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The relationship between total acidity, titratable acidity and pH in wine

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• This is an older paper, but worth revisiting given the impact of a wine's acid composition a pH on so many parameters, which Dr. Boulton summarizes like this:
- sourness, as well as organoleptic properties
- microbial stability
- incidence and extent of malolactic fermentation
- solubility of potassium bitartrate and calcium tartrate
- rates of formation and hydrolysis of esters
- ionization and rate of polymerization of anthocyanins
- protein instability in white wines.

• Dr. Boulton starts out by defining the terms involved.

Total acidity: proton equivalence of the amount of organic acid anions present in a wine. It is the number of protons (also called hydrogen ions, or simply H^+) that the organic acids (lactic, succinic, citric, acetic, and sulfurous acids) would contain if they were undissociated. It is calculated by measuring the acid anion concentration (by spectrometry or chromatography), expressing them as molar quantities (number of molecules per volume), and then multiplying by the number of protons that would result from complete dissociation.

Titratable acidity: number of protons recovered during a titration with a strong base to a specified endpoint. It can also be expressed as a molar quantity. Many people use titratable acidity and total acidity as synonyms, but they are not. The titratable acidity is always less than the total acidity, because not all of the hydrogen ions expected from the acids are found during the determination of titratable acidity. However, titratable acidity is easier to measure.

pH: logarithm of the concentration of free protons, expressed with a positive sign.

• This study proposes that the reason why not all (only some) of the hydrogen ions from the organic acids are detected by titration during titratable acidity determination is the **exchange of hydrogen ions from the acids in the berry with monovalent metal cations** (such as potassium and sodium). This exchange is thought to occur across the membranes of berry cells by a very special enzyme system called an ATPase (see Summary #223 of the third article in this series).

• If the above hypothesis were true, Dr. Boulton reasons, then the following would also be true:
- **Test #1**: the sum of sodium, potassium, and titratable hydrogen ions should be numerically equal to the number of hydrogen ions expected from the total acid composition, and
- **Test #2**: the pH measured in an array of wines should be similar to the predicted pH values (if one would take into account the ionization of the organic acids, the concentrations of potassium and sodium present, as well as the ethanol content able to affect the acid dissociation constants).

• The goal of the current study was to determine whether the above "exchange hypothesis" was able to "pass" these two tests. To that end, twenty one European wines were studied, including Algerian, French, German and Italian wines, representing white, red and rose wines of various degrees of sweetness.

• **Results Test #1**: the correlation between titratable acidity and total acidity for the wines tested showed considerable scatter. The slope of the line was 0.74, indicating that only 74% of the expected protons were recovered by titration. However, when titratable acidity was plotted against the titratable protons plus the sum of potassium and sodium, essentially all of the protons were accounted for. That is, the curve between titratable acidity and $[H^+ + K^+ + Na^+]$ had a perfect fit.

• **Results Test #2**: when the measured pH values of the wines were compared to the predicted values calculated assuming that both acid ionization equilibria and mineral exchange had taken place, the values were very close (within 0.1 to 0.2 units of error). This suggests that, indeed, an exchange of H+, K+ and Na+ does take place in the berry.

In brief, this article proposes that potassium and sodium ions enter the grape berry in exchange for protons from the acids in the berry. The author validates this hypothesis by showing that the 'predicted values' of titratable acidity and pH based on the relationships proposed, and the 'measured values', are in close agreement.

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