article on sulfites by Andrew Waterhouse a professor at UC Davis.