Cold Stability
Anything But Stable!

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What is Cold Stability?

• Cold stability refers to a wine’s tendency to precipitate solids when held cool.
• The major precipitates tend to be tartrates (potassium hydrogen tartrate, KHT, and occasionally calcium tartrate, CaT).
• However polymeric tannins and colour compounds may also be co-precipitated or included in the tartrate crystals.
Why it happens

• KHT (and CaT) naturally occur in grape juice.
• As the juice is fermented the increased alcohol lowers the solubility of the tartrates (and many other species). Most of the tartrate thus precipitates during fermentation.
• The wine at this point has an equilibrium amount of tartrate based on its solubility.
• However changes in temperature (colder less soluble) and pH can change this solubility leading to further precipitation.
Stabilization

- Customers don’t like tartrates appearing in bottles (in whites it is often mistaken for glass).
- To prevent this happening wine is often held at reduced temperature (often sub-zero) for a period of time to force precipitation of tartrates and thus make the wine stable to the conditions likely to be experienced in the hands of the consumer.
- Yeah, right!
Confounding Factors

• While the solubility of the tartrates is (relatively) easily defined there are a number of things that can prevent crystallization.

• Some sugars, proteins, polyphenols and polymers can inhibit either the formation of the crystal nucleus or the growth of the crystals.

• These may result in stable supersaturated solutions.

• To combat this wineries usually seed the cold stabilizing wine with KHT to force precipitation and speed the process.

• CaT and racemic KHT are also used to precipitate CaT.
Other Cold Stabilization Methods

- Electrodialysis (ED) is a method that removes the unstable species by forcing it across selective membranes under the influence of an electric field differential.
- Fluidized bed methods work by passing the wine through a bed of KHT at a reduced temperature to precipitate the unstable tartrates.
- However the end effect is still a net reduction in tartrate concentration below the cold solubility threshold.
Stability Measurement

- The role of the laboratory is to determine by testing whether a wine is stable or not.
- But the question is “what is stable”?
- Nearly any wine will precipitate tartrates if cooled low enough for long enough.
- Can other substances that precipitate out under cold conditions be considered instabilities?
- How long and how cold represents a reasonable test?
72 Hour Brine
(The Common Reference)

• Cool the wine for 72 hours at -3 to -4 degrees Celsius.
• Bring the wine back to 20 degrees allowing time for any precipitated colour compound to redissolve (reds).
• Visually inspect the sample for crystalline deposits and if present the wine is considered unstable.
• Is valid for both reds and whites.
• Sometimes need to use a microscope to determine if a deposit is crystalline or not.
Disadvantages of the Brine Method

• 3 days!

• No real measure of how unstable a product is, that is it is just a pass or fail.

• Must be careful that the glassware is not too clean! (need nucleation sites for crystallization.

• In reds it is open to some degree of interpretation.
KHT
CaT
Amorphous Colour Compounds
A Mix
Freeze Thaw

• The theory is that the sample is taken to just frozen (slushy) and then allowed to thaw to room temperature.
• The wine is unstable if any crystalline deposits form.
• It is relatively quick, taking as little as one hour.
The Disadvantages

- It corresponds with the brine test only about 80% of the time (if done carefully).
- It is very dependant on how quickly and how long the sample is frozen for.
  - Any sample will precipitate tartrates if frozen long enough.

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The Disadvantages

- Things that can affect freezing time include:
  - Sample size
  - Sample shape
  - Location in the freezer
  - Particulates
  - The phase of the moon (really, it can).

- To do it properly the samples must be very carefully monitored.

- It can be really difficult to get consistent red results.
Potassium (K) Methods

• These methods generally involve the measurement of the potassium concentration in the sample.
• Chill the wine to sub-zero and seed with KHT.
• The sample is stirred at low temperature and then retested for K.
• If the difference in relative or absolute K value is greater than some arbitrary value the wine is considered unstable.
• This value is often determined internally by trial.
Potassium Methods

• They work!
• At least for tartrates.
• Relatively fast.
• Can be used in modified form to monitor the cold stabilization process.
• Need reliable methods for K determination (flame emission photometry, AAs, ICP or ISE).
• Does not give an indication of other forms of cold stability (colour or tannin dropout).

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Conductivity Methods

• Similar to K methods except measure a change in conductivity rather than K.

• Since K+ and the tartrate anion are the greatest concentration of conducting ions the conductivity should be relatively proportional to KHT concentration.

• A common value for the cut-off in conductivity change for an unstable reading is around 4%.
Conductivity Methods

- They seem to correlate well for white wines.
- Reasonably quick (1 hour).
- Relatively inexpensive to set up ($7k).
- But:
  - Suffers from interference in reds
  - 53% false positives in a 300 wine study!!

Compared to brine test.
Concentration Product

• Essentially this involves using the concentrations of K, tartrates, alcohol and the pH to determine theoretical tartrate capacity of the wine and compare it to the real quantities.
• If the real exceeds the theoretical then the wine is unstable.
• Unfortunately experimentation has shown that wines have a greater capacity for tartrates than theoretically calculated.
• This is probably due to some of the crystallization inhibiting factors mentioned earlier.
• Also tells us nothing about CaT or other precipitates (the red problem).
Other Issues

• CaT instability is a very slow equilibrium and most tests don’t give an indication of this instability.
• This means that wines that have been stabilized and tested as such may still precipitate in bottle.
• Especially a problem in sparkling wines, which appear to have less inhibiting compounds.
• Most wineries try to control the problem by monitoring Ca levels.
The Red Issue

• Traditionally red wines have not been cold stabilized.
  – Hey we are not supposed to drink them cold are we?
• They also tend to spend a lot more time in tank and so self stabilize.
• Changes in style have meant that reds are being released much younger.
• International export means that wines can end up experiencing very cold temperatures for extended periods in transit.
• We can deal with the tartrate stability but the question is should we be calling persistent colour and tannin deposit unstable?
• Modern customers don’t like chunky bits no matter what they are.
What to do?

- The 72 hour brine test still appears to be the reference standard.
- K methods work reasonably well for whites and reds but do not address non-tartrate issues.
- Conductivity methods appear to be reliable for most white wines but suffer from interference in reds.
- CP methods are questionable but may have application in future spectroscopic approaches (FTIR).
- Need to look at what is most effective for your situation.