Acidity and pH of apple juice

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Acidity is an important property of apple juices, and is also easily measured. Whether for cidermaking or for blending fresh juice, it is always a good idea to have a measurement of acidity. Most notably, the acidity of the juice has an influence on:

> The perceived acidity in the taste of the fresh juice and of the finished cider: if the acidity is too low, the juice or cider will lack freshness. On the other hand, too much acidity may render the juice or cider too sharp and unpleasant to drink. We need to seek the right equilibrium.
> The type of acidity responsible for the tasting sensation is called *total acidity* (or TA) and is easily measured by titration.
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> The protection of cider from spoiling micro-organisms: a cider which has a low acidity level will be much more susceptible to be spoiled by such organisms.
> The type of acidity that governs this protection is the *pH* (potential Hydrogen) that measures the concentration of H^+ ions in a solution. The pH is related with the biochemical reactions that occur in the fermenting cider. It is easily measured with a pH-meter or with indicator strips.

So we can see that the total acidity is a property which is most useful for blending of fresh juice and cider, while pH is a property mostly useful in cider biochemistry. These two scales are very different: the pH scale is an inverse logarithmic scale where when the pH is reduced by one unity, the concentration of hydrogen ions is multiplied by ten. The total acidity is a linear scale where if the value is twice as large, the percieved acidity will also double.

Most apple juices have a pH between 3.0 for the more acidic juices and up to about 4.5 for the juices that contain very little acidity. On the TA scale, the acidity is often expressed as grams per litre (g/ℓ) of malic acid. The values measured may range from 1 g/ℓ for the least acidic juices to about 15 g/ℓ. The total acidity may also be expressed as a percentage: 1% total acidity being equal to 10 g/ℓ. In North America, another scale is also often used, which is the total acidity in tartaric acid equivalent. This is because most acidity titration kits sold in winemaking supply stores are calibrated for tartaric acid which is the main acid in grapes. But since in apples the main acid present is the malic acid, it makes more sense to use the malic acid scale. To convert the total acidity number from tartaric acid equivalent to malic acid we need to multiply the grams per litre of tartaric acid by 0.89.

In cider making, we usually try to maintain the TA of the blend between 4.5 and 7.5 g/ℓ of malic acid, with the lower figure more typical of English cider made with bittersweet apples, while the

higher figure would be more typical of North-American sparkling cider. For fresh juice or for sweet ciders and ice ciders, the acidity may be higher as the sugar will balance the acidity.

As it was mentioned earlier, the pH is related with the biochemistry of the fermentation. Research work was done, most notably by the Long Ashton research station in England during the years 1960 to about 1980, to study those aspects. From this research work, we may retain, for practical cidermaking purposes, the following important guidelines:

> When the pH is lower or equal to 3.0, the acidity is normally sufficient to protect the cider from the spoilage due to unwanted micro-organisms.
>
> If the pH is between 3.0 and 3.8, the acidity alone would not be enough for protection and the addition of sulfite (SO_2) is recommended to complete the protection. The recommended dosage of SO_2 varies from 50 ppm when the pH is closer to 3.0, and up to 180 ppm when the pH reaches 3.8.
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> If the pH of the juice is higher than 3.8, it is recommended to lower the pH to 3.8 by blending or by adding some malic acid, and then to add the recommended SO_2 dosage for a pH of 3.8.

There has been considerable discussion in the cider making community as to whether we could substitute one of the measurements for the other. In other words, can we use the result of a total acidity titration to assess the level of protection of a cider? Or, can we use the pH measurements in blending different varieties when seeking a certain level of acidity in the juice or in the finished cider?

Before we go further, I need to explain a few basic things about acid solutions. What is called a *strong acid* is a substance that, when in solution in water, will release one H^+ ion for each molecule of the acid. We then say it is fully dissociated. And if we know the dilution, we can compute the number of molecules and thus the mass of acid and the TA; and we can also compute the number of H^+ ions and the pH. So there will be a predictable and exact relationship between pH and TA for a particular strong acid, and this relationship will be such that when the TA is multiplied by ten, the pH will be reduced by one unit as this is how the pH scale is defined. Apple juice is however quite different: we are dealing with mostly malic acid, mixed with a few other acids present in lower concentrations. These acids are organic weak acids that can release either zero, one or two H^+ ions per molecule depending on the conditions and thus they are only partly dissociated. The difficulty is that we can't predict the extent of dissociation which depends on many factors (and I will skip these as it would become too complex). So, even if we know how many molecules of acid we have, we don't know how many H^+ ions they will have released. Hence we can't compute the pH from the TA. Then, the original question now becomes: although we can't theoretically obtain a predictable and exact relationship between pH and TA for apple juice, maybe there could be some sort of empirical relationship, meaning that the extent of dissociation of the acids would be fairly constant from a sample of juice to another.

As there were no definitive answer to this, I started gathering some data points to either confirm or infirm this possibility. Each data point had to give both measurements (i.e. TA and pH) from

the same sample of juice. I found some in the literature from the following references:

> Smock, R. M. and Neubert, A. M. (1950), *Apples and Apple Products*, Interscience Publishers, New York, 486 pages. In Table 38, page 338, there are 4 data points of commercial table apple varieties from USA, unspecified origin and date.
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> Beech, F.W. and Wood, D.E.S. (1979), *Tasting of Single Cultivar Ciders*, in the Proceedings of The Second Cider Workshop, 3rd October, 1979, Long Ashton Reasearch Station, UK. 9 data points from English cider apples.
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> Moyer, J. C. and Aitken, H. C. (1980), *Apple juice*, in Nelson and Tressler, *Fruit and Vegetable Juice Processing Technology*, 3rd edition, AVI Publishing, pp 212-267. In table 6.3 there are 9 data points from table apples grown in British Columbia in the years 1934-45, from Atkinson & Strachan, 1949. And in Table 6.5 there are 8 data points from tests done in New England, from Clague & Fellers, 1936.
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> Lea, A., *The Wittenham Hill Cider Pages* (http://www.cider.org.uk/). The page *Cider Apple Data* contains a table of 40 data points from the Geneva Station in New York, originally published by D. Downing in *Processed Apple Products*, AVI Van Nostrand, 1989. The measurements would probably have been done by the end of the 1970's from the apples grown in the Geneva Station. These include cider apples and standard eating apples.

In addition to these 70 published data points, I was able to gather quite a number of points from cider makers in England and North America after making requests throuth the *Cider Workshop* and the *Cider Digest* internet discussion forums, which I added to some data points I had taken myself. This gave me a total of 165 points, taken from different areas in North America and England, with time frame ranging from the 1930's to 2010, and from a diversified range of apples varieties and types.

These data points have then been plotted on a semi-log graph. The semi-log was chosen because the pH is a logarithmic scale and thus the resulting graph was linear. I was then able to draw a best fit straight line through these points with the slope adjusted so the pH would decrease by one unit when the total acidity is multiplied by 10 as per the theory of pH. This is the blue ligne on the graph. Its equation is:

$$pH = 4.3 - Ln(TA) / Ln(10)$$

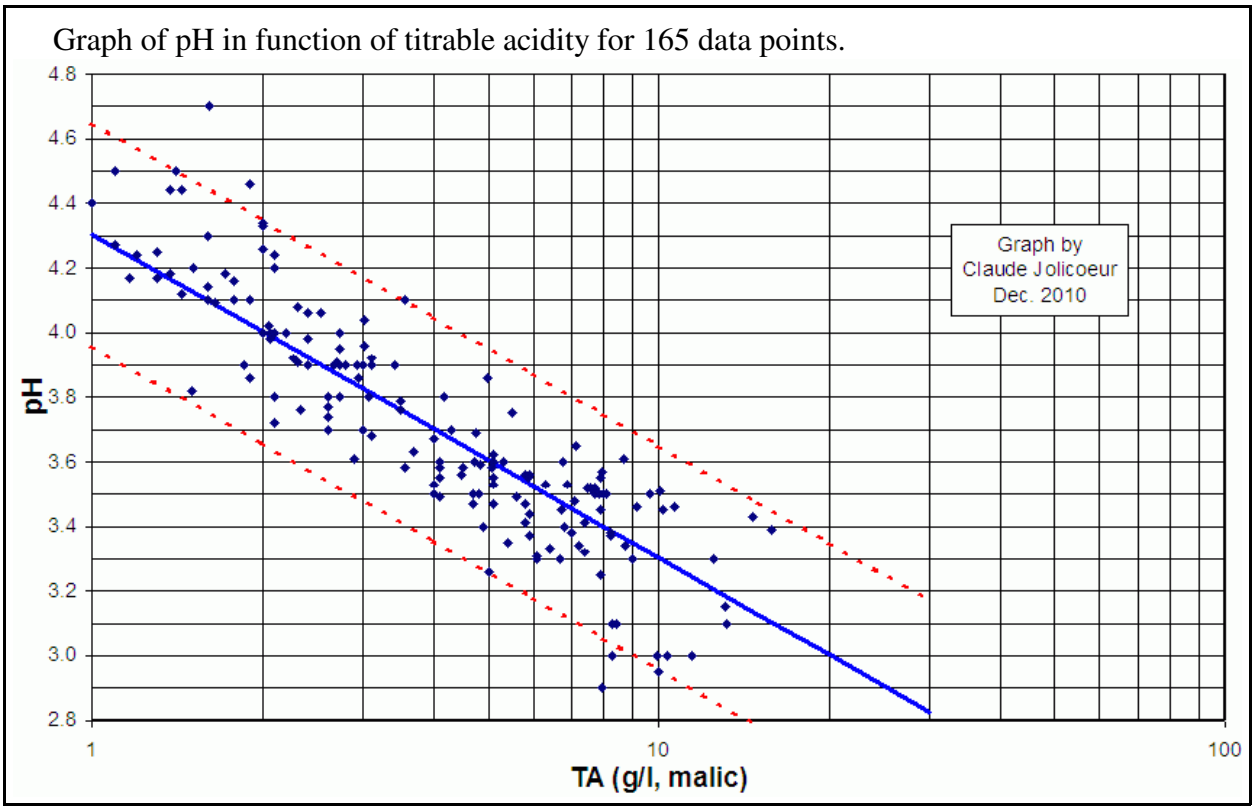
which can also be written:

$$pH = 4.3 - 0.4343\ Ln(TA)$$

Now, it can easily be seen that there is a lot of scatter of the data points around this mean line. To evaluate the amount of scatter, we compute the *standard deviation* of the data in relation to the mean line, which turns out to be 0.17 in pH units. Then, if this data follows a normal distribution curve, we may be able to say that 95% of the data points should be within 2 times the standard deviation from the mean line. The 2 red broken lines represent the mean plus or minus two times the standard deviation. Their equations are:

$pH_{MIN} = 3.96 - Ln(TA) / Ln(10)$; $pH_{MAX} = 4.64 - Ln(TA) / Ln(10)$

and the area between pH_{MIN} and pH_{MAX} is called the 95% confidence interval. And in effect, we can see that there are only a few data points outside this interval.



So, what this tells us is, if this data sample is truely representative, when we measure TA we could say that there is a probability of 95% that the pH would be between pH_{MIN} and pH_{MAX}, and there will be a difference of 0.68 in pH units between the 2 values. For example, with a TA of 7 g/ℓ (or 0.7% as malic), this will tell that the pH should be between 3.11 and 3.79, with a probability of 95%.

Unfortunately, in practice, this is not very useful because it could not help us in the dosage of the SO_2 required to protect this cider. With our example and a pH of 3.11 (the MIN value), a very small dose of SO_2 is required, while at a pH of 3.79, a dose near the maximum is required. The standard deviation is too large and in consequence the graph and equations cannot be used to dose the sulfite and skip the pH measurement.

Now, if we look at it the other way around, let's say we have a juice sample for which we have measured a pH of 3.6. Could this be any help in blending this cider? If we turn the equation around or if we look at the graph, we find that for this pH of 3.6, the 95% confidence interval would go from a TA of 2.3 and up to 11 grams per litre. Again this is way too wide to be of any practical use, as a TA of 2.3 g/ℓ is very low acidity and 11 g/ℓ is very high acidity. It cannot help

us figuring the best blend for this juice.

On a more positive note, this graph may be helpful to double check the acidity measurements. If we take both measurements (pH and TA) and plot this point on the graph, and see that the point is quite far from the mean line, we might make the measurements a second time to be sure it was done right.

In conclusion, this work confirms that both a pH and a TA measurement of acidity are necessary in cidermaking. These two measures each have their own use and one cannot be substituted for the other.

Many thanks to the cidermakers of the Cider Workshop and of the Cider Digest who provided a good part of the data points shown here.