

Winemaking 301

Prepared and Presented by: Frank Schieber, Amateur Winemaker MoundTop Microvinification Vermillion, SD www.moundtop.com schieber@usd.edu

Hosted by: Breezy Hills Vineyard & Winery Minden, Iowa

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Agenda

<u>рН</u>

What it is (and what it isn't). Role of pH in winemaking. pH meters and pH electrodes. Calibrating pH meters and measuring pH of wine.

Sulfur Dioxide (Free SO₂)

Protective benefits (antimicrobial; antioxidant). Free versus Bound SO₂. Critical role of wine pH. Molecular SO₂ vs. ionized HSO₃ (Bisulfite) Calculation of SO₂ additions – Need for empirical measurement. Accurate measurement of free SO₂ using Aeration-Oxidation (AO) Method.

Monitoring Fermentation with a Refractometer (vs. Hydrometer)

Refractometer approach is faster, just as accurate and more sanitary. Method, Apparatus, Software versus Tables (<u>www.moundtop.com</u>).



Residual Sugar

Verifying end of alcoholic fermentation. Quick & reasonably accurate determination using *Clinitest* tablets. Stabilization of "sweet" wines using potassium sorbate. (Caveat emptor: Friendly warning about commercial "wine conditioner")

Titratable Acidity (TA)

Definition. How knowing TA is useful. Tartaric acid ionization, pH and the cold stabilization process. Measuring TA in white wines (Color indicator method). Measuring TA in red wines (pH indicator method).



pH: Its Role in Winemaking

- Needed to manage sulfite levels in wines. ***
- Predict microbial stability (< 3.65).
- Determine wine's potential for MLF (> 3.3).
- Guides choice of wine style.
- Predicts a wine's potential for aging.
- Titration end-point for red wines.
- Guides cold stabilization decisions for red wines.
- <u>Viticulture</u>: Some winegrowers determine when to pick their grapes based upon pH.

pH: What is it?

- **pH** is an index that represents the concentration of "available" hydrogen ions (H⁺) in an water based solution (e.g., wine).
- [H⁺] = <u>concentration of hydrogen ions (mol/L)</u>
- $pH = log_{10}(1/[H^+]) = -log_{10}([H^+])$

pH is inversely related to H⁺ concentration ph is a logarithmic scale (1 unit = 10-fold change)

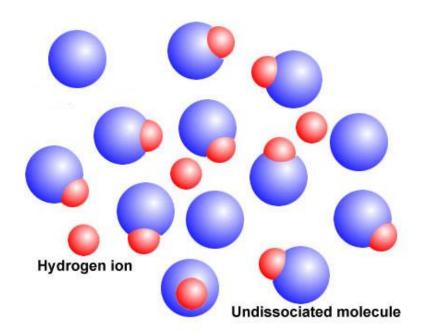
pH: What is it?

- **pH** of "pure" water is 7
 pH_{water} = log(1/[H⁺]) = log(1/0.0000001)
 = log(10,000,000) = 7
- If [H+] is greater than water's, then its pH < 7.
 Such solutions are acidic (e.g., wine).
- If [H+] is less than water's, then its pH > 7.
 Such solutions are **basic** (i.e., alkaline).
- Wine pH typically falls between 3-4.

pH: What it's Not!

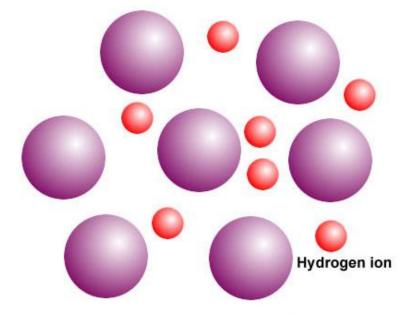
- **pH** is <u>not</u> a measure of the **AMOUNT** of acid in a solution such as wine.
- Winemakers usually describe the AMOUNT of acid in solution in terms of <u>Titratable Acidity</u> expressed in grams/liter (Discussed below).
- pH is better conceptualized as a measure of the STRENGTH of an acid (The more easily an acid "donates" its H⁺ ions in solution, the greater its relative reactivity).

Concentration of H⁺ = <u>Acid Strength</u>



Weak acids dissociate only slightly in aqueous solution. The majority of molecules remain undissociated.

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Low [H+] = High pH
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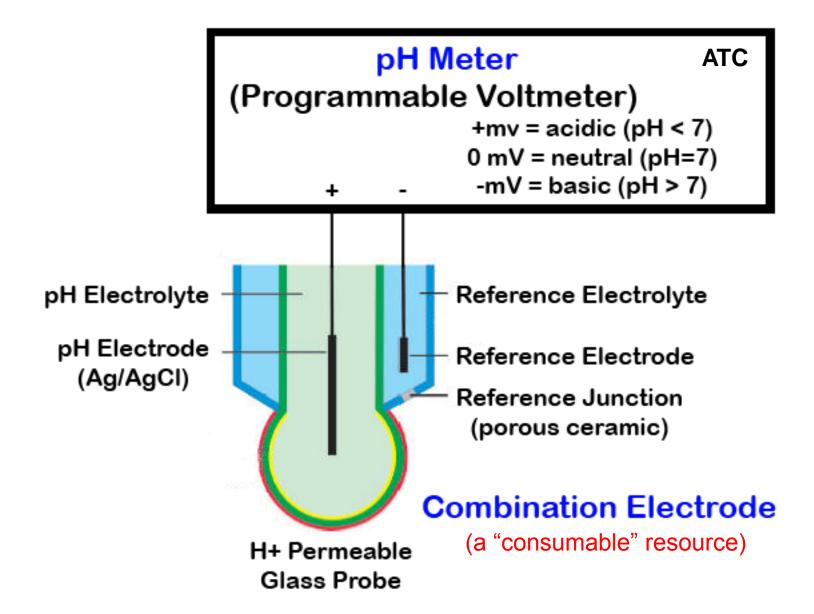


Strong acids are assumed to dissociate completely when in aqueous solution.

High [H+] = Low pH

Source: http://www.chem.ubc.ca/courseware/pH

Measuring pH



Laboratory Quality pH Meter/Probe (Yet, portable enough for field use)



High Quality "used" <u>meters</u> are readily available on eBay.

<u>Caveat Emptor</u>: Most pH <u>electrodes</u> available on eBay are "expired". It's OK to look for a meter on eBay but buy a FRESH/NEW probe from a reliable retailer.

pH Meter Calibration Video

Source: http://valleyvintner.com



pH Electrode Maintenance Conditioning a New Probe/Electrode

- Rinse off dried crystals with water (Don't rub with cloth or paper towel)
- Soak electrode in distilled water for 1 hour ***
- Soak in Buffer 4 for 5 min
- Soak in Buffer 7 for 5 min
- Calibrate

pH Electrode Maintenance Short- and Long-Term Storage

- Never let glass "bulb" dry-out
- Store electrode in <u>Storage Solution</u> recommended by manufacturer or in <u>Buffer 4</u>
- For maximum lifespan: Replace storage solution every 6-8 weeks
- <u>Never store electrode in water</u> for more than an hour (especially distilled water). This will leach ions from internal electrolyte solution.

pH Electrode Maintenance Sluggish or Drifting Performance

- Soak in 0.1 M HCl solution for 1 hour (Removes protein build-up from glass bulb)
- Soak in hot (50°C) Buffer 4 for 1 hour (Clear blockage from reference junction)
- Allow electrode to cool down and Recalibrate.
 If performance doesn't improve, it's probably time to secure a new pH electrode.

Sulfur Dioxide (Free SO₂)

Critical Role of SO₂ for Winemaking

• <u>Antimicrobial</u>

Inhibits many types of bacteria/wild yeast.

• <u>Antioxidant</u>

Prevents browning (pre/post fermentation). Inhibits formation of acetaldehyde (and bindsup any that does form); minimizing "Sherrylike" aromas.

- <u>Preserves fruitiness</u> (Varietal character).
- Well tolerated by commercial yeast strains.

Factors Complicating SO₂ Management

- Understanding "Free" vs. "Bound" SO₂.
 <u>Only "Free" SO₂ provides "insurance"</u> against future wine damage.
- Estimation of Free SO₂ can't be done by formula alone. <u>Quantitative measurement</u> is necessary.
- Free SO₂ ionizes into two separate components: <u>Molecular SO₂ vs. Bisulfite</u>.
- Molecular SO₂ level is <u>highly pH dependent</u>.

Free vs. Bound SO₂

Total SO₂ =

Amount of SO₂ added by the winemaker (plus trace amounts produces by yeast)

Proportion of SO₂ that has interacted with "bad actors" and prevented them from damaging the wine. Hence, this portion of the SO₂ is no longer available to protect against future insults.

Bound SO₂ + Free SO₂

"Unused" SO₂ that is still available to inhibit microbes and oxidizing agents that can potentially damage the wine.

("Insurance Policy")

Several Varieties of Free SO₂

- Molecular SO₂ (non-ionized)
 Responsible for <u>antimicrobial</u> properties
- **Bisulfite** (ionized form) Responsible for <u>antioxidant</u> properties
- Sulfite (doubly ionized form)
 Virtually non-existent at wine pH

Ionization of Sulfur Dioxide in Water (Reaction responsible for various forms of Free SO₂)

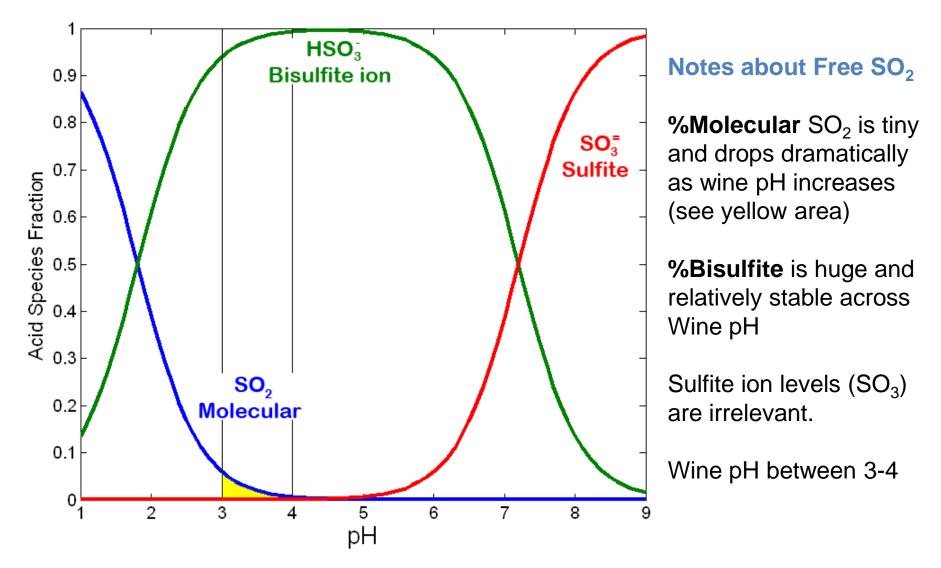
$$H_2O + SO_2 \xrightarrow{pKa = 1.81} HSO_3^- \xrightarrow{pKa = 7.2} SO_3^=$$

| Molecular | Bisulfite | Sulfite |
|-----------------|-----------|---------|
| (dissolved gas) | ion | ion |

The heck you say?

Ionization of Free SO₂ (Let's describe it with a picture)





Research shows that the Molecular fraction of Free SO₂ must be maintained at 0.8 mg/L (PPM) in order to provide adequate antimicrobial protection. Distribution of Free SO₂ "Species" as a function of Wine pH (also shown: mg/L of Free SO₂ Required to yield 0.8 mg/L Molecular SO₂)

| рН | %Bisulfite | %Molecular | | |
|-----|------------|-------------------------------|---------------|--|
| 3.0 | 93.9 | 6.1 | 13 mg/L (PPM) | |
| 3.1 | 95.1 | 4.9 | 16 | |
| 3.2 | 96.1 | 3.9 | 21 | |
| 3.3 | 96.9 | 3.1 | 26 | |
| 3.4 | 97.5 | 2.5 | 32 | |
| 3.5 | 98.0 | 2.0 | 40 | |
| 3.6 | 98.4 | 1.6 | 50 | |
| 3.7 | 98.7 | 1.3 | 62 | |
| 3.8 | 98.9 | 1.0 | 80 | |
| 3.9 | 99.1 | 0.8 | 100 | |
| 4.0 | 99.3 | 0.6 | 133 | |
| | | Free SO ₂ Required | | |
| | | for 0.8 mg/L Molecular | | |
| | | - | | |
| | | | | |

Free SO₂ Req'd (mg/L) = 0.013534 * exp(2.2867 * pH) (R² = 0.999)

Maintaining 0.8 mg/L Molecular SO₂ is the key to managing sulfite additions to wine.

How do we achieve this?

Case Study #1

Red wine with pH=3.6 has just finished MLF.

Reference to Table/Equation indicates that 50 PPM of free SO_2 is required to achieve the target concentration of 0.8 PPM molecular SO_2

Since <u>about HALF of the first 60 PPM of SO₂ added to a wine immediately</u> <u>becomes bound-up</u>, we need to add approximately:

 $(0.5)(60 \text{ PPM}) + 20 \text{ PPM} = 80 \text{ PPM SO}_2 \text{ addition to achieve}$ goal level of 50 PPM free SO₂

Add 80 PPM SO_2 to the wine.

Test free SO₂ to verify (e.g., Aeration-Oxidation test demonstrated below).

Case Study #2

At the second racking, a wine has a pH of 3.4 and a previous SO_2 addition history of 90 PPM.

Reference to the appropriate table reveals that a wine with a pH=3.4 requires 32 PPM to achieve the target level of 0.8 PPM molecular SO₂.

Laboratory test of the wine reveals a current free SO₂ level of 20 PPM.

Compute the required SO_2 addition as follows:

addition = SO_2 req'd for 0.8 molecular – current free SO_2 level addition = 32 - 20 = 12 PPM

12 mg/L of SO_2 must be added to the wine to achieve ideal level.

How do we make the physical adjustment to the wine once we know the size of the free SO₂ addition required to achieve a concentration 0.8 mg/L molecular?

Forms of SO₂ Used in Winemaking

- Liquified SO₂ gas (under high pressure)
- 5% Sulfurous acid (H₂SO₃) solution

(The above are not practical for the amateur)

 Potassium metabisulfite (KMeta) powder (57% SO₂ by weight when dissolved in water)

Case Study #3 40 PPM SO₂ Addition using KMeta

Problem:

How much KMeta powder must be added to 10 gallons of wine to raise the current free SO_2 level by 40 PPM?

Solution: Remember...1 PPM = 1 mg/L

(40 mg/L SO₂ Req'd * 10 gal. of wine * 3.785 L/gal) / 0.57 KMeta concentration

(40 * 10 * 3.785) / 0.57 = 1414/0.57 = 2656 mg of KMeta required

Accurate yet inexpensive 100 g scales with 0.01 gram precision are readily available.

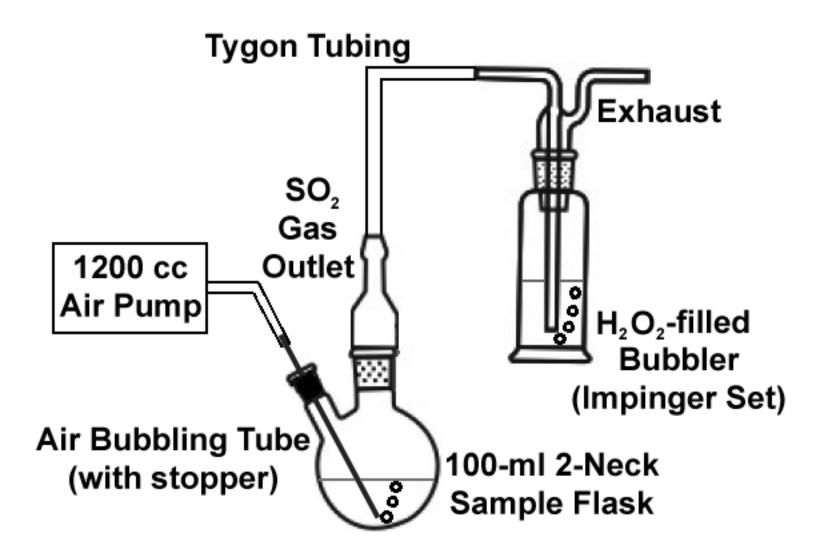


Downsides of SO₂

- Not effective against bacteria at high pH (Consider Lysozyme treatment)
- Disagreeable taste/aroma at higher levels
- Some individuals are hypersensitive to sulfites (headaches; allergic reactions)
- Legal limit for Total SO₂ (350 mg/L USA) (350 PPM?...A seriously oxidized wine!!!)

Aeration-Oxidation Apparatus

(Determination of Free SO₂)



Logic of A-O Procedure

Add 20 ml (volumetric) wine sample to a 2-neck flask.

Add 10 ml (nominal) of phosphoric acid (25%) to the wine sample. This reduces the pH and converts the free SO_2 to the molecular form.

Purge acidified wine sample of its SO_2 gas by bubbling air through it.

Capture the air used to collect the SO_2 gas and bubble it through a 0.3% hydrogen peroxide (H_2O_2) solution.

The SO₂ entering the H₂O₂ is immediately converted to sulfuric acid: SO₂ + H₂O₂ \rightarrow SO₃ + H₂O \rightarrow H₂SO₄ (i.e., sulfuric acid)

After 15 min. all of the SO_2 has been volatized from the wine sample.

The amount of SO_2 in the original wine sample can be quantified by measuring the volume of 0.01 N sodium hydroxide (NaOH) required to neutralize the sulfuric acid now in the H_2O_2 trap. This is a achieved using titration techniques and a special dual-color indicator.

Step-by-Step Aeration-Oxidation (Aspiration) Procedure

- See handout detailing A-O Procedure
- Download from:

http://www.moundtop.com/so2/SO2-Aspiration-Procedure2.pdf

AO Free SO₂ Method Video

(Source: www.valleyvintner.com)

Measuring Free S02 with the ValleyVintner,LLC "Aeration Oxidation" System.

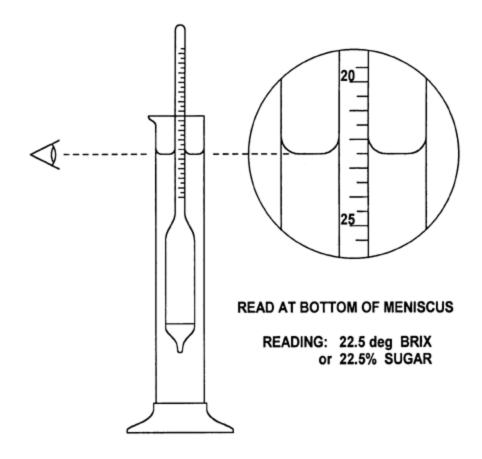
Monitoring Fermentation using a Refractometer

Why Monitor Fermentation?

- Initial Brix predicts <u>potential alcohol</u> (and guides <u>chapitalization</u> decisions)
- When to add yeast nutrients (1/3 Brix down)
- Determine <u>rate of fermentation</u> (color extraction; "stuck" fermentation risk)
- <u>H₂S intervention (too late for more nutrients?</u>)
- Estimate <u>press date</u> (logistics) and MLF inoculation date
- Determine <u>end-of-primary-fermentation</u> (Racking decisions)

Classical Hydrometer Approach

BRIX / BALLING HYDROMETER





Classical Hydrometer Approach

- Measurement based upon relationship between sugar/alcohol concentration and <u>specific gravity (i.e., density)</u> of a solution
- Decreases in %sugar (Brix) and increases in %alcohol BOTH lead to a reduction in the specific gravity of wine (Hence, the hydrometer sinks deeper into the wine as the fermentation process progresses)

Classical Hydrometer Approach

• <u>Apparatus</u>:

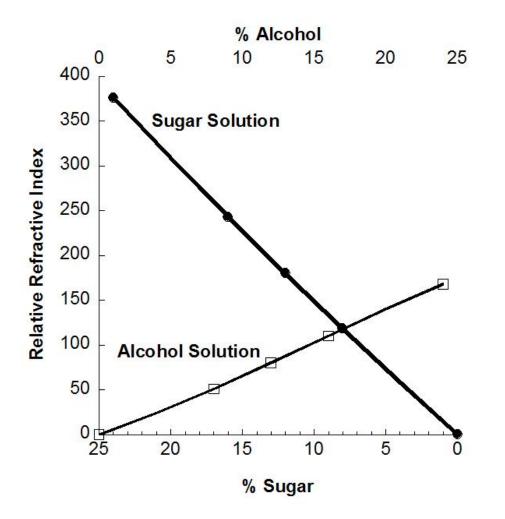
250 ml sampling jar, winemaking hydrometer, thermometer, wine thief, temperature chart

• <u>Problems</u>:

Wastes a lot of wine; requires manual temperature compensation; messy; difficult to maintain optimal sanitation

- Refractometry is an alternative approach to measuring both the %sugar and %alcohol in a solution
- <u>Problem</u>:

As fermentation progresses, the drop in %sugar causes a decrease in the refractive index of wine; while the accumulation of alcohol causes an increase (Ambiguity)



As fermentation progresses, the depletion of sugar and the accumulation of alcohol "push" the refractive index of wine in opposite directions.

If this process could be accurately "modeled", then a refractometer could be used in lieu of a hydrometer to monitor the progress of fermentation.

Refractometer Approach (<u>The Model Equations</u>)

%estimate SG using current (rbrix) and original brix (obrix) readings sg=1.001843-(0.002318474*obrix)-(0.000007775*(obrix^2))

- (0.00000034*(obrix^3))+(0.00574*(rbrix))+(0.00003344*(rbrix^2))
- + (0.00000086*(rbrix^3));

%compute and apply temperature correction to SG estimate tcorr=1.313454-(0.132674*tempf)+0.002057793*(tempf^2) -(0.000002627634*(tempf^3)); sgc=sg+(tcorr*0.001);

%estimate true brix using temperature corrected SG value tbrix=-676.67+(1286.4*sgc)-(800.47*(sgc^2))+(190.74*(sgc^3));

Notes

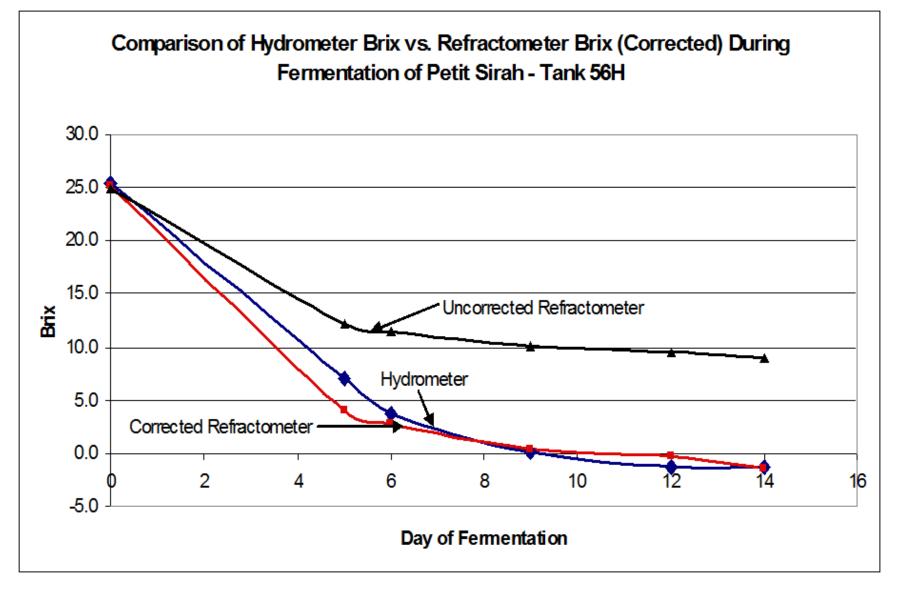
These equations are used in the spreadsheet implemented by ValleyVintner.com and can also be found at <u>http://www.primetab.com/formulas</u>.

 Record Initial Brix (Prior to pitching yeast)

- Draw a few drops of wine using sanitized pipette
- Read Refractometer Brix
- Enter reading into computer spreadsheet.
- Computer model estimates true Brix & S.G.







Source: Barry Gump, "Tips for Small Winery Labs"

- Accurate
- Fast
- Less clean-up
- Optimal sanitation can be maintained
- Verify finish with residual sugar test (Just like with hydrometry)

<u>Spreadsheet available from</u>: <u>http://valleyvintner.com/Refrac_Hydro/Refract_Hydro.htm</u>

<u>Refractometer Fermentation Tables available from</u>: <u>http://www.moundtop.com/fermentation/RBRIX-Fermentation-Tables.pdf</u> (No computer/spreadsheet needed if Tables are used)

Residual Sugar

Residual Sugar (RS)

Definition

The concentration of sugar remaining after fermentation is allowed to "finish".

- A "dry" table wine will finish with 0.1-0.3% RS
- It's considered to be "dry" because the residual sugars are non-fermentable (i.e., pentose sugars)

Residual Sugar

Categories of Wine Sweetness

| Dry White | 0.1 – 0.2% | 1-2 g/L |
|-------------|------------|-------------|
| Dry Red | 0.2 – 0.3% | 2-3 g/L *** |
| Off-Dry | 1.0 – 3.0% | 10-30 g/L |
| Sweet | > 3% | > 30 g/L |
| Port/Sherry | 5-15% | 50-150 g/L |
| Dessert/ | 10-20% | 100-200 g/L |
| Ice wines | | _ |

Risk of Refermentation in the Bottle

- If fermentable sugars (~0.5% or greater) and yeast remain in your wine, a second fermentation is likely to occur (Unexpected fizzy, yeasty wine upon opening).
- Viable yeast populations in "finished" wine are highly variable and require careful microscopic analysis to quantify (Usually unavailable to the small winemaking operation).
- <u>Filtration at 1 micron (or smaller; absolute) is necessary to</u> remove 99% of viable yeast. This is difficult to achieve without expensive filtration equipment.

Accurate Measurement of Residual Sugar Level

- The estimates of sugar remaining at the end of fermentation obtained via hydrometer or refractometer are NOT ACCURATE ENOUGH for the determination of trace amounts of residual sugar that could lead to an unwanted refermentation.
- <u>Clinitest Tablets</u> (developed for testing the sugar content of urine in diabetics) provide a fast, inexpensive and accurate means for measuring residual sugar levels of wine. The tablets contain copper and self-heating compounds that react with sugar. The <u>color of the product produced</u> by this reaction is related to the amount of sugar in the wine sample.
- Precision level = 0.1% RS

Clinitest Procedure

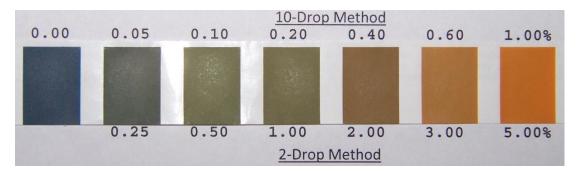
• <u>Apparatus</u>: Clinitest tablets, large-format test tube, eye dropper, Clinitest color chart (,distilled water).

<u>Procedure</u>:

- 1) Add 10 drops (0.5 ml) of wine sample to a test tube
- 2) Drop 1 Clinitest tablet into the same test tube.
- 3) Observe heat-producing reaction and wait for it to finish. (Gently shaking in circular motion) (Caution: HOT)
- 4) Match final color of test tube contents to <u>Clinitest color</u> <u>chart</u> to determine %sugar level.
- (If brownish "pass thru" occurs the %sugar exceeds 1% and you must retest using a 1:5 dilution)

Clinitest Procedure

Clinitest Color Chart (Facsimile)



<u>Warning</u>: Don't use photocopied, scanned or online copies of the Clinitest chart since the colors will probably not be accurately reproduced. An accurate chart is supplied with each bottle of Clinitest tablets.

See <u>http://www.moundtop.com/sugar/ResidualSugar-procedure.pdf</u> for details.

Potassium Sorbate Stabilization of Sweet Wines

- If residual sugar exceeds the "dry" level, any viable yeast cells remaining in the wine can be inhibited using <u>sorbic acid</u>.
- Obviously, "back sweetened" wines will need to be stabilized with a yeast inhibitor also.
- Amateur winemakers can add sorbic acid to their wine via a granular white compound called <u>potassium sorbate</u> (aka K-Sorbate).
- <u>Sorbic acid does NOT kill viable yeast cells</u>. Instead, it <u>INHIBITS their reproduction</u> by interfering with their ability to "bud off" daughter cells.
- Sorbic acid does not kill most forms of bacteria. Hence, it is NOT A SUBSTITUTE FOR FREE SO₂

Potassium Sorbate Stabilization

- The amount of potassium sorbate needed to inhibit yeast reproduction depends upon several factors, including pH and %alcohol level.
- Increases in pH from 3.0 to 3.7 are accompanied by a reduction in the proportion of "molecular" sorbic acid from 98 to 93%, respectively.
- Hence, the <u>role of **pH** can be ignored for wines with pH <= 3.7</u>

Potassium Sorbate Stabilization

The amount of molecular sorbic acid available for yeast inhibition increases significantly as **%alcohol** increases from 10 to 14%. Hence, the minimum required sorbate dosage is highly dependent upon the level of alcohol.

| Alcohol | Sorbic Acid Req'd |
|---------|-------------------|
| (%) | (mg/L) |
| 10 | 150 |
| 11 | 125 |
| 12 | 100 |
| 13 | 75 |
| 14 | 50 |

(Source: Peynaud, 1980)

Potassium Sorbate Dosage

- K-Sorbate contains **74% sorbic acid** (by weight) when dissolved in water.
- K-Sorbate req'd (mg) = (Sorbic acid req'd (mg/L) * gallons of wine * 3.785 L/gal) / 0.74
- The sensory threshold ("bubble gum") for sorbic acid is approximately 150 mg/L (Margalit, 1996).
- Legal max. = 300 mg/L.
- <u>Caution</u>: "Geranium leaf" fault if MLF occurs in a sorbated wine.
- <u>Warning</u>: Avoid the use of "Wine Conditioner" products (sugar confound; limited shelf-life)

K-Sorbate Case Study

Clinitest assessment of a **10 gallon** batch of white wine reveals that it has **0.7% residual sugar**. The %alcohol of the wine, based upon "potential alcohol" calculated from the prefermentation Brix level, indicates that the wine contains **11% alcohol** by volume. How much potassium sorbate must be added to this wine to inhibit a secondary yeast fermentation?

<u>Step 1</u>.

Minimum sorbic acid requirement for 11% alcohol is 125 mg/L. (See Table)

<u>Step 2</u>.

K-Sorbate (mg) = (125 mg/L * 10 gallons * 3.785 L/gal) / 0.74 = 6395 mg

<u>Step 3</u>.

Dissolve 6.4 g of potassium sorbate in a small amount of water and thoroughly stir into wine.

Titratable Acidity

Titratable Acidity (Why is TA useful to know?)

- Guides harvest decision-making.
- Dictates compatible wine "styles".
- Determines if must treatment is required prior to fermentation.
- Diagnose "unplanned" MLF during bulk aging.

Note:

TA should never trump sensory evaluation!!!

Titratable Acidity (Amount of Acid in Wine)

- Grapes contain significant amounts of acid
- Tartaric and malic acid account for 90% of TA
- Acid concentration of grapes varies from 4-16 g/L

Less than 6 g/L typically tastes flat/flabby

Greater than 9 g/L typically too tart

Acidity Titratable

- Low acid wines can be augmented by the addition of tartaric acid.
- Best to add tartaric acid before fermentation.
- Most wines can tolerate an addition of 1-2 g/L before developing a "manipulated" flavor.

Acidity Titratable

- High acid wines are much more difficult:
- Best controlled in the <u>vineyard</u> (e.g., hang time)
- Modest adjustment via <u>calcium carbonate</u> prior to fermentation (also: *Acidex*; *Sihadex*)
- Moderate post-fermentation reductions <u>MLF</u> (1-2 g/L) <u>Potassium bicarbonate (1-2 g/L)</u>
- <u>Yeast</u> selection (Malic acid metabolizing)
- <u>Blending</u> with low acid base wine

Relationship between TA and pH

- Wine TA and pH are "loosely" coupled.
- High TA tends to be related to low pH.
- High pH/High TA grapes are not all that uncommon in some regions/harvests (e.g., cool nights; rain just before harvest).
- pH decreases accompanying tartaric acid addition are <u>highly unpredictable</u> (due to complex chemical buffering).
 BENCH TRIALS ARE ABSOLUTELY NECESSARY!

Logic of TA Titration Procedure

- Measure a small wine sample (e.g., 5 ml)
- Add <u>sodium hydroxide</u> (NaOH) base solution to the wine until the acid is "neutralized" (<u>pH=8.2</u>)
- 2 molecules of NaOH (OH⁻ ions) are required to neutralize one molecule of tartaric acid (2 H⁺ ions)
- Concentration of tartaric and/or malic acid can be accurately estimated by the <u>volume of NaOH</u> <u>needed to neutralize the wine sample</u>

TA Calculation

TA (g/L) = (ml NaOH)(N NaOH)(mol. wt. H₂T)(mol H₂T/equiv)

(ml Wine Sample)

<u>Given</u>:

NaOH concentration = 0.1 N (equivalents/L) mol. wt. tartaric acid $(H_2T) = 150$ g mol H₂T per equivalent NaOH = 0.5 volume of wine sample = 5 ml

TA (g/L) = (ml NaOH) (0.1 NaOH eq/L)(150 g/mol)(0.5 mol/eq)

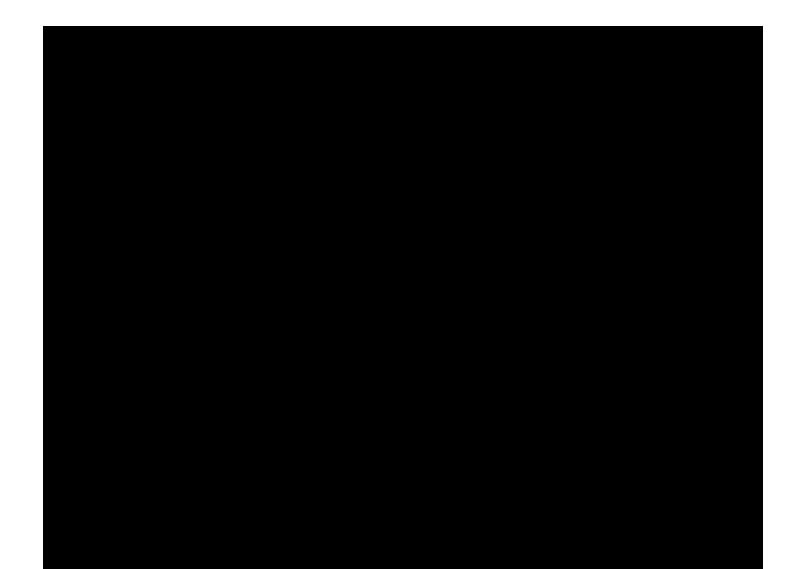
(5 ml Wine)

TA (g/L) = (ml NaOH) * 1.5

[Simplified Formula]

%TA (g/100ml) = TA/10

Titration Procedure Video



Tartrate Instability

- The solubility of tartaric acid in wine varies dramatically with changes in temperature and %alcohol.
- Solubility decreases as temperature falls.
- Solubility decreases as %alcohol increases.
- As a result of the increase in %alcohol following fermentation, many wines become <u>supersaturated with tartaric acid</u>. This condition leads to "tartrate instability".

Tartrate Instability

- Supersaturated tartaric acid will eventually "fall out" of solution.
- Formation of unsightly (but harmless) sediment of yellowish or reddish crystals composed primarily of potassium <u>bitartrate</u> (KHT) (a product of tartaric acid chemistry)

How can the winemaker avoid the precipitation of bitartrate sediment in their bottled wine?

Cold Stabilization

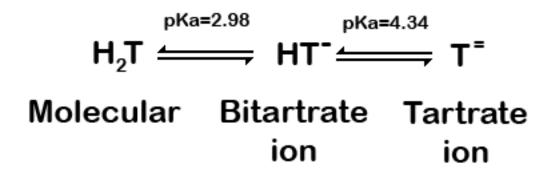
- Some of the excess bitartrates can be "coerced" out of the wine (prior to bottling) by reducing the temperature of the wine to just above the freezing point (e.g., 25° F) and holding it there for about 2 weeks.
- Chilling the wine significantly reduces the solubility of the bitartrates and forces them to precipitate in the tank/carboy (rather than in the bottle). Followed by racking/filtering.

Effects of Cold Stabilization on pH

- If the wine pH > 3.65
 Cold stabilization causes an <u>increase in pH</u>.
- If the wine pH < 3.65
 Cold stabilization causes a <u>decrease in pH</u>.
- How can this be?

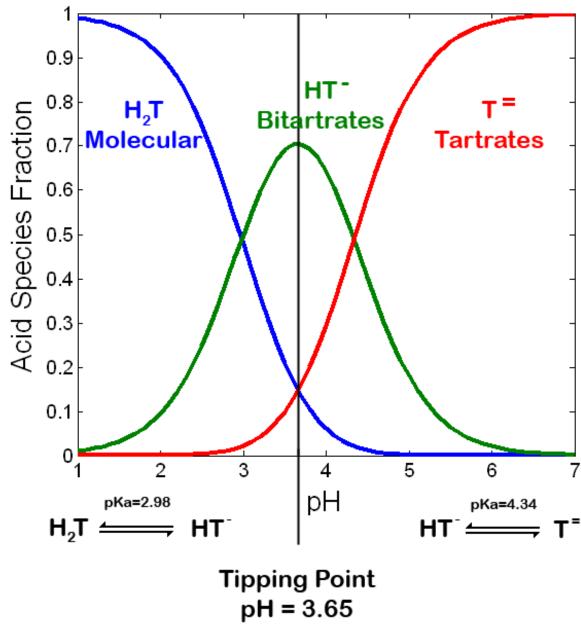
Effects of Cold Stabilization on pH

- To explain the bidirectional influence on pH we'll need to do a bit of "heavy lifting"
- We'll begin with the equation describing the equilibrium of various "species" of tartaric acid:



Now let's see a graphical display of this relationship...

Distribution of Tartaric Acid Species: Molecular, Partially and Fully Dissociated Ions



- Cold causes Bitartrates to precipitate out
- Chemical reactions work to maintain equilibrium

When **pH < 3.65** the dominant equilibrium reaction converts H_2T to HT^- Each such conversion adds a free H⁺ ion to wine (Decreasing pH)

When **pH > 3.65** the dominant equilibrium reaction converts $T^{=}$ to HT^{-} . Each such conversion consumes a free H⁺ ion (Increasing the pH)