The general relationship between potassium, sodium, and pH in grape juice and wine

By: Roger Boulton

• In this article, Dr. Boulton reveals the very complex relationships between pH, total acidity, and potassium (K^+) sodium (Na^+) concentrations in a juice or wine.

• In a previous article, the author introduced us to a key player in this story, surprisingly up to here overlooked: **potassium and sodium cations.** The key message in that article was that titratable acidity is lower than total acidity (that is, not all protons from the acids present in a wine can be titrated) because some of them have been exchanged by metal cations such as potassium and sodium. As a result, the total acidity of a wine was equal to the amount of titratable protons <u>plus</u> the concentrations of potassium and sodium cations.

$$\textbf{Total acidity} \quad = \quad \textbf{[H}^+\textbf{] titratable} \quad + \quad \textbf{[K}^+\textbf{]} \quad + \quad \textbf{[Na}^+\textbf{]}$$

• In the current article, the author introduces us to another key player also previously overlooked - what he calls the '**extent of exchange**'. To effectively determine the influence of K+ and Na+ on pH, it is first necessary to express the concentrations of potassium and sodium in relation to the total acidity present in the wine, that is, determine what <u>fraction</u> of the total acidity is due to an exchange of protons by potassium and sodium.

$$\textbf{Extent of exchange} \quad = \quad \frac{\textbf{[K+]} \; + \; \textbf{[Na+]}}{\textbf{[H+]} \; + \; \textbf{[K+]} \; + \; \textbf{[Na+]}}$$

• Finally, we also need to keep in mind that pH is going to depend, besides on the extent of exchange, on the **amount and strength of the acids** present in a wine. Dr. Boulton proposes that the extent of exchange, couple to the knowledge of the amount and strength of the acids in a wine, should allow the correct prediction of wine's pH.

$$\textbf{pH} \quad = \quad \textbf{f} \quad [\quad \textbf{extent of exchange} \text{ (the higher the extent of exchange, the higher the pH),}$$
$$\textbf{acid concentration} \text{ (the higher the acid concentration, the lower the pH),}$$
$$\textbf{strength of acids present} \text{ (the higher the strength, the lower the pH)} \quad]$$

• To prove the above point, Dr. Boulton plots out the measured pH of 95 juices and 125 wines against either their potassium concentration alone (sodium is negligible by comparison), or else against their extent of exchange (for various malic to lactic acids ratios), and compares the results.

• **Results**. When the pH values of the various wines were plotted against just their concentration of K, the pH was practically independent of K concentration. However, when the pH values were plotted against the extent of exchange, there was a better, more predictable relationship. In other words, the **measured pH was a reflection of the extent to which protons from the total acidity were exchanged by potassium and sodium ions.** This curve, therefore, allows a general prediction of the pH of a wine based on their concentration of K and Na, as well as on the proportion of them that have been exchange by protons.

• In general, the extent of exchange of a wine is lower than that of the corresponding juice because of the loss of potassium in the wine due to potassium bitartrate precipitation. Similarly, the pH of a wine is generally higher than that of the corresponding juice because of the formation during fermentation of weak acids (partially dissociated into protons) at the expense of strong acids.

• To end the article, Dr. Boulton touches on some of the real applications of the above findings, both in the vineyard and in the winery. For instance, the above three equations (in pink) should allow us to predict what would happen to a wine's pH and titratable acidity in a variety of situations, which are summarized below.

What happens to pH and TA during:				
		pH	TA	Comments *
VINEYARD	Acid synthesis in the berry		↑	
	Acid degradation (malate respiration or gluconeogenesis)	-- or ↑	↓	pH can remain constant if the ratio tartaric:malic rises; or it can rise if there is mineral uptake
	Uptake of K or Na	↑	↓	TA falls while extent of exchange increases
	Post-veraison rainfall	--	↓	TA falls as acidity is diluted in swollen berries, no change in pH
WINERY	Wine dilution with water	--	↓	pH does not change because K and Na are diluted at the same degree as TA
	Yeast fermentation (by itself)	↑		Weaker acids (e.g. succinic) are formed at the expense of stronger ones
	Malolactic fermentation	↑	↓	
	Precipitation of potassium bitartrate	--, ↑ or ↓	↓	Interesting case in which effect on pH depends entirely on original wine pH: if original pH<3.8, then pH drops; if original pH>3.8, then pH increases; and if original pH=3.8, then there is no change in pH
	Extended skin contact	↑	↓	Skin is rich in K+, and there is more extent of exchange
	Actual fermentation (weak acid formation and bitartrate precipitation combined)	↑ or ↓	↓	Depending on the extent of two opposing forces: weak acid formation dominates, which raises pH, or bitartrate precipitation dominates, which lowers pH
	Wine contamination	--	↑	TA due to formation of acetic and other acids, but impact on pH is negligible due to wine buffering capacity

* Please read discussion in original text for further explanation