Wine acids, not just tartaric

Titratable acidity
One of the most common, simple and useful wine analyses is the measure of titratable acidity (TA). Most wine producers have some ability to measure it, either by simple titration with a pH meter or by more sophisticated equipment such as auto-titrators or FTIR spectrophotometers. The result is used in a wide range of wine production decisions including harvest timing, acid adjustments and cold stabilisation.

For convenience, titratable acidity is usually expressed in grams per litre of tartaric acid, but this can obscure the fact that it is not a single acid measure. Titratable acidity is made up of contributions from tartaric, malic, succinic, lactic, acetic and citric acids, with minor contributions from a range of other acids. It is dependent not only on the physical amount of each acid present, but also the number of protons each has to contribute to the titration. For example, each molecule of acetic acid has only one proton, compared to two for tartaric and three for citric acid. Each acid also differs in its strength (its tendency to lose its protons) and hence its impact on pH and flavour.

Tartaric, malic and citric acids are derived from grapes while succinic, lactic and acetic acid are formed through yeast and bacterial activity. The relative proportions of these acids in wine can have a significant impact on flavour as well as the outcomes of winemaking interventions such as acid adjustments and cold stabilisation. Because they also influence wine pH, they can also affect many fining processes.

Organic acid survey
To gain some insight into the typical profile of organic acids seen in wine, AWRI Commercial Services reviewed the results for 277 wines analysed for their organic acid profile over the past five years. The values found are summarised in Table 1 and Figure 1. The wines in the dataset were submitted by clients of AWRI Commercial Services and therefore do not necessarily include the same wines across the five vintages.

Table 1. Summary of the organic acid values found for 277 wines analysed over the last five years at the AWRI Commercial Services laboratory.

<table>
<thead>
<tr>
<th></th>
<th>mean</th>
<th>median</th>
<th>min</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tartaric (g/L)</td>
<td>2.70</td>
<td>2.5</td>
<td>1.0</td>
<td>7.3</td>
</tr>
<tr>
<td>Malic (g/L)</td>
<td>1.27</td>
<td>1.3</td>
<td>&lt;0.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Succinic (g/L)</td>
<td>1.15</td>
<td>1.2</td>
<td>&lt;0.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Lactic (g/L)</td>
<td>0.80</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Acetic (g/L)</td>
<td>0.40</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Citric (g/L)</td>
<td>0.12</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Vintage to vintage variation

The survey also examined how the proportions of the different acids varied from vintage to vintage (Figure 2). These data showed that tartaric acid contributes between 30% and 45% of the overall measured titratable acidity.

Vintage to vintage differences in the proportions of organic acids making up TA can affect the dynamics of a number of winemaking processes. For example, decisions on the need for acid additions in the early stages of winemaking are usually made based on an assessment of the amount of acid that will naturally ‘fall out’ during processing and fermentation. This drop in acid occurs mostly through precipitation of tartrates; the other acids are relatively more soluble and not likely to precipitate. This means if the proportion of tartrates varies from year to year, the changes in TA (and the associated pH) will also vary and this can affect wine style. A clear understanding of the proportion of tartaric acid that makes up the TA is also important when making decisions on the best process to use for cold stabilisation.

Figure 1. The relative proportions of different organic acids found in red and white wines.

Figure 2. Relative contributions of different organic acids to titratable acidity across vintages 2010-2015.
Contributions from acids other than tartaric

Another variable contributor to TA is malic acid which is known to be affected by the growing conditions experienced by the grape and can also be produced during primary fermentation by some yeasts. The quantity of lactic acid also varies, given that it is formed through bacterial fermentation of malic acid. Not all wines undergo malolactic fermentation (MLF), with red wines more likely than white to undergo this step; this is reflected in Figure 1 which shows a higher contribution from lactic acid in red wines than white wines.

Taken together, lactic and malic acid were found to make up between 24% and 38% of measured TA. Having an understanding of the amount of malic acid in wine (and the amount of lactic acid produced during secondary fermentation) can be valuable in understanding the true meaning of the TA result for a given wine. Because the malic to lactic acid conversion drives a significant change in pH (0.1 to 0.2 units, depending on the amount converted), flavour and stylistic outcomes can be affected by the concentrations of these acids. Conveniently, malic acid is relatively easy to analyse in many wineries and, through subtraction, it can provide an indication of the amount of tartaric acid present, given that the proportions of the other organic acids have been found to be much less variable. Lactic acid is more difficult to quantify in most winery laboratories; however using the initial and final amount of malic acid before and after secondary fermentation allows a reasonable estimate to be made.

The contribution of succinic acid to titratable acidity was found to vary between 19% and 23%. While this variation is not large, the overall contribution to TA is significant because succinic acid does not precipitate during cold stabilisation. As a relatively low strength acid, it also makes a lesser contribution to pH than the equivalent amount of tartaric acid, which can have impacts on wine flavour and style. While the vintage variations in succinic acid were not large, the amounts measured in individual wines varied by almost 3 g/L, a range which has the potential to have a significant impact on wine flavour. There is currently not a simple process available to wineries to measure succinic acid and instead the analysis is usually conducted by high performance liquid chromatography or ion chromatography at commercial analytical laboratories. Analysis of succinic acid can be useful in determining if this acid is the cause of anomalous behaviour in a wine such as unexpected changes in pH and TA during fermentation, cold stabilisation or secondary fermentation.

The contribution of acetic acid to TA is relatively low because most wineries actively work to avoid its formation. Its concentration does not vary greatly from vintage to vintage, apart from areas affected by heatwaves, as it tends to be more a function of winemaking practice.
However, it does contribute to between 6% and 9% of measured TA on average and high values should be taken into account when interpreting TA results.

Citric acid is only present in very small quantities (if at all) and therefore its contribution to TA is limited.

**TA – not as simple as it might seem**
Once you start thinking about the organic acids involved, the ‘simple’ analytical measure of titratable acidity starts to look much more complex. Key points to take away are that tartaric acid is only about half the story and that the contributions of malic, lactic, succinic and acetic acids should be considered and can vary from vintage to vintage. If a wine is behaving in an unexpected way in terms of its cold stability or pH/TA changes during winemaking, it may be useful to have a sample analysed for organic acids, to gain more detailed information than the blunt measure of TA can provide. This information can be used to develop strategies to achieve desired flavour and stylistic outcomes. Such strategies could include pH adjustment and the choice of the most suitable organic acid to use, alternative cold stabilisation techniques to achieve the desired changes in pH and TA, or understanding of the likely impacts of deacidification processes.


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