"pH and Wine quality"

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Wine acidity. pH

Acidity

- All the acid substances from must and wine
- titratable acidity, volatile acidity, pH
- content of dissociated and undissociated acids
- buffer capacity of each of the different acids.

Total acidity

- (inorganic e.g. phosphoric acid and organic including amino acids)
- estimation with NaOH solution
- important for the state of tartaric and malic acid
- both dicarboxylic acids partially dissociated
- pK values (50% of the hydrogen ions are dissociated)
- 3.04 and 4.34 for tartaric acid
- 3.46 and 5.1 for malic acid.

TA

- A high TA is 1.0% too tart and too sour for consumption
- A low TA, say 0.4%, in flat tasting wine
- red wines are about 0.6%
- white wines are usually a little higher

Titratable acidity

- determined by neutralization NaOH colored reagent (e.g. phenolphthalein)
- pH-metry, potentiometry
- neutralization of all titratable acids (excluding CO_2 and free and combined SO_2)
- usually expressed as tartaric acid (g/L) or as sulfuric acid in France
- repeatability ??? great amounts of colored or suspended matter

pH

pH depends on three main factors:

- the total amount of acid present,
- the ratio of malic acid to tartaric acid, and
- the amount of potassium present

- little acid and excess potassium show high pH values.
- more tartaric acid, less malic acid, less potassium and more titratable acid has lower pH values
- pH values range from 2.9 to 4.2 (preferable 3.0 to 3.5)

Low pH

- inhibits bacteria
- sugar fermentation progress more evenly
- malolactic fermentation easier to control
- direct influence on the hot stability of wine (protein precipitates)

Protein stability

- isoelectric point, or isoionic point, of the protein (pH, the positive and negative charges are equal and the protein is least soluble)
- isoelectric properties influence: their natural tendency to precipitate and affinity to be removed with various agents
- difference between the juice or wine pH and the isoelectric point of the protein fraction has to be maximum

Bentonite treatment

- removes excess protein
- pH increases, bentonite is less effective (add larger amounts)
- too much bentonite because it can strip wines of their unique aromas and flavors

- Hydrating bentonite - hot water - pH-adjusted 3.0
- reduction in viscosity of the bentonite slurry may aid in its dispersement
- lowered pH is an aid in preventing biological growth within the bentonite slurry.
- water that has a low mineral content should to avoid bentonite clumping
- dissolved minerals (cations) detrimentally affect the hydration, the viscosity, and the binding ability - discussion!

Effects of pH levels on wine quality

Wine Characteristic	**Low pH (3.0 - 3.4)**	**High pH (3.6 - 4.0)**
Oxidation	Less	More
Amount of color	More	Less
Kind of color	Ruby	Browner
Yeast Fermentation	Unaffected	Unaffected
Protein Stability	More stable	Less stable
Bacterial Growth	Less	More
Bacterial Fermentation	Less	More

- pH “Classical” measurements in the must
- A pH electrode gets dirty very rapidly when measuring the pH of must
- Sediments deposit on the sensitive pH measuring bulb and on the pH electrode junction
- A dirty pH electrode can give inaccurate results that are up to 0.5 pH

Volatile acidity

- VA comprises mainly acetic acid
- lesser quantities of butyric, formic and propionic acids
- vinegary edge to the wine 1.5 g/L of acetic acid
- smell appallingly of nail varnish 250 mg/L ethyl acetate.

- not possible to make a wine without any VA
- normal fermentation, wine yeast S. cerevisiae produces up to 100 mg/L acetic acid.
- under high sugar conditions higher levels acetic acid
- Lactic acid bacteria, produce small amounts of acetic acid.
- if alcoholic fermentation stops then this potential for acetic acid production is greatly increased

- concomitant formation of other, sometimes unpleasant, aroma compounds (see ethyl acetate and acetaldehyde)
- These compounds have much lower sensory threshold than acetic acid—both acetaldehyde and ethyl acetate are detectable at less than 200 mg/L in wine
- both acetic acid and acetaldehyde are toxic to Saccharomyces cerevisiae and may lead to stuck fermentations.

Acetic acid

- Volatile acidity refers to the steam distillable acids present in wine, primarily acetic acid but also lactic, formic, butyric, and propionic acids.
- The average level of acetic acid in a new dry table wine is less than 400 mg/L, though levels may range from undetectable up to 3g/L.
- **U.S. legal limits of Volatile Acidity:**
  - Red Table Wine 1.2 g/L
  - White Table Wine 1.1 g/L
- The aroma threshold for acetic acid in red wine varies from 600 mg/L and 900 mg/L, depending on the variety and style.

Origins of acetic acid

- Sulfur dioxide, which is usually present in wine, can chemically trap acetaldehyde, causing an accumulation of this intermediate at the expense of its further oxidation to acetic acid
- Ethanol concentrations above 10% become increasingly inhibitory to the growth of acetic acid bacteria and their ability to oxidize ethanol.
- The optimum pH for ethanol oxidation by acetic acid bacteria appears to be *ca* pH 5.0, but substantial activity has been reported in the range.

Origins of acetic acid

- Acetobacter aceti - able to convert both glucose and ethanol to acetic acid
- Yeast found in the vineyard - Kloeckera, Hansenula, and Metschnikowia - are able to produce large amounts of acetic acid and ethyl acetate early in a fermentation
- Most lactic acid bacteria will produce acetic acid from glucose if they are present when there is still significant amounts of sugar
- Brettanomyces is a strong producer of acetic acid.

Origins of acetic acid

- *Acetobacter aceti* and *Acetobacter pasteurianus* completely oxidizes lactic, pyruvic, and acetic acids via the tricarboxylic acid (TCA) cycle
- optimum pH for the oxidation of organic acids by acetic acid bacteria *ca* 6.0, there - this metabolism can still operate in the pH range 3.5 to 4.0
- Decarboxylation of amino acids to amines and the degradation of proteins to amino acids

Sulfur

the level of molecular sulfur dioxide varies with pH

pH of wine	% of free SO_2 in molecular form
3.0	6.0
3.2	4.0
3.4	2.5
3.6	1.5
3.8	1.0
4.0	0.6

-The level of molecular sulfur dioxide needed to stop bacterial growth and prevent any oxidation is at least **0.6ppm**

the level of free SO_2 needed to give **0.8ppm** molecular SO_2

pH	Free SO_2
3.0	13
3.1	16
3.2	21
3.3	26
3.4	32
3.5	40
3.6	50
3.7	60

recommended:

- 14% alcohol minimum of 0,6 ppm molecular SO_2
- 12% alcohol minimum of 0,8 ppm molecular SO_2

White wines

- pH 3.0 - 3.2 10 to 20 ppm free SO_2
- pH 3.2 - 3.4 20 to 30
- pH 3.4 - 3.5 30 to 50

Red wines

pH 3.4 – 3.6 10 to 20 ppm free SO_2
or
50 to 150 ppm total SO_2

Organic acids

- main acids in grapes are tartaric, malic, citric, gluconic, keto-guconic, mucic, coumaric and caffeic
- D-tartaric acid (Ta.A) and L-malic acid (MA) 90% or more of the total acids (TA)
- ratio depends mainly on the environment
- no significant difference among the top six cultivars (Merlot, Cabernet Sauvignon, Shiraz, Chardonnay, Pinotage, Sauvignon blanc)
- ratio of Ta.A to MA can range from 0,6 to 3,4 the bigger values lead to a better quality

- after veraison, malic acid decreases strongly - its production ceases while respiration increases
- tartaric acid decreases only slightly due to dilution and some conversion of the free acid to salt forms (calcium rather than potassium)
- Tartaric precipitation induces a decrease in the buffering capacity of wine
- bitartrate stabilization induces a decrease in the total acidity with a lowering of the pH ranging from 0.05 to 0.15

Tartaric acid

- found in almost no fruit but the grape and here it is the predominate acid
- in German it is called Weinsaure or “wine acid”
- contributes to a wine's color, aseptic stability and taste
- non-grape wines are made with raisins or grape juice
- unripe grapes 15g/L, Must (north) 6g/L, (south) 2-3g/L

Malic acid

- fruit acid (in German is named Apfelsaure or “apple acid”)
- found in apples and other fruits. It is also found in plants - anion malate, key intermediate in Krebs cycle located in the cells' mitochondria
- one of the most widespread acids among the many fruits and vegetables from which wines are made

- juice of green grapes, before the color change, more than 20 g/l malic acid
- warmer climates (1–2 g/l) in the ripened fruit
- cooler climates (4 – 6.5 g/l)
- excess - "greenish," reducing MA is"toning down" or "smoothing out"
- 20-30% is respired during fermentation.
- If still too much malic, a malolactic fermentation MLF can be encouraged
- MLF can reduce malic and increase lactic by a factor of five

Lactic acid

- milder in taste than malic
- two-edged sword:
  - mild sour taste counteracts the harsher tartness of malic,
  - it can invite infection by certain lactic bacteria that produce odors suggestive of spoiled milk or sauerkraut.
- some winemakers dissuade MLF with the same vigor that others invite it

Sugars. BRIX

- Both the Brix and Balling scales, Australia and the USA
- describe the percentage of the grape juice accounting for by dissolved solids
- Juice 18º Brix - the solids (of which 90% are sugars) account for 18% of the solution.
- nothing to do with percentage of alcohol that may be achieved with fermentation, although this is described by the Baumé scale.

Conditions

- sugar (^{0}Brix) is perhaps the most important parameter
- pH above 3.6 are potentially unstable
- Sugar/acid ratio and total acidity are also important
- Generally (California standards)
  - white wine 19-23 Brix, $\geq$ 0.7% acidity , and pH $\leq$ 3.3.
  - red wine grapes are 20.5-23.5 Brix, $\geq$ 0.65 % acidity, and pH $\leq$ 3.4
- minimum of 15 Brix for processing.

Experimental criteria

- the product of the Brix value times the square of the pH is in the range of 220 to 260
- For example, a 22º Brix juice at pH 3.2 would yield a value of 225.3
- Late harvest fruit at a higher pH (24ºBrix at pH 3.6, for example) would yield a value (311) outside of this range

BRIX and alcohol

- multiplying the degrees Brix of red musts by about 0.55 and white juice by about 0.60
- E.g. white wine produced from 22º Brix juice is about 0.60x22 = 13.2% alcohol (if fermented to dryness)

TA and sugar level.

- the Brix value divided by the TA (g/100 ml tartaric acid equivalents) should yield a number around 30–32 for table wine production
- For a juice at 22ºBrix with a TA value of 0.8, the number obtained would be 27.5
- For a 24ºBrix juice or must, the TA value could not drop much below 0.8
- Other authors suggest that this value can be higher (37–38) for late harvest fruit

Potassium

- Its concentration in wine ranges from 200-2000 mg/L
- All wines differ in their "holding" or retention capacity for tartrate salts in solution
- If the holding capacity is exceeded, these salts will precipitate "tartrate casse“
- Solubility dependent primarily upon the alcohol content, pH, the temperature of the wine, and the interactive effects of various cations and anions
- The percentage of tartrate present as potassium bitartrate (KHT) is maximum at pH 3.7

Anthocyanins

- red pigments in grape skins, important role in the colour of wine
- in equilibrium at wine pH, with only 25% or less in the red, flavylium form
- SO_2 forms a colourless bisulphite addition compound with the flavylium ion - reaction is reversible
- color of young red wines is entirely due to the monomeric grape anthocyanins
- polymeric pigment forms in aged red wines - progressive decline in the amount of anthocyanins

- In wine at pH, (3.0 - 3.8), oak lactones exist almost entirely in the aroma-active lactone form
- High pH the open chain form of the *cis*-isomer lactonised relatively slowly
- wines treated with oak chips or shavings continue to develop “oakiness” by additional formation of *cis*-oak lactone once the chips or shavings are removed.