Cold Stability
Anything But Stable!

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Fosters Wine Estates

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?

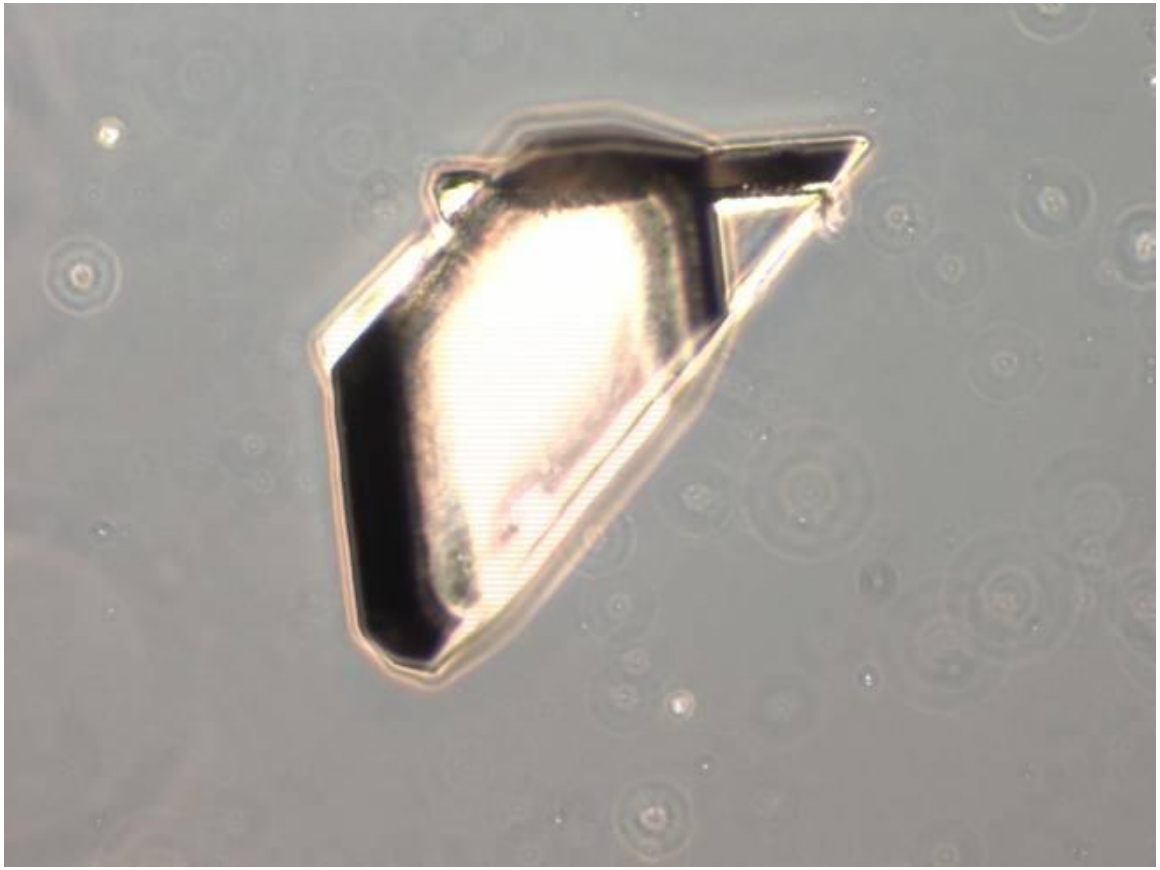
72 Hour Brine (The Common Reference)

- 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.

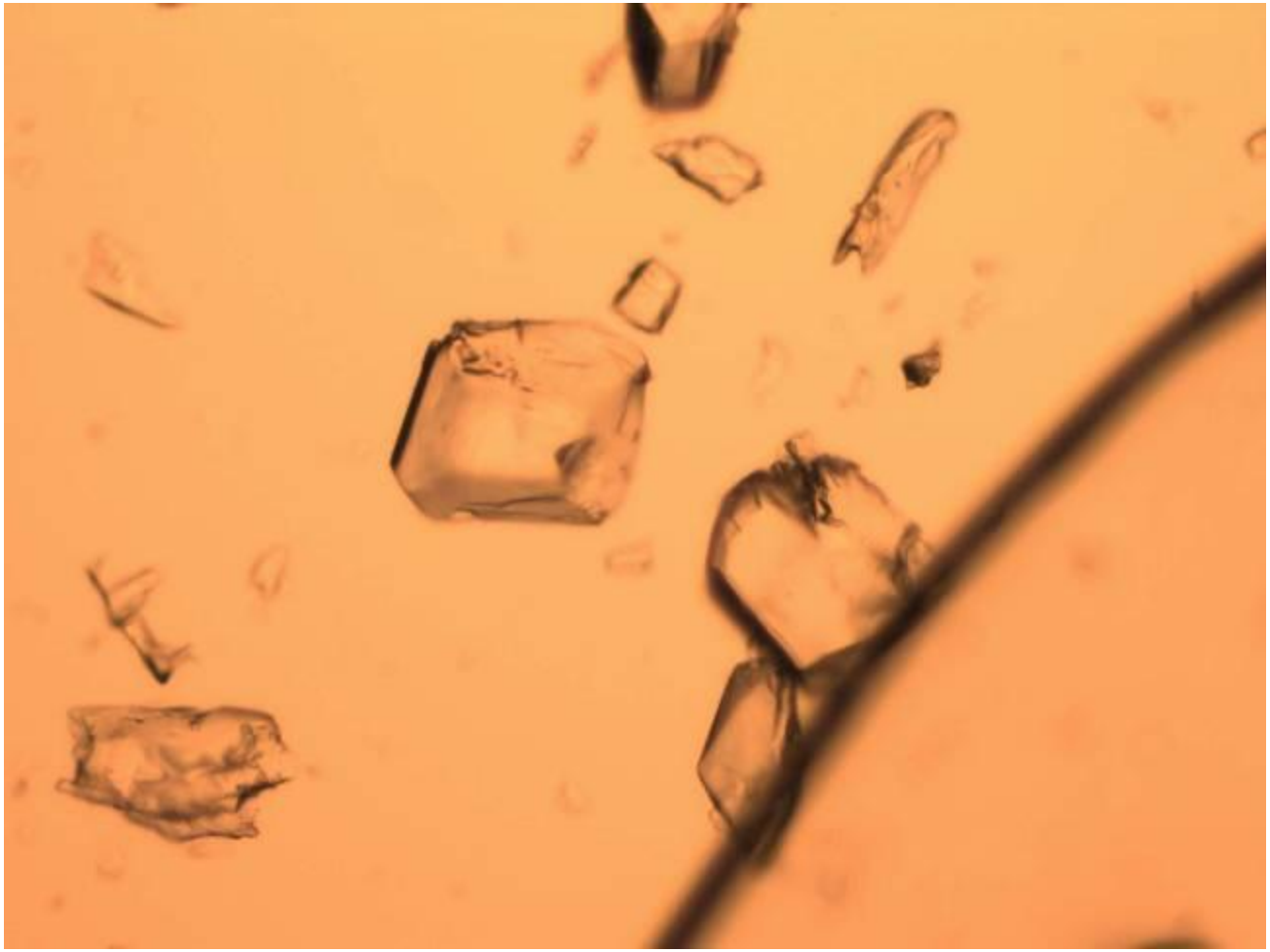
Disadvantages of the Brine Method

- 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.

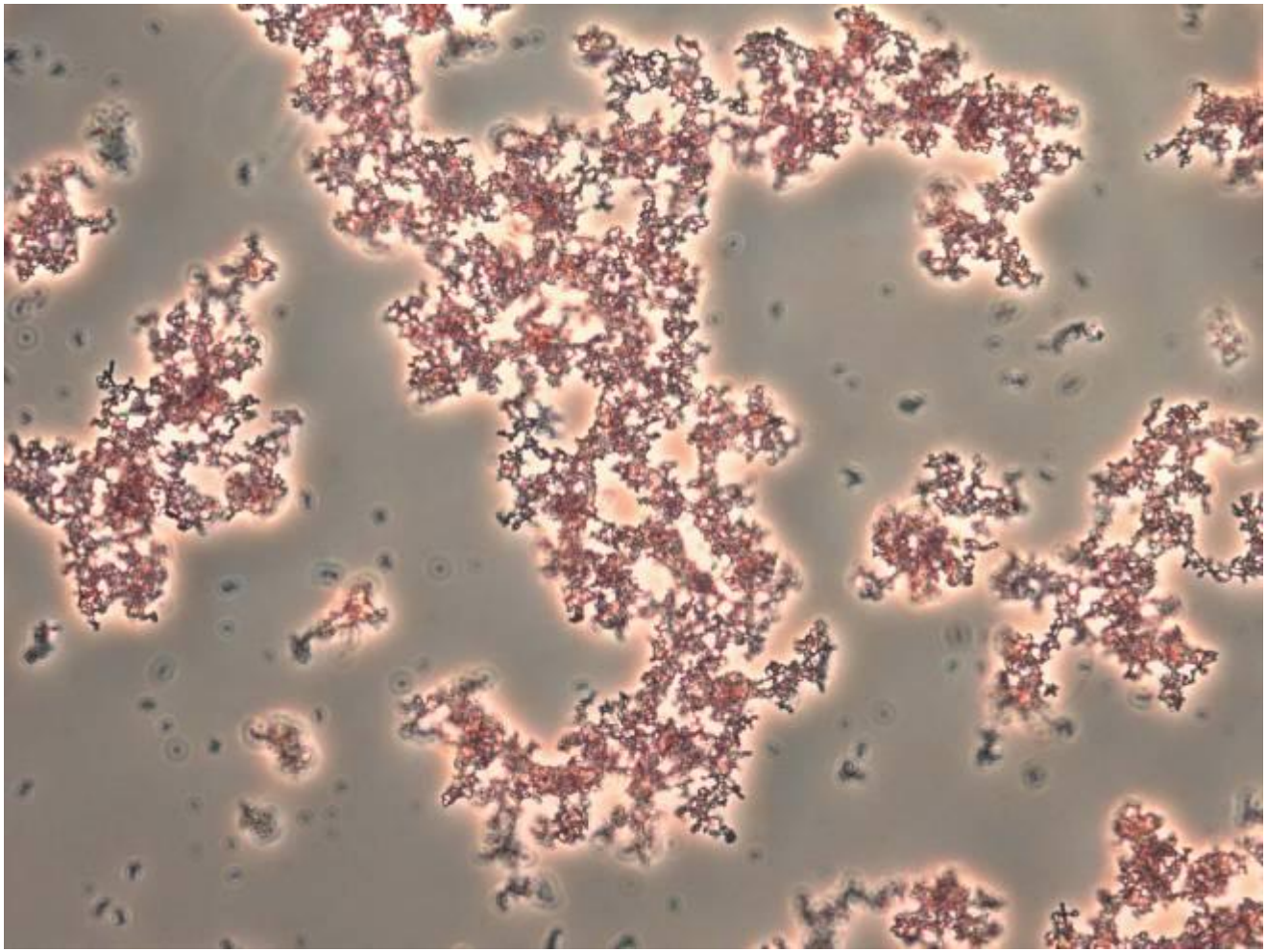
KHT



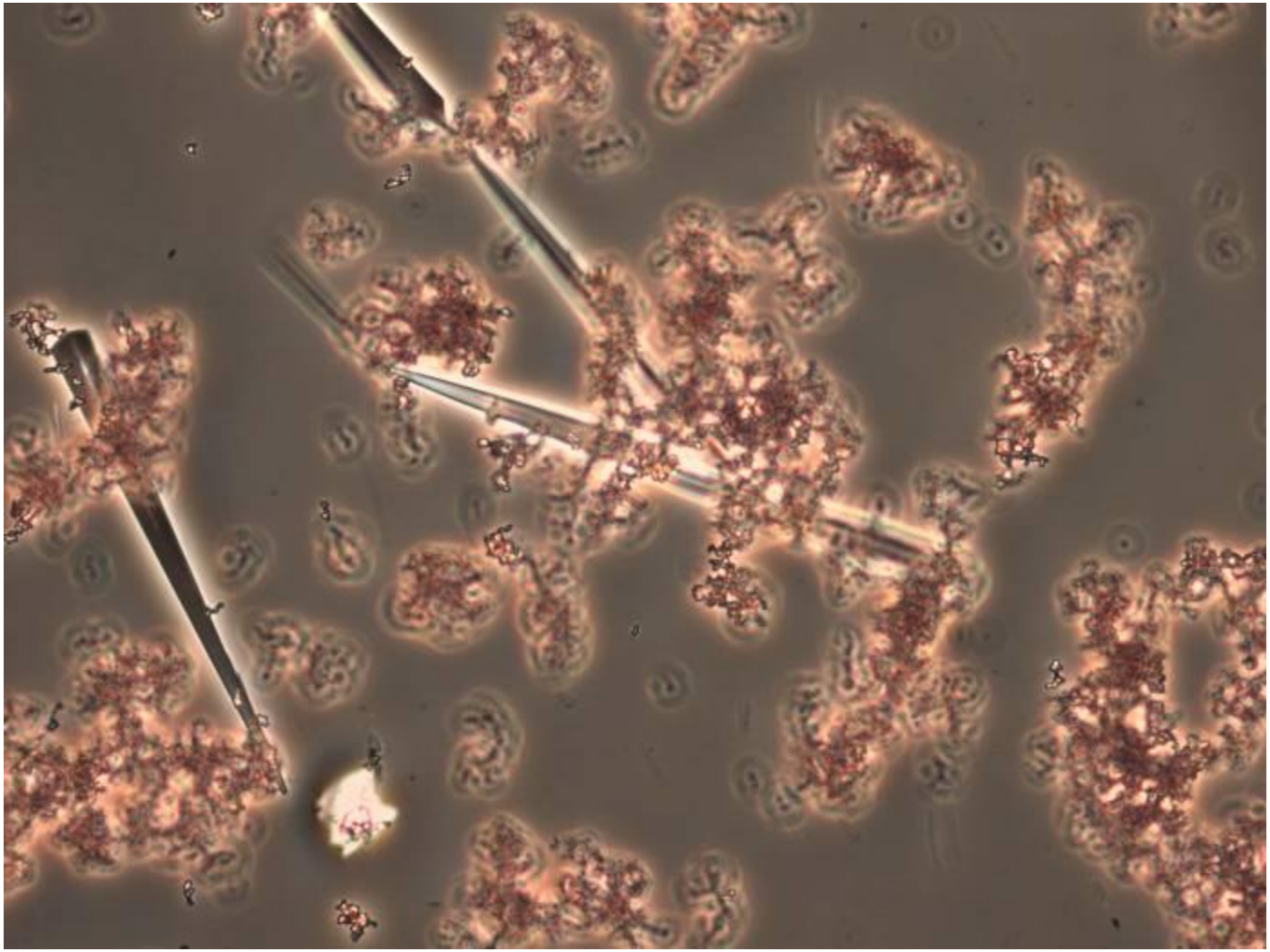
CaT



Amorphous Colour Compounds



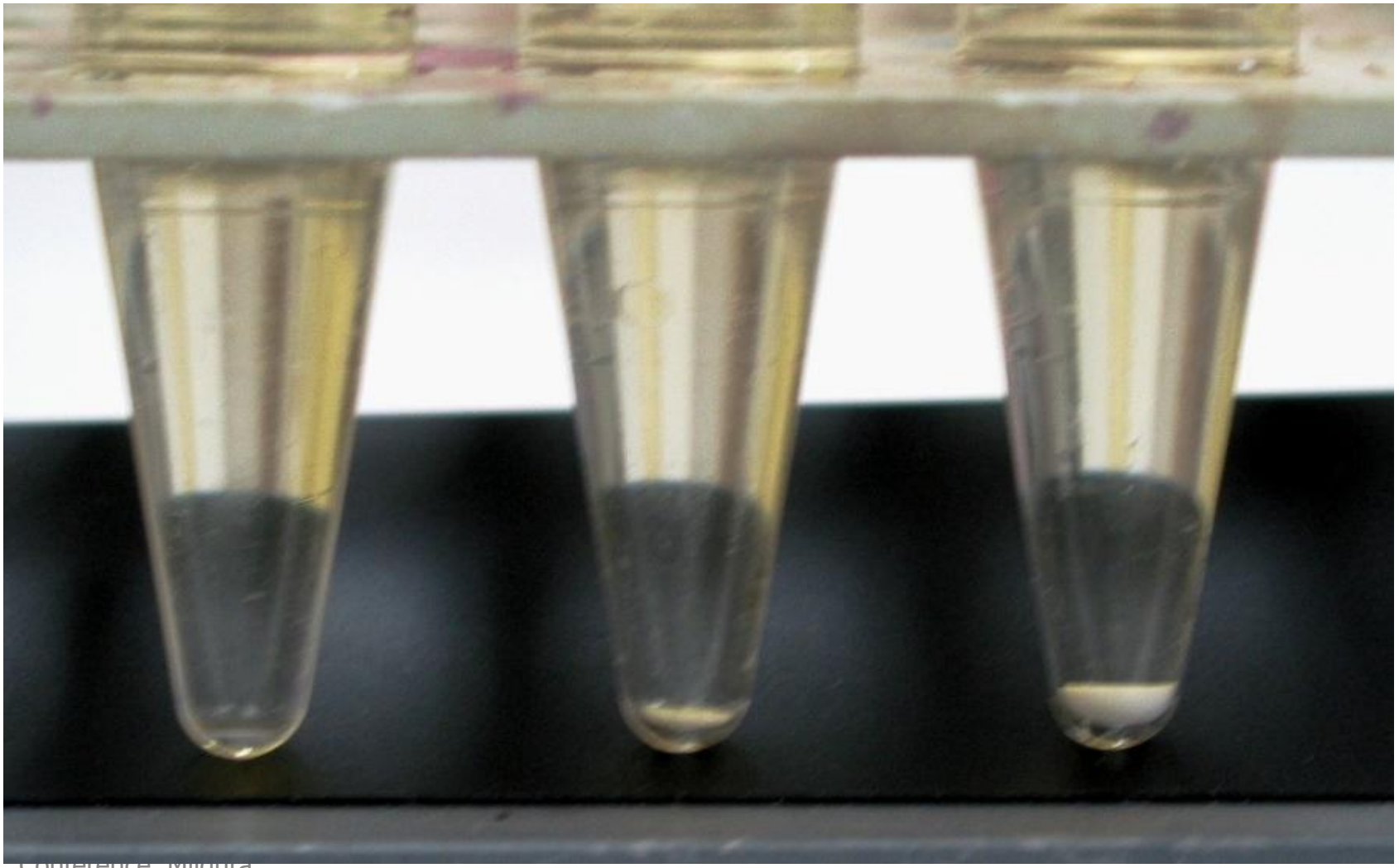
A Mix



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



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).

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 the 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 sparking 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.