Alternative DIY methods of Acid Titration for Cider

Titration to determine the acid content of wine or cider involves using a base (alkali) solution to neutralise the acid in a sample, then knowing how much base was used to do this, the amount of acid in the sample can be calculated.

In basic terms…

Concentration of the acid x Volume of acid = Concentration of the base x Volume of the base (expressed as Ca x Va = Cb x Vb) If any three of these factors are known, the equation can be rearranged, and the fourth factor calculated.

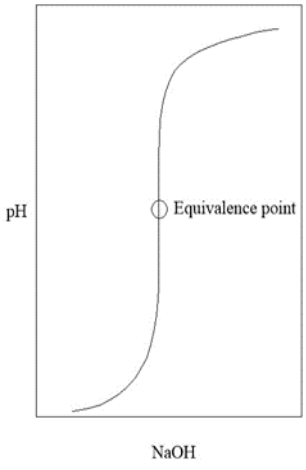
Titratable Acidity test kits from Brewcraft, Cellar Science, etc, make this easy to do by supplying a Sodium Hydroxide (NaOH) base solution to neutralise the Acid, an indicator solution such as phenolphthalein to show when the acid is neutralised, appropriate sized syringes etc for making the measurements, and instructions on how to do the titration.

The NaOH concentration in kits is usually 0.1N or 0.2N expressed as moles per litre (a mole is a very large number used in chemistry, a bit like using “dozen” for eggs or “bushels” for apples). The molecular weight of Tartaric acid is also known (the kits are usually intended for titrating Wine), so instructions are given for determining the concentration or Total Acidity g/L of Tartaric Acid. Multiplying Tartaric Acid g/L by 0.89 converts the result into Malic Acid (cider) g/L.

Now for the practical bit if you don’t have a kit… NaOH is readily available in dry powder or flake form (eBay or Hardware Store) and is commonly known as caustic soda or lye. It is used in various grades and purities ranging from commercial through to scientific depending on the application (i.e. cleaning drains vs making soap vs scientific).

Unfortunately, here in OZ (and possibly elsewhere in the World where it may be difficult to get titration kits) liquid NaOH (and phenolphthalein indicator) are classified as dangerous products by the postal authorities and can’t easily be sent through the mail. So, apart from buying yet another TA test kit (if they are available), the chemicals can be hard to get in small quantities, so alternatives are needed. The simple approach to this problem is to make up a base solution that is the equivalent of 4g of dry NaOH per litre of distilled water for a 0.1N concentration (or 8g for a 0.2N concentration) and use readily available indicators like Bromothymol Blue (BMB) or Phenol Red (PR). These indicators are commonly used for testing pool or aquarium water.

The useful thing about titration for wine or cider (a weak acid and strong base) is that the curve of pH vs the amount of base (NaOH) added to the wine or cider is somewhat “S” shaped and as shown here, is almost vertical where the acid and base neutralise each other (which is known as the equivalence point).



This means that any indicator which changes colour somewhere around the equivalence point will work, because the pH changes quickly (as the sample being tested goes through neutral from being acidic to alkaline). Near the equivalence point only a small additional amount of base causes the change. For a NaOH vs Malic Acid titration this sensitive “vertical” area extends from around pH6 to pH10. In an alkaline solution, BMB changes colour to blue, PR to red and phenolphthalein to pink so they all indicate when enough NaOH is added to neutralise the sample and send it just slightly alkaline.

Instead of indicator solutions, a pH meter can be used to indicate the pH change at equivalence point (e.g., pH8.2 for phenolphthalein) however because of the physical size of some pH meters, a larger sample of cider may be needed than that used with indicator solutions.

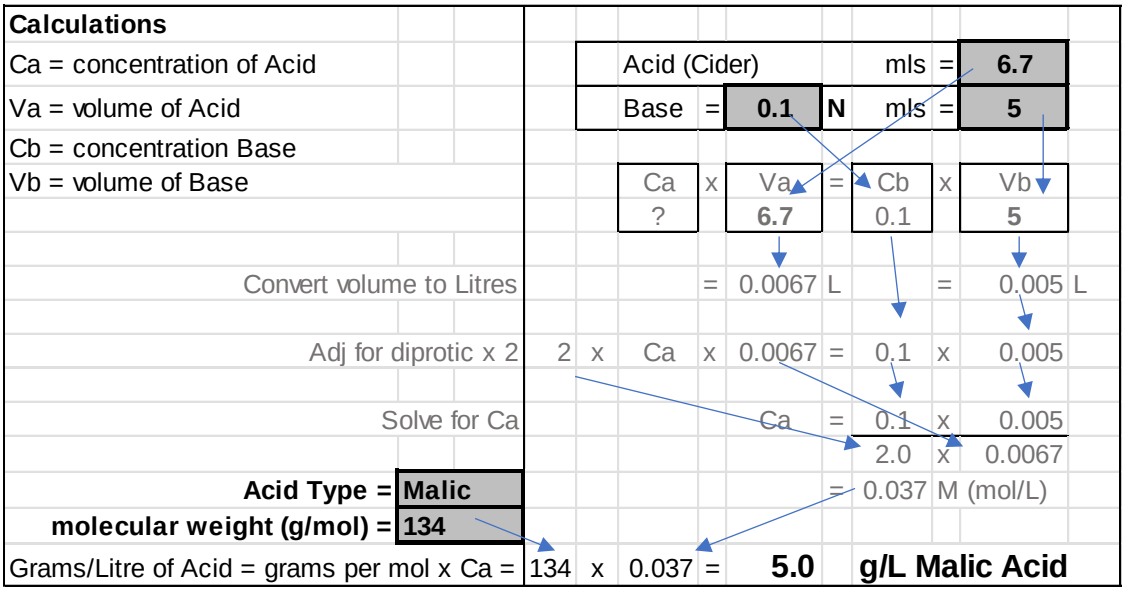
My chemistry is a bit clunky, but I understand that Malic Acid (Cider) and Tartaric Acid (Wine) are diprotic (one molecule of acid reacts with two molecules of base). So, after all the calculations are done to convert acidity into g/L the resulting formula commonly used in winemaking titration is **ml of NaOH x 0.75 = TA (g/L)** for a "standard" 10ml sample of Tartaric Acid and using 0.1N NaOH.

The same formula for Malic Acid uses a multiplier of **0.67**. (By way of explanation, the molecular weight of Tartaric Acid is 150 g/mole and because it is diprotic, the multiplier in the equation is only 0.75, and similarly the equivalent multiplier for Malic Acid with a molecular weight of 134 g/mole, is 0.67. Note that 134/150 = 0.89 is the factor mentioned previously for adjusting results to Malic Acid with Wine TA kits that have instructions for titrating Tartaric Acid).

Different brands of test kits have different approaches which use different amounts of sample or chemical to achieve the desired result. Also, Vinolab.hr has a useful calculator for determining the TA of wine (Tartaric Acid) for any sample size and NaOH concentration.

As an example, a simple method suggested by Andrew Lea for Cider is to have a sample size of 6.7ml and titrate with 0.1N NaOH which results in millilitres of NaOH equalling Malic Acid TA in g/L. Claude Jolicoeur suggests a similar method for minimising the use of NaOH and getting more tests out of a kit. He suggests a sample of 2.68 ml of sample and multiplying the amount of 0.2N NaOH used by five to get Malic Acid g/L (or any combination like this). Note that in these cases the sample size is derived from the molecular weight of Malic Acid to simplify the maths for Cider.

Following is a spreadsheet and calculations that I use. It can be used for any sample size (just plug the variables into the shaded boxes). Unfortunately, Excel files don't attach to HBT posts, but I am sure that anyone familiar with spreadsheets can figure it out if they want to use it).



The potential error when measuring small quantities accurately with syringes doesn't appear to be significant. Using an acid sample of approximately 5g/L (made up by dissolving 1 gram of malic acid in 200ml of tap water) and trialling DIY alternatives against the Cellar Science kit as a control, showed no difference in measured g/L. The Andrew Lea method was used so for practical purposes, the DIY approach to titration seems to be acceptable for Craft Cider Making purposes.

The result of the trial was…

Cellar Science, 0.1N NaOH solution with phenolphthalein indicator	**TA = 5.2g/L**
"DIY 0.1N NaOH solution" with phenolphthalein indicator	TA = 5.2g/L
"DIY 0.1N NaOH solution" with Bromothymol Blue or Phenyl Red indicator	TA = 5.2g/L

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