

ACID

version 6.4

User Manual



Innovative Winery Solutions

Napa, California

www.winerysolutions.com

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INTRODUCTION

IWS

IWS is a personal project begun decades ago as an automated fermentation monitoring system. I learned to code to create that system, and subsequently applied software design to other winemaking questions. There are now just two IWS products: ACID and FILTER. Each is a computer application designed to shed light on a very specific area of wine production. ACID forecasts changes in wine acidity, and FILTER predicts the performance of filtrations. They were created from a single perspective - that there are aspects of winemaking which can be assessed more precisely than is possible with traditional methods. It is my feeling that tools built with this in mind will lead to a greater understanding of the nature of wine, to a reduction in the level of processing of wines, and to making the winery cellar a nicer and more efficient place to work.

ACID

ACID is a unique approach to describing wine acidity. It is based on the chemistry of organic acids in an ethanol solution rather than on guidelines developed from wine histories. This provides a comprehensive picture of changes in wine chemistry, a picture which can be relied upon to give an unparalleled understanding of acid adjustments and malolactic fermentations. Since ACID is based on chemistry, this picture remains clear from season to season and from vineyard to vineyard. With it winemakers can put themselves in control of the acidity of their wines even before calling a pick date.

GETTING STARTED

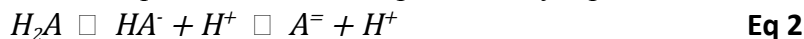
The Model

The job of ACID is to calculate the pH and TA of wines after an acid adjustment or malolactic fermentation. A mathematical model was created to accomplish this. This model is the machinery that drives ACID. It may be treated as a black box, but some understanding of the approach will enhance the utility of the program. Some important concepts central to the model are outlined below.

Wines vary in their resistance to pH change. This resistance is called buffer capacity and is easily measured in any lab as a TA is being run; procedures are given in Appendix 1. It is defined as the concentration of free protons required to cause a unit change in pH. Wines carrying higher buffer capacities will require larger additions to effect the same pH change. The units ACID uses to express buffer capacity are millimolar per pH unit. Wines typically have buffer capacities ranging between 30 and 60 $\text{mmolar}/\text{pH unit}$. So, for example, a wine with a BC of 50 $\text{mmolar}/\text{pH unit}$ and a pH of 4.00 would require 25 mmoles of protons per liter to change the pH to 3.50 (Equation 1).

$$(4.00 - 3.50) \times 50 = 25 \quad \text{Eq 1}$$

This information is all that is necessary to calculate the pH change resulting from the addition of a strong mineral acid like hydrochloric. However tartaric and malic acids do not behave like hydrochloric. These diprotic, organic acids exist in an equilibrium of three species in solution. The equilibrium is pictured in Equation 2 where *A* represents any diprotic acid.



The concentration of each of the species is calculable and based on the pH of the wine. The ratio of the three species determines how many free protons (H^+) an acid addition will generate. The free protons, in turn, change the pH as dictated by the buffer capacity.

The above concept is the backbone of all of the calculations performed by ACID. There are however other factors besides pH which have some influence on the behavior of tartaric and malic acids in wine. These include ethanol concentration, ionic strength, potassium concentration, and tartrate concentration. ACID considers these effects as well.

The Basics

This section contains a brief orientation to the organization of ACID. Reading this section, *The Basics*, and the next, *Your First Wine*, will allow a person to navigate through the program. For a detailed description of each command see Appendix 2.

Each wine being considered by the user is represented by a window. These windows can be moved and resized manually. In addition, ACID can arrange all open windows in a tiled or cascaded arrangement, making them easier to view.

Each window contains a table which follows the pH, TA, malic acid, potassium, and buffer capacity of the wine through whatever treatments the user selects for that wine. A treatment is any adjustment made to the acidity of a wine. There are three treatments available with ACID Classic - tartaric acid addition, malolactic fermentation, and potassium bitartrate precipitation. ACID Pro adds to that list additions of malic acid and potassium bicarbonate.

Your First Wine

Perhaps the best way to become acquainted with the ACID system is to look at an example. One of the most fundamental questions on which ACID can shed some light is, "What will the pH and TA of my wine be after a malolactic fermentation?" This first example will demonstrate how to answer that question.

The data from this example is taken from a Sauvignon Blanc in barrel during the 1993 harvest.

It is necessary to be somewhat familiar with the laboratory procedures found in Appendix 1 before going through this example.

Entering the initial data

The first step is to enter the data from the buffer capacity titration of the wine. Table 1 outlines the data entry procedure step by step. The lab procedure is found in Appendix 1.

The first column is for mouse use, the second for keyboard commands (as an alternative to the mouse) and data entry, and the third describes what is happening with the program.

Menu Choice or Mouse Selection	Hot Key or Keyboard Entry	Result
Calculations, Buffer Capacity Regression	<i>Ctrl R</i>	Enter Buffer Capacity Regression Data dialog box appears
select "4" below "n"	-	indicates that there are four data points to be entered
first pH box	<tab>	ready for first pH value
-	3.430	first pH value entered
second pH box	<tab>	ready for second pH value
-	3.489	second pH value entered
third pH box	<tab>	ready for third pH value
-	3.561	third pH value entered
fourth pH box	<tab>	ready for fourth pH value
-	3.621	fourth pH value entered
first buret box	<tab> 5 times	ready for first buret value
-	7.2	first buret value entered
second buret box	<tab>	ready for second buret value
-	7.4	second buret value entered
third buret box	<tab>	ready for third buret value
-	7.6	third buret value entered
fourth buret box	<tab>	ready for fourth buret value
-	7.8	fourth buret value entered
OK	<rtn>	accept data as entered; BC and r values reported
-	-	record the buffer capacity (61.6 ^{mM} / _{pH})
OK	<rtn>	close dialog box

Table 1-Cookbook to calculate buffer capacity for first example

With the calculated buffer capacity you can now enter the starting data for this example wine. Table 2 is a cookbook to perform the data entry.

It is important to use the units that ACID is expecting. Wherever possible ACID uses grams per liter for concentrations; that includes potassium and TA, as well as tartaric and malic. Alcohol is expressed as $\frac{\% \text{ volume}}{\text{volume}}$. If working with a juice, rather than a wine, then the potential alcohol should be entered.

Ionic strength, while important to consider, is not something measured in each sample. Wines and juices typically range between 75 and 85. In practice most adjustment decisions will not be affected by even wider ranges than that. Values chosen over the years by users range from 60 to 100 and results are satisfactory at both ends of that spectrum. It is recommended that a value of 80 be used for all wines and juices being considered in ACID.

Menu Choice or Mouse Selection	Hot Key or Keyboard Entry	Result
Wine, New	-	Initial Data dialog box appears
Wine Name	-	ready for wine name
-	<i>1993 SB</i>	wine name entered
pH	<tab>	ready for pH
-	<i>3.21</i>	pH entered
TA	<tab>	ready for TA
-	<i>7.8</i>	TA ($\frac{g}{l}$) entered
Malic	<tab>	ready for malic acid concentration
-	<i>2.08</i>	malic acid ($\frac{g}{l}$) entered
K+	<tab>	ready for potassium concentration
-	<i>1.2</i>	potassium ($\frac{g}{l}$) entered
Buf Cpy	<tab>	ready for buffer capacity
-	<i>61.6</i>	buffer capacity ($\frac{mM}{pH}$) entered
Alcohol	<tab>	ready for alcohol concentration
-	<i>13.3</i>	alcohol ($\frac{\% v}{v}$) entered
Tartaric	<tab>	ready for tartaric acid concentration
-	<i>8</i>	tartaric acid ($\frac{g}{l}$) entered
Ionic Strength	<tab>	ready for ionic strength
-	<i>80</i>	ionic strength (mM) entered
OK	<rtn>	accept data as entered; new wine window appears

Table 2-Cookbook to enter laboratory data for first example

Performing a treatment

A window is now displayed containing a table showing the initial data for the wine named "1993 SB." ACID will calculate changes in pH, TA, MA, K⁺ and BC for any treatment which is performed on this wine. The treatment to be performed in this example is a malolactic fermentation. Table 3 will take you through this.

Menu Choice or Mouse Selection	Hot Key or Keyboard Entry	Result
Treatments, MLF	<i>Ctrl-F</i>	MLF dialog box appears
-	<i>0</i>	expected malic concentration entered
OK	<i><rtn></i>	accept data as entered results now appear in table

Table 3-Cookbook to perform a MLF on the first example

ACID should now show this wine finishing malolactic with a pH of 3.26 and a TA of 6.64.

SOLUTIONS

Several example wine files are included with the installation to help demonstrate ACID's utility. They are there to shed light on what is possible. They are entry points into a wider understanding about wine acidity. The wider understanding can lead to questions that otherwise would remain unasked, and it can answer them. The example files are located in the folder titled IWS ACID in your documents folder

Timing

Many winemakers have a preference for adding tartaric acid as early as possible, using phrases like "lack of integration" and "raw acid taste" to describe later additions. Since ACID is a comprehensive description of wine behavior, including malolactic fermentation, all necessary acid adjustments may be made at the beginning of a wine's life.

Aside from the above winemaker anecdotes there are more specific reasons to make additions early. The range of malolactic organisms that can grow in a wine increases as pH rises. The populations that may grow at higher pH's are often spoilage organisms like Lactobacillus. On the other hand if pH is too low malolactic may not proceed at all. So the ability to control the pH of a young wine or juice contributes to the control of fermentations.

In addition, the pH of a red must affects the extraction and retention of phenolics from skins and seeds. Quite different wines can arise from the same fruit with no difference other than the pH in the fermentor. Virtually everything that happens in wines and juices is to some extent governed by their pH, so it should come as no surprise that the eventual fate of anthocyanins and other phenolics is influenced by the pH of their environment.

Production Tool

The editing feature of ACID may be used to analyze any number of wines without starting from scratch each time, like typing a letter from a starting form rather than a blank sheet. The file "red.acd" will be used to demonstrate this.

To begin strike *Ctrl-O* or select Open from the Wine menu to open a file. Navigate to the IWS ACID folder contained in your My Documents folder, then on to Examples, and open the file named "red.acd". This wine is a fictional red wine which, as can be seen from the initial data, has not yet completed malolactic fermentation. The question to be answered is, "How much tartaric acid is to be added to the wine?" Let's assume the winemaker has decided to shoot for a post-malolactic pH of 3.70. ACID estimates that it would require a 2.09 $\frac{g}{l}$ addition to accomplish this.

Now let's say there is another red to be analyzed with a pH of 3.80, TA of 6.00, MA of 3.00, K^+ of 2.00 and a BC of 50.0. The first step is to edit the initial data. Strike *Ctrl-E* or select Edit from the Treatments menu. Now select treatment zero and OK with the mouse. A dialog box comes up allowing you to edit the initial data. Change the name to "red2", the pH to "3.80" and the MA to "3.00". ACID now shows this wine finishing malolactic with a pH of 3.73. Remember the winemaker wanted to aim for 3.70 so the acid addition must be changed. Once again strike *Alt-E* or use the mouse. This time select treatment number one to be edited. Type 3.57 as the

target pH. This provides a final pH of 3.70 and recommends a 1.65 g/l addition.

Tartaric vs. Malic

A malic acid addition will raise the TA of a wine more than a tartaric addition for a given pH change. It will also mean greater changes during a subsequent malolactic fermentation. So how should a winemaker decide which acid, or what mixture of acids, to add? The answer is that at the juice stage he or she must have a target pH and TA in mind for the final wine, and have a tool which considers wine acid holistically. The file "white.acd" will be used to illustrate this.

Retrieve the file for the wine "white" as done in the previous example for the wine "red." A look at the wine reveals a mix of tartaric and malic is required to bring this wine to a final TA of 7.00 and pH of 3.24.

If there were a second white wine to be analyzed, with a starting pH of 3.23, what additions would be required to finish with the same TA and pH? Edit the initial data to change the pH from 3.30 to 3.23 and the name to "white2". The table shows a finishing TA of 6.85. Edit treatment number two to a target TA of 9.20. This will bring the finishing TA to 7.00 with a pH of 3.24. A 1.97 g/l addition of malic acid is what's needed to bring this wine to the same target acidity.

Wines Are Individuals

The amount of tartaric acid necessary to effect a given pH change, or even a given TA change, is different for different wines. Buffer capacity, pH, potassium concentration and tartaric acid concentration will all influence the efficiency of a tartaric acid addition.

If any windows are open close them all and open files for the wines "white3" and "red3". Notice for the white wine 1.56 g/l of tartaric acid is required to lower the pH by 0.1 unit, while the red requires only 0.74 g/l. With the larger addition to the white it is no surprise that the TA rises more in this wine, but the greater TA cannot be accounted for solely by the larger addition. 81% of the acid added to the white is measured as a rise in the TA while in the red the efficiency is 64%.

The reason for the higher efficiency in the white is that less of the added acid precipitates. The higher pH and K⁺ values of the red make the added acid less stable in the solution. The higher buffer capacity and lower alcohol of the white require a larger addition to effect the same pH change. Each bit of potassium bitartrate that precipitates from the white puts far more pressure on the pH of that wine than is applied by the same precipitation in the red. All of these factors affect one another. The chemistry works in concert to make each wine behave in its own way.

Greater Understanding

The TA drop during a malolactic fermentation is a function of the concentration of malic acid in the wine, but what affects the pH change of a wine during a malolactic fermentation? Obviously higher malic acid concentrations and lower buffer capacities would lead to bigger pH shifts. An interesting result of the ACID calculations, though, is that the starting pH also has an effect on the magnitude of the pH shift during malolactic fermentation.

Open files for the wines “white4” and “red4”. Even though the wines start with the same malic acid concentration and buffer capacity, the pH shift is quite different in the two wines, about 60 higher in the red than the white. This is simply a function of how malic and lactic acids behave at different pHs.

ACID may be used in a similar manner to gain an understanding of how any other treatment is affected by the chemistry of the wine in which it is performed.

LIMITATIONS

When adjusting the acidity of a juice or young wine it is important to bear in mind changes which ACID does not consider that can occur during fermentation, aging, and finishing. These changes may be difficult to predict, but the collection of data describing them should allow for ever more precise estimates. Some areas winemakers should consider are outlined below and others may exist.

During a yeast fermentation there are acidity changes. Anecdotal evidence suggests that they are quite variable, with TA tending to rise by a few tenths ($\frac{\%}{1}$) and pH drifting either direction. These changes may be attributed to consumption and production of organic acids, especially succinic and malic.

Potassium bitartrate precipitation is likely to be an important effect during cold settling and fermentation, and is definitely important during cold stabilization. During precipitation TA will fall and pH may change as well. ACID will calculate changes in acidity expected as a result of a potassium bitartrate precipitation; the problem however is predicting the extent of the precipitation.

The greatest changes to the acidity of a fermenting red must be brought about by the extraction of acids from the skins and flesh of berries. These acids will cause both the TA and the pH to rise. Typical changes might be around 1.0 $\frac{\%}{1}$ of TA gained and a pH rise of 0.2 units, but vary widely with cultivar, ripeness, vintage, and vineyards. A winemaker would be best served by performing a version of the extraction in the laboratory, rather than trying to use a rule of thumb to guess at its extent. This is easily done by placing a sample of whole berries into a blender, then centrifuging the resulting slurry.

It is strongly recommended that such an extraction be made part of the sample preparation for red fruit when using ACID. If a winemaker does choose to use juice chemistry as a starting point when considering acid additions to red musts, and is using ACID to help make decisions, it is important to target pH and not TA. If a given TA is targeted the rise in TA from the skins will cause the winemaker to overshoot his or her target and the wine will require deacidification. If pH is targeted and it rises during the fermentation a second acid addition at press time will be the final adjustment necessary for that wine.

It is not only the acidity of the whole fruit sample that is different from a juice sample. Brix and nitrogen status can both be dramatically different from juice to whole fruit as well. More informed, and simply better, harvest and crush decisions can be made with the use of a blender and centrifuge.

Some error is inherent in any sort of measurement. In the lab every analysis carries its own interferences and precision. pH electrodes are generally considered accurate to only 0.02

units and those measurements are foundational for these calculations, and for the resulting decisions. Time should be taken to be sure that all laboratory personnel are performing analyses according to the same protocol to keep the analyses as precise as possible, and sampling must be performed with thought and care to be certain the sample represents the wine in question. Even with all of that in place, each data set on which ACID works is the result of many measurements, and each measurement will always carry some level of error. ACID is affected by the sum of all of those errors.

APPENDIX 1 - TA/Buffer Capacity Procedure

Discussion

Degassing the wine, as described here, is not a part of performing TA's at many, perhaps most, wineries. It will however provide for more precise results, and more consistent results over time. TA values will also be a bit lower if degassing is employed. If TA is a factor in making decisions regarding young wines then it is essential.

For batch degassing good results can be obtained with an ultrasonic cleaner. With samples in 15 ml glass tubes, running the cleaner for 10 minutes at 35°C is generally sufficient, but duration and temperature may vary from unit to unit.

Figure 1 shows a typical TA titration curve. The reciprocal of the slope of the curve at any point on the line is the buffer capacity of the diluted wine being titrated. There is a sharp drop in buffer capacity toward the end of the titration (above about pH 5.0), and at pH's below about 3.2 the buffer capacity of a wine begins to fall off as well. In addition, there is variation even within the 3.2 to 5.0 range. The effect all this has on the measured buffer capacity of a wine is minimized by using a small volume of titrant when performing buffer capacity titrations.

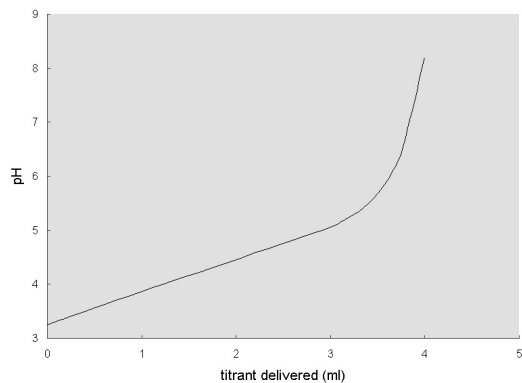


Fig 1 - TA titration curve

IWS recommends that four points be collected and that, with a standard TA procedure using 5 mls of wine and 0.1 N titrant, the increment be ~0.1 ml of titrant. It is best to collect pH data to the nearest thousandth (eg. 3.792). While that last digit has no significance with the limitations of the accuracy of measuring pH, it is significant when looking at the change in pH during the titration - that is to say the difference from one point to the next.

Procedure

- *samples must be centrifuged or filtered*
- degas sample for at least three minutes (on a stir plate, under vacuum); *more than three minutes is necessary for fermenting musts or sparkling wines*
- measure 100 ml of distilled water in a graduated cylinder and put it into a narrow 200 ml beaker with a half inch stir bar
- place the beaker on a stir plate under a buret containing standardized 0.1 N NaOH, put a pH electrode into the beaker and begin stirring
- add a couple of drops of phenolphthalein as a help, and check on the pH meter
- with a drop or less of titrant bring to a pH of approximately 8.2 (± 0.3 is fine at this point in the procedure); dilute acid should be made available to lower the pH if necessary
- pipet 5 ml of degassed wine into the beaker
- record the pH and buret reading as the first point of the buffer capacity titration
- deliver an increment of titrant by turning the stopcock through 180° and record the pH and buret reading; it is recommended that the increment be kept under 0.1 ml
- repeat the previous step until four points have been taken
- once the buffer capacity data has been collected continue the titration to an endpoint of 8.2 and record the final value

Calculations

ACID will perform a linear regression to find the slope of the titration curve and calculate the resulting buffer capacity of the wine. If the correlation (r) of the regression is not 0.95 or higher, then the data is likely faulty.

TA is calculated using the following equation:

$$TA = (75 \times V \times N) \div v \quad \text{Eq 3}$$

where: TA = titratable acidity ($\frac{\text{g tartaric acid}}{\text{l}}$)

V = volume of sodium hydroxide used for the titration (ml)

N = normality of the sodium hydroxide titrant

v = volume of the wine sample (ml)

Reagents

Phenolphthalein solution

0.1 N NaOH

0.1 N HCl (for standardizing)

May be diluted at about 1:1 to create dilute acid for adjusting the starting pH downward.

APPENDIX 2 - Command and Control Reference

Some commands are only available to users of ACID Pro. Those menu selections are indicated with an asterisk (*).

Wine Menu

Open

Action: Retrieves a wine file.
Keyboard shortcut: *Ctrl-O*

New

Action: Used to create a window representing a new wine. First a dialog box is brought up which allows the user to enter the initial data for the new wine. Then the new window is created with the data inserted into the table.
Keyboard shortcut: *Ctrl-N*

Close

Action: Closes the currently highlighted window.

Save

Action: Saves the currently active window to disk.
Keyboard shortcut: *Ctrl-S*

Save as...

Action: Opens a dialog box to allow the wine to be saved under a new file name

Exit

Action: Quits the program

Treatments Menu

Tartaric Addition

Action: Calculates the result of a tartaric acid addition to the wine in the active window and places the results in the table of that window. It is important to remember that the target pH or TA is just that, a target. The table must be consulted for the actual results of the addition indicated.
Keyboard shortcut: *Ctrl-T*

Malic Addition *

Action: Calculates the result of a malic acid addition to the wine in the active window.
Keyboard shortcut: *Ctrl-M*

L-Malic Addition *

Action: Calculates the result of a malic acid addition to the wine in the active window.

Keyboard shortcut: *Ctrl-L*

Malolactic Fermentation

Action: Calculates the result of a malolactic fermentation occurring in the wine contained in the active window.

Keyboard shortcut: *Ctrl-F*

Potassium Bitartrate Precipitation

Action: Calculates the result of potassium bitartrate precipitation occurring in the wine contained in the active window.

Keyboard shortcut: *Ctrl-P*

Potassium Carbonate Addition *

Action: Calculates the result of a potassium carbonate addition to the wine in the active window.

Keyboard shortcut: *<none>*

Hydrated Potassium Carbonate *

Action: Calculates the result of a potassium carbonate addition to the wine in the active window - if the K_2CO_3 is fully hydrated ($K_2CO_3 \cdot 1.5H_2O$).

Keyboard shortcut: *<none>*

Edit

Action: Allows user to change target values for any treatment in the active window or to change the initial data for the wine. If a change is to be made in the type of treatment it must be deleted and reentered.

Keyboard shortcut: *Ctrl-E*

Delete

Action: Deletes the last treatment in the active window.

Set Default Values

Action: Generates a dialog box which allows the user to set the default values for alcohol, tartaric acid, and ionic strength; these values will be inserted into the initial data when a new wine is requested. Also the dialog box allows the user to set whether or not ACID will display these values for each wine.

Keyboard shortcut: *Ctrl-V*

Calculations Menu

Buffer Capacity Regression

Action: Calculates a buffer capacity based on titration data.

Keyboard shortcut: *Ctrl-R*

Set Buffer Capacity Constants

Action: ACID needs to know the molarity of the titrant used and how much the wine was diluted during the TA titration in order to calculate a buffer capacity; this command brings up a dialog box which allows those values to be entered.

Keyboard shortcut: *Ctrl-C*

BC/TA *

Action: Like TA, buffer capacity is a property of the wine that arises from its composition. In a juice, where virtually all of the acidity is accounted for by tartaric and malic acids, this relationship can be calculated if one knows the concentration of the acids, pH, potential alcohol, and ionic strength. In practice the TA and BC tend to be higher when determined via titration than by this calculation. *Only valid for juices.*

Tartaric/K+ *

Action: TA is the summation of hydrogen ions in the wine. If one knows the malic acid concentration and the TA of a juice then one can attribute the portion of the TA that is not accounted for by the malic acid entirely to tartaric acid. From there one can determine potassium. The approach is that malate and tartrate in a juice need a certain quantity of counter ions, most of which is potassium. This is designed for a winery lab that is performing wet chemistry only, where tartaric acid and potassium concentrations are otherwise not available. *Only valid for juices.*

View Menu

Cascade

Action: Arranges all open windows in a stacked arrangement with all window titles (file names) visible.

Tile Horizontally

Action: Arranges all open windows in a stacked arrangement, maximizing the area visible for each.

Tile Vertically

Action: Arranges all open windows side by side, maximizing the area visible for each.