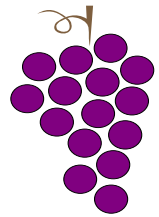

Acidity in Wine

- Measurement
- Adjustments
- Wine balance

By
Jacques Mercier

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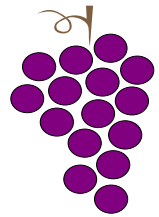

1 - Definitions:

- ***pH*** *(hydrogen potential)*: log [1/H^+], where [H^+] is the concentration of hydrogen ions in the wine coming from dissociation of acids in water/wine:

  $H_2A \Leftrightarrow H^+ + HA^-$ (note that $\Delta pH = 1 \Rightarrow \Delta[H^+] = 10$)

- ***Acid Strength***: How much an acid dissociates in water/wine. Strong acids (sulfuric) dissociate more (i.e., produce more [H^+] or decrease pH more) than weak acids (organic acids in wine).

- ***Buffer capacity***: resistance to pH change from acidity change.

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1 – **Definitions** (cont.'d):

- ***Total Acidity***: Sum of all organic acids contained in wine (mainly tartaric, malic and a bit of citric from grapes, as well as acetic, lactic, succinic & carbonic from fermentation) and their salts (e.g., tartrates).

- ***Titratable Acidity*** *(T.A.)* = $[H^+] + [HA^-]$, or portion of total acidity which can be neutralized by a strong base (NaOH in this case). T.A . is smaller than total acidity because part of the total acidity is neutralized by potassium (e.g., potassium bitartrate)

- ***Units:*** % or grams per liter (g/L).
  0.1% = 1 g/L.

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2 - How are Acidity and pH related ?

a) **Formal Relationship** (derived from theory):

- Simple part of relationship:
  Increase in acidity ⇔ Decrease in pH
- Complex part of relationship:

T.A. ⇔ **Buffering** ⇔ **pH**

Buffering depends on:

- *Total acidity (↑)*
- *Potassium concentration (↑)*
- *Acid mix (Tartaric > Citric > Malic > Lactic > Acetic, in terms of acid strength)*
- *Alcohol (↓)*

The higher the buffering the less the pH will decrease when adding acid.

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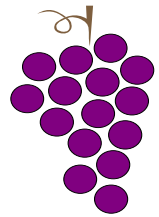

2 - How are Acidity and pH related ? (cont.'d)

b) Empirical Relationship (derived from observation/experiments):

- Calibrate an eye-dropper (how many drops does it take to collect a know volume, 5ml for example) => Divide by number of drops to get volume per drop.

- Knowing that 2.5mg tartaric acid will increase acidity of 25ml of wine by 0.1g/L, you can mix an acid solution for which each drop contains 2.5mg tartaric acid.

Example: If measured volume of a drop is 0.05ml, then the concentration of such a solution to be mixed would need to be 50g/L (2.5mg divided by 0.05ml) => Dissolve 5g tartaric acid into 50ml d.w. , then bring volume up to 100ml.

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2 - How are Acidity and pH related ? (cont.'d)

b) Empirical Relationship (derived from observation/experiments):

- Put 25ml wine in a container (wine glass), successively adding one drop of the the solution (to increase the T.A. by 0.1g/L each time). Measure the pH after each drop and this will give you an empirical relationship between T.A. and pH (how much acid is needed to decrease pH by a know amount) for this particular wine in that pH range. Typical values are: ΔT.A.=1g/L => ΔpH = 0.1 for tartaric and 0.08 for malic/citric, but need to be measured as above so as to not add too much acid.

Note: It is also recommended to evaluate the taste impact (increased tartness) of adding acid to decrease pH by filling more than one sample wine glass and adding 1 drop in the 1st glass, 2 drops in the 2nd glass, etc., and then compare the taste of each glass.

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3 - Does tartness taste depend on T.A. and/or pH ?

a) Definition refresher:

$[H^+] + [HA^-] \Rightarrow$ T.A.

$[H^+] \Rightarrow$ pH

b) For weak acids in wine: $[HA^-] \sim 100 \times [H^+]$

c) Control tasting experiments have shown that the impact of increasing $[H^+]$ on tartness is about 10 times the impact of increasing acidity.

d) Combining b) and c) => Tartness depends mostly (~90%) on acidity and a little bit (~10%) on pH

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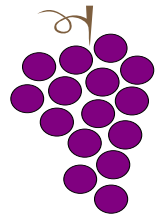

4 - Desirable T.A. and pH ranges:

a) **Red Wines**:
pH: 3.3 - 3.8 and T.A.: 5-7 g/L

b) **White Wines**:
pH: 3.1 - 3.4 and T.A.: 6-9 g/L

5 - Reasons for adjusting pH and acidity

a) **First**: To adjust tartness of wine, either up or down depending on desired style.

b) **Second**: To bring the pH down to a value where reasonable amount of SO2 (i.e., below tasting threshold of 40-50ppm FSO2) can be used to stabilize the wine from undesirable chemical and microbial change and allow it to age gracefully.

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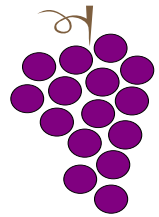

6 - Effect of various wine acids on pH:

- The order in which wine acids will decrease pH is as follows:
  Tartaric > Citric > Malic > Lactic

- Less tartaric acid is needed to reduce the pH than other acids
  Useful if goal is to reduce pH for stability reasons, while increasing tartness as little as possible.

-ML Fermentation (malic => lactic) will increase pH (& VA).

- More citric or malic acid needs to be added than tartaric acid to obtain same pH decrease. Since ML consumes 50% of the added malic acid and can convert some of citric acid into acetic acid, these should preferably be added after ML completion or only if ML has been inhibited. So, beware of adding before ML the infamous "acid blend" (tartaric/malic/citric in 1:1:1 proportions) still found in some winemaking supply stores.

7 - Effect of potassium bitartrate precipitation on pH

-Tartaric acid is the only acid which will precipitate (as potassium bitartrate) during fermentation. Useful if goal is to lower pH without increasing tartness as much. So, it is preferable to add tartaric acid before fermentation because even more can be added to decrease the pH without increasing the tartness of the finished wine as much as other acids.

Since precipitation also reduces potassium, an even greater pH reduction is achieved by reducing the buffering capacity.

7 - Effect of potassium bitartrate precipitation on pH (cont.'d)

Cold stabilization (T=26oF for a few wks) will also reduce tartaric acid (and potassium) level via potassium bitartrate precipitation. If pH > 3.65 already, pH will increase during cold stabilization, as expected (less acid => higher pH). However, if pH < 3.65 already, pH will actually decrease. Useful if goal is to decrease acidity and pH at same time, such as in high pH / high acid wines (high potassium &/or high malic wines). pH must be decreased < 3.65 first for this to work.

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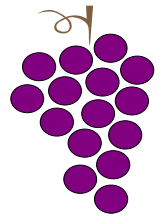

Acid Measurements: Titration

Principle:

Add an alkaline acid neutralizer (NaOH, a base) to a known wine volume sample, until acid in wine is neutralized (see end point below). NaOH volume required for neutralization is recorded and gives a measure of the acid content in wine.

Make sure to mix wine must or juice well before taking your sample.

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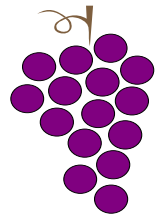

Acid Measurements: Titration (cont.'d)
Base (NaOH):

Shelf life and storage: very sensitive to air. Store bulk of quantity in an evacuated bottle, in fridge. Pour what you need for each measurement session in a smaller bottle.

Strength of store bought varies widely (anywhere from 60% to 120% full strength) either from inadequate storage or error in mixing.

Note: *Above can be substantial sources of error.*

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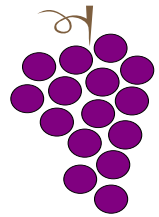

Acid Measurements (cont.'d) : Titration

Base (NaOH):

Calibration of NaOH solution:

- Mix your own NaOH solutions (m.w.=40, so 4 g/L => 0.1N, use dist.w.),
  and/or
- Before every measurement session, calibrate your NaOH solution with a very stable acid standard of a known concentration:
  - Potassium acid biphthalate (20.4 g/L => 0.1N).
  - Tartaric acid (6 g/L) (but is not as stable over long range)
- Use calibration factor to correct result. Factor will slowly decrease with time (i.e., you will need more and more NaOH to titrate same acid strength).

Solves most inconsistency problems.

For fermenting wine (i.e., carbonic acid from CO2 increases reading):
Boil sample (mw oven) or evacuate sample (measure sample before boiling).

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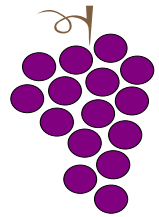

Acid Measurements (cont.'d) - **Titration End point:**

Colour indicator (phenolphthalene) --> Turns red when acid is neutralized and solution becomes alkaline. Works well for whites, but more difficult with red wines.

Note: It is OK to dilute red wine in distilled water to see red wine end-point (red to dark blue) better (amount of acidity titrated is not change by adding water, but mixing is slower => need to agitate more).

pH meter: End point reached as pH = 8.2. Very accurate, but need to add NaOH more slowly and agitate more (stirrer) to allow pH meter to Follow. Beware, pH changes really fast as you approach 8.2 (a single drop of NaOH makes a difference).

Note: For pH meter calibration, buy pre-measured 0.3 & 0.7 standards powder then dilute in 100ml (incl. powder vol.) distilled water (much cheaper). Use bottle rinser of each standard to rinse probe before immerging into respective standard (eliminates cross-contamination creep of standards). Leave probe in ph = 3.0 standard between measurements to monitor drift and correct for it.

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Titration Formula

C_{sample}	N_{NaOH}	Vs (mL)	C_{sample}
$g/L = \frac{75 \times V_{NaOH} \times N_{NaOH}}{V_{sample}}$	0.1	10	$g/L = 0.75 \times V_{NaOH}$

C_{sample} for V_{NaOH} = 10ml (Full Scale)	NaOH Solution	KHP Solution
7.5 g/L	**For 0.1N:** 3g of NaOH in 750mL.	**For 0.1N**: 7.66g of KHP in 375mL or 10.21g of KHP in 500mL

N (normality): Mass of acid or base that can accept or donate exactly one mole of protons (H + ions):
For NaOH, it is the gram equivalent weight (molecular weight - 40) per liter of solution.

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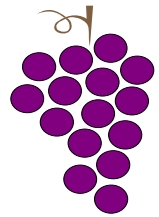

Acid adjustments

Targets:

	Malolactic Fermentation ?	Must/Juice	Wine
Reds	Yes (most, if too acidic)	7.5-8.5 g/L	6.5-7g/L
	No (Gamay, low acidity red)	7-8 g/L	"
Whites	Yes (mostly Chardonnay)	8-9 g/L	~7 g/L
	No (most)	8-9 g/L	7-7.5 g/L

When to adjust

Before vs After fermentation

Before --> Coarse adjustments (> 1 g/L).
--> Ideal time (best integration).

After --> Fine adjustments (<1 g/L).
--> Can taste layered if too much.

Musts (reds) vs juices (mostly whites)

Must --> Final volume not known before pressing (depends on yield)
--> Proceed with caution (see below).

Juices --> Straightforward (final volume already known).

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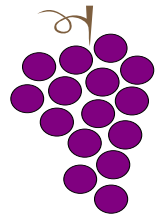

Acid adjustments

Not enough Acid *?*

Right kind of acid:
Tartaric --> most reds/whites.
MalicTar. (50/50) --> German (Riesling, Gewurz), Gamay.

Addition procedure:
For juices (mostly whites): just measure and add required quantity.
For red musts (two-part addition procedure):

Measure acidity.
Add half of required quantity and **mix well.**
Remeasure and recalculate how much acidity has changed from 1st half of addition, then recalculate 2nd half.
Add rest and mix well.

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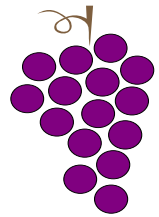

Acid adjustments

Too much Acid ? Reduce by (in order of ease):

Alcoholic Fermentation (decr. by 0.5-1.0g/L).

Cold stabilization (reduces tartaric acid by ~0.5g/L, also reduces potassium concentration):
Put in fridge for 2-3 weeks @ about 28oF, then rack cold (40-45oF).
Be careful when racking cold, because even if oxidation is slower, oxygen pick-up is much faster.

Malolactic fermentation:
Total acid reduction depends on malic acid present.
Adds complexity (for Chardonnay, sometimes Sauvignon Blanc, most reds, except low acid wines from hot climates or low tannin reds).
Reduces fruitiness (by decreasing malic acid).

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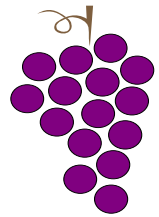

Acid adjustments

Too much Acid ? (cont.'d) Reduce by (in order of ease):

Add sugar, just enough to balance acidity.

---> Crucial to have enough acidity, otherwise the wine will taste cloying and lack structure, tasting like candy. Equally important for fruit wines. Perform test trial to determine best balance.

Carbonates:

Potassium (add to wine, decr. limit --> 3g/L, tartaric acid reduction only). If too much used --> can add saltiness to taste.

Calcium (add to must, mostly tartaric reduction, some malic, can be chalky, takes longer)

Ageing (e.g., acidic Riesling can age for 5-10 years before they smooth out, but then they can be absolutely superb !).

More Alcohol (i.e., increase starting sugar).

Acidex (complicated, but effective, removes both tartaric and malic equally).

Blending --> you can always blend with a more/less acidic wine.

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Flavor Perception:

	Location	Length
Sweetness	Tip of tongue	Immediate, but does not persist
Acidity	Side of tongue	Quick, lasts longer
Saltiness	Side of tip of tongue	Quick, lasts longer
Bitterness	Back of tongue	Slow, lasts the longest

Taste Interaction Matrix

	Acidity	Sweetness	Alcohol	Bitterness	Tannin
Acidity		-	+	+	+
Sweetness	-			-	-
Alcohol	-	+		-	-
Bitterness	+	-			
Tannin	+				
High Temperature	+	+ (whites)	+ (reds)		
Low Temperature	- (whites)	-			+ (reds)

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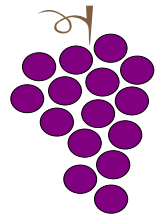

In words:

-Acidity decreases the perception of sweetness (and vice-versa):
Off-dry & dessert wine balance:
Too much acid => too harsh/sharp.
Too much sugar => cloying, sugary, flabby.

- Acidity perception is enhanced by tannins, so needs to be lower for reds than for whites, except for lower tannin red varieties, such as: Barbera, Pinot Noir, Gamay.
- The less tannic a wine is, the more acidity it can support (Barbera) or the higher a red wine is in tannin, the lower should its acidity be.
- The combination of high acidity and high tannins make for the harshest and most astringent wines (e.g., unripe Cab).
- Alcohol enhances the perception of sweetness (Port, Zin).
- As high alcohol "fruit bombs" age, the fruit declines and the perception of alcohol increases, making them poor aging candidates.

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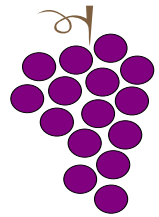

In words (cont.'d):

-A wine tolerates acidity better when its alcohol content is higher (e.g., Barbera, Pinot Noir, Gamay).
- More tannin is more acceptable if acidity is low and alcohol is high or, for a higher alcohol wine, low acidity is more acceptable when tannin is high (Petite Sirah).
- High Temperature:
  - Alcohol more apparent in red wines and tend to dominate more.
    - (poor summer temperature control in some restaurants)
  - Sweet white wines taste sweeter.
- Low Temperature:
  - Enhances tannin perception in reds (e.g., Victorian Xmas).
  - Makes sweet white wines taste dryer but more acidic.

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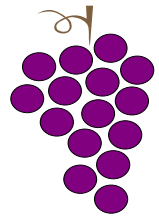

Useful links:

- **General lab supplies:**
  www.sciencelab.com,
  www.wine.awscientific.com
  www.labdepotinc.com
  www.cynmar.com
- **Scales:**
  www.americanweigh.com
- **Auto-leveling titration buret:**
  www.sciencelab.com/page/S/PVAR/10-208-20 (Part #10-208-22, 10ml & amber bottle)
- **pH meters (Hanna):**

  Portable: www.hannainst.com/usa/prods2.cfm?ProdCode=HI%2098113&id=002003

  Benchtop: www.hannainst.com/usa/prods2.cfm?ProdCode=HI%20222&id=002001

  Cleaning Solution for Wine Deposits: www.hannainst.com/usa/prods2.cfm?id=002001&ProdCode=HI%2070635L

  Cleaning Solution for Wine Stains: www.hannainst.com/usa/prods2.cfm?id=002001&ProdCode=HI%2070636L
- **pH buffer solutions capsules & envelopes** (to mix your own pH buffer calibration solutions):
  www.wine-testing-supplies.com/cat--pH-Buffers--pHbuffers.html
- **Sodium hydroxide pellets** (to mix your own titration solutions):
  www.sciencelab.com/page/S/PVAR/SLS4090
  www.wine-testing-supplies.com/item--Sodium-Hydroxide-Pellets-ACS-Reagent-250-5001--sodiumhydroxidepellets.html