Ask the AWRI: Winemaking with high pH, high TA and high potassium fruit

Some winemakers across Australia noted unusual behaviour in acidity when making acid adjustments to red musts during the 2018 vintage. Acid additions often resulted in a rise instead of a decrease in pH, and a much higher titratable acidity (TA) than expected. This behaviour was caused by high potassium concentrations in fruit. This column summarises the winemaking issues experienced when working with grapes that have elevated potassium levels and high pH.

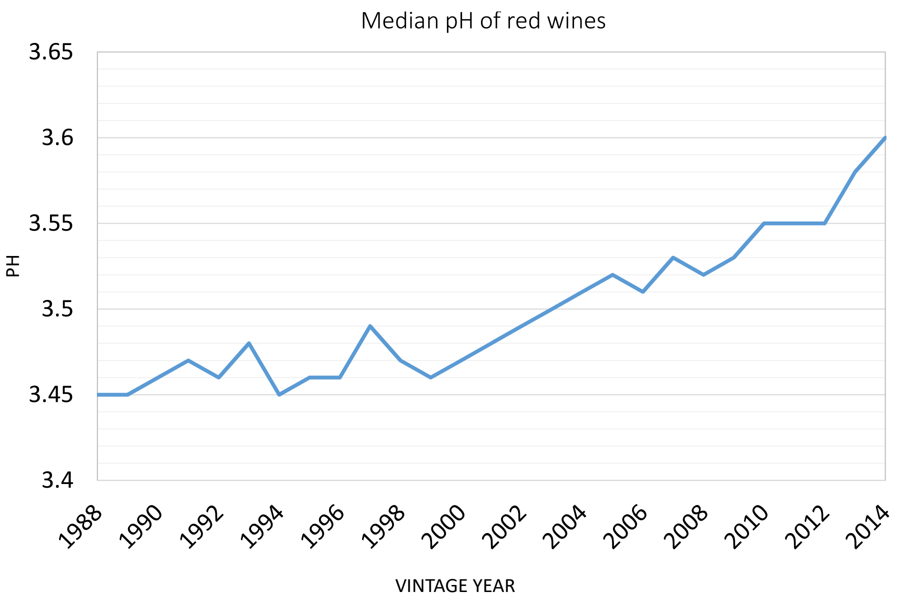
How have pH and TA levels in Australian red wines changed over time?

When Australia transitioned from mainly fortified to dry red table wine production in the 1960s and 70s, high pH was a common issue. This caused a range of microbiological instabilities which then led to changes in winemaking practices, particularly adoption of refrigeration, acid additions and judicious SO_2 management. Average pH in red wine was then around 3.45 from 1980-2000. Since 2000, there has been a gradual and continual increase in wine pH, with a median value of 3.62 reported in 2014 vintage Australian red wines (Godden *et al.* 2015).

During this time the titratable acidity (TA) has remained relatively constant at around 6.0-6.4g/L. The TA consists of approximately 40% tartaric acid, 30% malic/lactic acid and 20% succinic acid, with cooler years often resulting in a doubling of malic acid concentration. A pH shift of 0.2 units might not sound like much, but in the log scale of pH this is reducing the acidity, or the amount of hydrogen ions in the wine, by nearly half. Some have also correlated this pH shift with climatic changes. It's important to be aware that higher pH musts and wines face increased risk of bacterial spoilage and growth of *Brettanomyces* sp. yeast. There are also negative effects on colour stability.

What are typical potassium levels in grapes and wine?

Potassium concentrations in Australian Shiraz grape juice range between 1800 and 3600mg/L (Walker and Blackmore 2012). Red grape skins contain higher concentrations than berry pulp, around 9000mg/L, and finished red wines contain around 900 to 1100mg/L (Conde *et al.* 2007) and (Wilkes and Wheal 2018). Walker and Clingleffer (2016)



Median pH in Australian red wine (n=37,000). Data from Table S4, Supporting Information, Godden et al. 2015

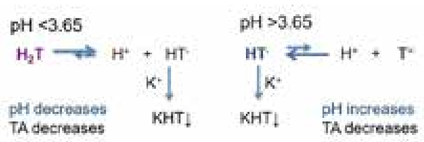
indicate that potassium levels in red wine are generally 20% lower than initial juice measurements. Much higher potassium levels were reported in Australian wine in the 1970s, particularly from warmer regions; however, with the current trend for grapes to ripen and be harvested earlier, there may be less time for potassium to accumulate in grape berries. In the 2018 vintage, potassium concentrations in many red wines were around 1800 mg/L, or close to double the average amount.

What happens to acid and potassium concentrations during fermentation?

In the first three days of a red wine ferment, potassium concentrations tend to increase by 50-120% as potassium is extracted from the grape skins into the must. The concentration then starts to decrease as potassium bitartrate (KHT) begins to precipitate out of the wine, removing a hydrogen ion, and thus increasing the pH of the must. The tartaric acid concentration thus also decreases to about half the original amount by the end of fermentation. There is potential for further potassium extraction at the end of ferment due to the presence of alcohol and increased temperature (Iland 1984) and there can also be a pH increase at this time as malic acid is converted to lactic acid, if malolactic fermentation (MLF) begins during the primary ferment.

What happens when tartaric acid is added to must?

Tartaric acid is a weak organic acid. When added to a liquid, tartaric acid disassociates into a mixture of three forms: tartaric acid (H_2T), bitartrate (HT^-) and tartrate ($T^=$) forms, with different amounts of the three forms existing at different pH levels.



For a grape must at pH3.01, there is approximately 50% H_2T and 50% HT^-. At pH4.37 there is no H_2T and approximately 50% HT^- and 50% $T^=$. At the midpoint of these two pH values, pH3.65, there is a big shift in these two distributions.

When tartaric acid is added to wines at pH below 3.65, a large amount exists as H_2T. This then releases a free hydrogen ion into the wine which decreases the pH, and a HT^- ion which binds to potassium, forming KHT. KHT precipitation effectively removes tartaric acid from the liquid, and thus a decrease is observed in the titratable acidity. The tartaric acid equilibrium in the wine then seeks to balance or replace this precipitated KHT by disassociating more H_2T into even more hydrogen ions, which further decreases the pH.

When tartaric acid is added to wines at pH above 3.65, the acid exists predominantly in the HT^- ion form. The HT^- ion scavenges potassium and the added acid effectively all precipitates out as KHT. This removes tartaric acid from the liquid, and decreases the titratable acidity. The tartaric acid equilibrium in the wine then seeks to balance or replace this precipitated KHT by actually removing existing hydrogen and $T^=$ ions in the wine to form more HT^- ion, which thus increases the pH.

How should winemakers adjust the pH/TA balance in high potassium ferments?

It is recommended to adjust must to pH<3.5 with tartaric acid as early as possible before fermentation begins, so long as this does not result in a TA above 7.5g/L. This will generally result in wines with pH 3.5 to 3.6 and a decrease in TA of 0.56g/L per 1g/L malic post-MLF. If the TA is above 7.5g/L, then pH should be adjusted even further to 3.4, given that large amounts of KHT precipitation will be expected during the ferment. This sometimes might require up to 4g/L of tartaric acid; however, this large acid adjustment is still more cost-effective than alternatives such as ion removal technologies. As KHT precipitation occurs and during cold stabilisation, the TA will decrease and return to more normal levels.

For more information on acidity and pH, check out the winemaking FAQs on the AWRI website. For assistance with any other technical grapegrowing or winemaking question, contact the AWRI helpdesk on helpdesk@awri.com.au or 08 8 313 6600.

References

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