Measurement of TA and pH

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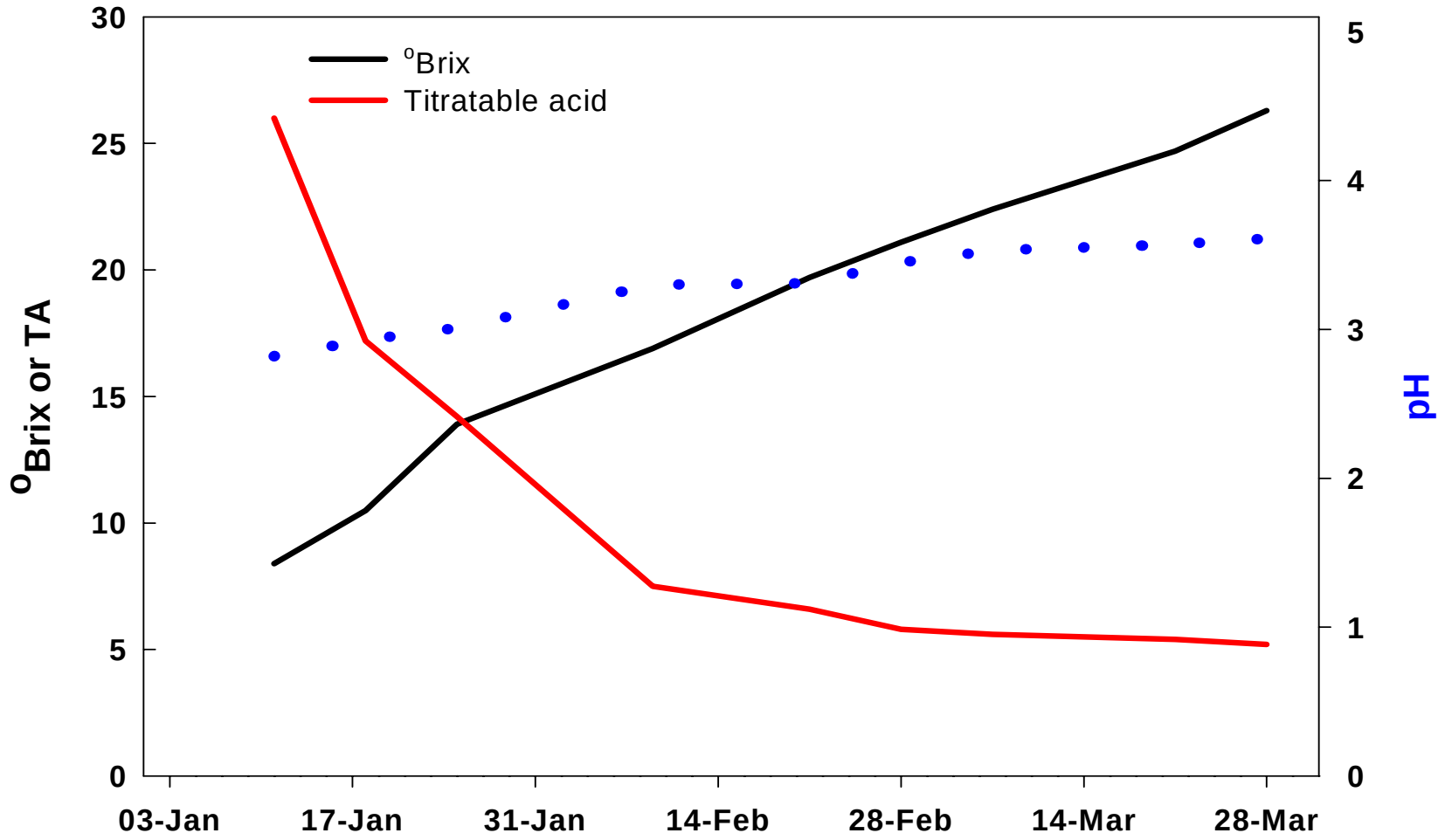
As °Brix rises, TA drops, pH increases



Why are acid & pH important ?

- Acid
  - Wine acidity to balance alcohol & residual sugar
- Importance of low pH in juice and wines
  - Increase antimicrobial action of SO2
  - Increase colour expression in young red wines
  - Selection of desirable micro-organisms
  - Enhanced clarification of juices and wines
  - Enhanced expression of fruit character
  - Promote balance of wine colour

What is pH & titratable acidity?

- pH – the equilibrium measure of hydrogen ion concentration in a juice or wine
- Titratable acidity measures the total amount of protons available in a juice or wine, and is expressed as g/L tartaric acid equivalent
- TA not to be confused with Total Acidity which is a measure of the Total organic acids in a juice or wine.

Acids found in grapes

ACID	COMMENTS
Tartrates: H_2T **(Tartaric acid)** KHT **(Potassium bitartrate)** K_2T **(Di-Potassium tartrate)**	Occurs naturally in grapes; strongest of natural acids; biosynthesis unclear Added during winemaking
Malic acid H_2M	Occurs naturally in grapes; declines post-veraison, lost in wine by MLF
Citric acid H_3C	Occurs naturally, but at very low level. Not an export additive.

Acids in wines

ACID	COMMENTS
Lactic acid, HL	Arises during MLF; minor yeast product
Acetic acid, HOAc	Produced by all yeast and some bacteria
Succinic, pyruvic acids	Very small amounts during alcoholic fermentation
Ascorbic acid	Added as an antioxidant
Carbonic acid	CO_2 in the wine
Sulphurous acid	SO_2 in the wine

+ acids in grapes

Acids in grapes

- **Primarily Tartaric & Malic acid**
- **Measured by determining the concentration of titratable hydrogen ions in juice**
  - **Depends on concentration of**
    - **tartaric acid and bitartrate**
    - **malic acid**
- **Usually expressed as g/l as tartaric acid**
- **Normally determined by titration with Sodium Hydroxide (NaOH) to a pH end-point of 8.2**

Not all acids are the same

- The strength of an acid determines the concentration of protons (H+ ions) released into solution
- Stronger acids release more protons into solution
- H_2T, H_2M are stronger acids than KHT

eg. $H_2T + 2NaOH \rightarrow Na_2T + 2H_2O$

$KHT + NaOH \rightarrow NaKT + H_2O$

pH is not related to Titratable acidity

Juice pH	Titratable Acidity (g/L as H_2T)	Tartrate +Malate (g/L)
3.15	6.6	7.1
3.21	6.5	8.2
3.54	6.6	10.0
3.96	6.2	8.2

pH ≠ Titratable acid

As the form of the tartrate changes, the pH will change, as the replacement of protons by K in this case lowers the TA and raises the pH of the solution

1g/L	Tartaric acid H_2T	Potassium bitartrate KHT	Di-Potassium tartrate K_2T	Malic acid H_2M
TA	1	0.5	0	1.12
pH	2.68	3.58	6.53	2.84

Sampling

- Exposed berries will have higher pH, lower acidity than shaded.
- Water stress will increase pH
- Hot weather will cause rapid decline in TA
- Avoid sampling in heat of the day
- Don’t get samples too hot (or too cold).

Sample preparation

- Usually on same sample lot as ^{o}Brix
- Precise volumetric equipment
- Fresh samples preferred
  - Refrigerate if storing overnight
- Use same extraction process between sampling times
- Centrifuged sample if possible
- Temperature correction for pH
- Regular calibration of pH meter & NaOH solutions
  - Keep pH buffers cool/refrigerated

Calculations

$$g/l = \frac{ml\ NaOH \times normality\ NaOH \times 0.075^{*} \times 1000}{Sample\ volume\ (ml)}$$

$$Eg\ \frac{15 \times 0.1 \times 0.075 \times 1000}{10} = 11.25\ g/L$$

*** = eqivalent weight of tartaric acid**

(If 0.13N NaOH & 10 ml sample is used:

ml NaOH added = g/l)

- **Can also be measured by manual titration with NaOH using Phenolphthalein indicator**

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Sources of errors

- Non-representative sample
- Incorrect NaOH concentration
- Incorrect sample volume
- Too rapid titration
- pH meter not accurately calibrated for end-point titrations >8
- Poor electrodes
- Gas in wine sample

pH

- What is pH?

The pH is the negative logarithm of the concentration of free Hydrogen ions in a juice or wine.

$$pH = -\log[H^+]$$

ie pH 3 is 10x more acidic than pH 4
(*cf* Richter Scale for earthquakes)

Already shown that the pH of juice can be very different at similar levels of TA
depending on the amounts and proportions of tartaric acid, potassium bitartrate, di-potassium tartrate & malic acid

pH can influence TA

- Balance between H_2T, HT^- & T^{2-} depends on pH. (& H_2M etc)
  - Below pH 3.56 KHT precipitates causing TA to decrease & pH drops
  - Above pH 3.56 KHT precipitates causing TA to decrease & pH rises

How to measure pH

- **Only way is with a pH meter**
  - **Numerous types available**
    - **Hand-held, bench top**
    - **Manual vs autosampling**
    - **Combined vs reference electrode types**

Sources of error

- Non-representative sample
- pH meter not accurately calibrated for end-point titrations
  - Buffers incorrect
  - Not calibrated for pH's 3-4
- Poor electrodes
  - Reference cell dry.