Cold Stabilization Testing has Many Options

One new technique is showing good potential

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AS WINEMAKERS, WE ARE very concerned about how our products are perceived by consumers. Nothing drives a winemaker crazier than when customers start calling the winery about "glass" in their bottle of wine when he or she knows that every effort has been taken to assure that the wine is cold stable. It is for this reason that testing protocols have evolved over time. In many cases, those protocols have become very elaborate and are sometimes quite expensive.

The major challenge with cold stabilization procedures is that a wine may pass one cold stability test but then fail another test under different conditions or using a different procedure. Which test was correct? Unfortunately, it is possible that both can be right.

Why is Determining Cold Stability So Difficult?

Tartaric acid in wine has a unique property: it is capable of becoming supersaturated in an alcohol/water mixture. As more and more compounds are added to the mixture, the situation becomes complicated. Some compounds hasten precipitation while others delay precipitation.

Wine, as a complex beverage, makes this problem a difficult one to solve easily. It is as if the ions in wine are in a dance, floating in a solution and constantly in motion. In supersaturation, the dance floor is crowded, and theoretically, some of the ions should just pair up with their counterpart and "get off the floor." In a supersaturated solution, the ions just do not line up in exactly the right position to have that reaction take place, at least permanently. They come together and part again and again until enough come together in close proximity and proper alignment so that, as a group, they form a crystal. One crystal can float; many sticking together may fall out of solution.

Cold conditions bring the ions closer together, which increase the probability that they will align to form crystals. Other insoluble materials, such as a piece of dust, cork or a sharp edge, can act as a nucleation point and may allow the creation of strange crystal-like formations.

Over the years, nine general procedures have been developed to help winemakers decide if a wine is cold stable. Six of the procedures are analytical tests while three are cellar management techniques (see Box).

PROCEDURES TO HELP WINEMAKERS DETERMINE COLD STABILITY

1. **Analytical Methods**
   a. Cold Hold (with/without precipitation)
   b. Freeze/Thaw
   c. Refrigeration/Brine Test
   d. Conductivity (Contact Process)
   e. Concentration Product
   f. Saturation Point (TSat)
2. **Cellar Management**
   a. Refrigeration
   b. Electrodialysis
   c. Inhibitors

Analytical Methods

COLD HOLD

One of the original methods employed was the cold hold technique. Although this is a test method because it takes weeks to months, it is usually implemented as both a test and a process. In the days before refrigeration, winemakers noticed that wines that were held longer in cold temperatures had fewer crystals form in the bottle. Wineries in cool/cold climates could just open the doors to let cold air in or put the tanks outside. For wineries with warmer winter temperatures or winemakers who want more control over the process, it takes a very large amount of energy to cool large volumes of wine to proper temperatures.

Regardless of a winery's location, this method comes with several concerns. Does it get cold enough and for long enough to cool the wine to the right temperature? If it does, then the winemaker and the winery staff must make sure that the precipitation occurs on time and that the crystals are removed before the wine warms up. If the outside temperatures do not get cold enough for a sufficient length of time, does the winery have the resources to provide refrigeration to get the cooling process where it needs to be? Otherwise, another cold stabilization method must be employed.

Due to energy concerns, this method is more popular in colder regions. Whereas it is possible to just hold the wine at these low temperatures, many wineries that employ this method also add cream of tartar or potassium bitartrate to act as seed crystals.

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FREEZE/THAW

An early test of cold stability used by winemakers was to filter a wine and then freeze it for a certain length of time, usually 12 hours. After thawing the wine, a small amount of precipitate could initially be observed. After the wine was warmed for an hour to room temperature, it was swirled, and the crystals were either reabsorbed, or the crystals remained. In the first case, the wine was judged as cold stable, and in the latter case, it was not stable.

However, using this test that is based on the visibility of crystals is not reliably accurate. It is possible for there to be microcrystals in the wine that are not visible and not big enough to fall out. The winemaker wants there to be a good result and may accept the test as proving cold stability when, in reality, the wine is in a marginal condition, and it is only a matter of time before precipitates fall out.

REFRIGERATION/BRINE TEST

The next non-instrument test involves the creation of a refrigerated liquid that can be held at - 4°C for three days. If, at the end of that time, the same criteria of crystals that were formed then redissolve on warming, or no crystals are observed, the test is said to pass. Some laboratories that use this test have developed a system of grading where: 10 or fewer small crystals is borderline; more than 10, but not visible to the naked eye, are judged as unstable; and visible crystals, obviously, not stable as well.

CONDUCTIVITY TEST

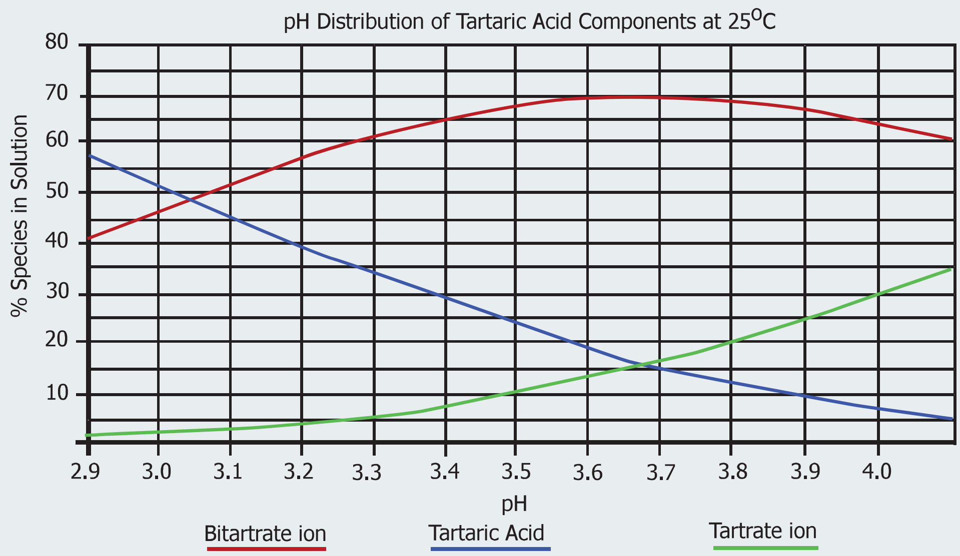
A relatively simple test to determine the degree of cold instability in a wine uses a measure of the wine's conductivity at a specific temperature. Different temperatures give different degrees of conductivity. As temperature falls, conductivity is reduced.

Using a stirred cell from Chemglass (**FIGURE 1**), a wine is reduced to its test temperature set point. A conductivity meter measures conductivity, and then potassium bitartrate (KHT) is added. The stirred cell continues for a standard time. Although some variability exists, the set point ranges from white wines (at about 0°C) to red wines (about 5°C), and the testing time is usually about 30 minutes. The amount of KHT added to the stirred cell is up to 4 g/L. If a wine has not been treated, the higher amount is added. If, after this run, the conductivity has not dropped more than 4 percent from the point where the stirred cell reached the test temperature, the wine is usually

FIGURE 1: A Hanna Instrument Edge pH, Conductivity and Dissolved Oxygen meter is used with a Chemglass stirred cell to do a conductivity test to determine the stability of a rosé wine in the lab at Tamanend Wine.

FIGURE 2: The graph of tartaric acid dissolution species illustrates the complexity of the ion's availability for potential crystallization and the influence of those ions on wine stability. The concentration product calculation can determine the percent contribution of each ionic species at specific alcohol, water, pH and ion concentrations at the different levels of each component.

It is important to note the inflection point of all three lines at a pH of about 3.65. This graph shows why a wine that has an initial pH above 3.65, once cold stabilization occurs, will have an ending pH higher than before cold stabilization. Conversely, when the wine's pH is below 3.65, the pH will actually drop. Depending on the wine style desired, judicious addition of tartaric acid at cold stabilization can dramatically influence the final pH of a wine at bottling.



considered stable. To rule out marginal cold instability, a second test at 1g/L KHT is indicated when conductivity is at or above the 4 percent level. Studies show that the amount of KHT above 4g/L does not significantly increase chances of a wine being more stable.

In my lab, I use the Hanna Instrument Edge, pH, Conductivity and Dissolved Oxygen meter. Having one meter with the three probes is convenient for most smaller labs. Other labs that perform larger volumes of the same test have opted for dedicated meters for each use. The 200ml stirred cell in **FIGURE 1** is connected to the wine lab's glycol system. An alternative is a table-top lab refrigerated cooler.

CONCENTRATION PRODUCT

Another method that relies on more sophisticated instrumentation determines the tartaric acid concentration product (CP_{KHT}). In this test, the concentration product is calculated by using the following equation:

$$CP_{KHT} = ((\text{Potassium, mol/L}) \times (\text{Tartaric acid, mol/L}) \times (\%\ \text{bitartrate ion}))/100 = ((\text{Potassium, mg/L})/39.1 \times 1000) \times ((\text{Tartaric acid, g/L})/150.1) \times ((\%\ \text{bitartrate ion})/100)$$

Tartaric acid instability is driven by the four measures of pH, alcohol, water and the amount of each species of tartaric acid as shown in **FIGURE 2**. There are many choices of equipment available to use to determine each of these elements. Because of the cost of these more sophisticated instruments, these analyses are primarily conducted in commercial wine laboratories.

This test procedure does appear to provide a more definitive test of cold instability. However, winemakers should remember that the fouling or delaying of cold stability by some compounds or the acceleration of it by other compounds in the wine means there is no clear benefit from this test over others, and it is, therefore, no more or less accurate.

SATURATION POINT (TSAT)

Each of the testing procedures described above has its measure of uncertainty, but even more uncertain is the future of that wine. In 2006, Ribereau-Gayon and his team of researchers described a conductivity methodology to determine a wine's tartrate concentration at room temperature that can be absorbed.[1] That information, combined with an Erbsloh EasyKrista test (available from IDL Consulting in the United States), can give an indication of the temperature at which precipitates will fall out of a wine (**FIGURE 3**).

The lower the temperature, the better the TSat test predicts a more stable wine. Conversely, the higher the temperature, the less stable the wine because of the many other competing elements in that wine, which can increase the probability of a precipitate forming. A pass or fail result is not a guarantee for the future—it only indicates the propensity of the wine at one point in time.

EASYKRISTA TEST FOR FUTURE WINE COLD STABILITY

KHT stability	White and rosé wine	Red wine
Stable	<12	<15
Unstable	12-16	15-20
Very unstable	16-20	20
Extremely unstable	20	–

FIGURE 3: The Erbslöh EasyKrista test assesses the crystal stability in wine using a conductivity meter.

Cellar Management of Cold Stability

REFRIGERATION

It takes 12,000 BTU to reduce a ton of water 1°F so that a wine can be chilled under mechanical refrigeration. To understand the impact on a winery's electric bill, that translates roughly into 3.515 KWh. Because of this expense, many wineries in climates with mild winters have been looking for alternatives.

Many wineries, especially in wine regions east of the Rocky Mountains, rely on cold winter temperatures to stabilize their wines. The cost of this method is low; but as mentioned above, this is a slow process.

Wineries that are looking for more convenient ways to achieve a secure cold stability for their wines add KHT to the wine, then stir, rack and filter the wine as soon as it passes their internal test procedures. It is important that wineries do this, before the temperature rises, to prevent the re-solubilization of KHT, which could potentially cause the wine to become unstable again.

Tartrates present another problem for wineries when precipitation occurs in unstable wines. Over time, wine tanks will accumulate large amounts of bitartrate crystals on the walls and at the bottom of the tank. Cleaning out those tanks can take a lot of effort. While there may be a greater volume of tartrate crystals after refrigeration is used to achieve cold stability, those crystals will form even without chilling. If a wine tank has a highly polished mirror finish on the inside, all that is necessary to achieve a spotless cleanliness on the tank's interior is water at 150°F. The crystals will "melt" off the tank, with no scrubbing required. This method is also more sustainable because it does not add harsh chemicals into the winery's wastewater system.

ELECTRODIALYSIS

For many years, larger wineries have used electrodialysis to achieve cold stability. It is definitely a great tool but often is too costly for many wineries. Oenodia is the company that offers this equipment for winery use. They have also developed a portable system that can arrive at a winery and cold-stabilize all of the winery's wine at one time.

This system uses a sophisticated set of membrane stacks that alternate fluid layers, one for wine and then one on either side of the wine layer that contains a brine. When this stack passes a direct current charge through the wine, the brine path acts as an electrical conductor and pushes the ions in the wine through the membrane to remove potassium and tartrate ions. The membranes are designed to let only these specific ions to pass through them.

While electrodialysis occurs quickly and at cellar temperature, it needs to take place after all blending is completed. For a smaller winery, all wines that need this cold stability treatment must be completely finished before the service arrives in order to avoid adding setup charges to the cost of production.

Another issue associated with electrodialysis is waste stream. In the past, electrodialysis produced a weak brine solution in approximately the same volume as the wine treated, and that brine had to be discarded. Oenodia now includes reverse osmosis in their service protocol to concentrate the liquid in its waste stream. Nevertheless, this is a concern that should be considered before proceeding with this processing method.

STABILITY AMENDMENTS

In the last several years, a number of compounds have been used to provide some degree of cold stability to a wine. These products include carboxymethylcellulose (CMC), mannoproteins, gum Arabic and metatartaric acid. With the exception of the latter compound, all are approved for use in this country. These compounds have not received a great deal of popularity because of inconsistent results in providing long-term complete cold stabilization. Instead, they are often added as an extra level of protection.

When CMC came on the market, followed closely with news that the mannoproteins also provided protection, there was considerable interest in these two items. However, both products were quickly proven to be somewhat temporary in their ability to prevent crystal formation. There were many wineries and brokers that found the protective function of these compounds was temporary, within a two- to four-year time horizon. Many had to call back wines because CMC did not confer permanent protection.

Within the last year, potassium polyaspartate (KPA) was approved for use in the United States and Canada, after having been approved in Europe for several years. In this country, KPA is marketed by Enartis. This product could be a real game changer for the wine industry.

Zenith, Enartis' brand name for this product, comes in two types: one for white wine (Zenith Uno) and one for red wine (Zenith Color). It is produced by recovering L-aspartic acid from a fermentation, which is next converted into polysuccinimide. That is then converted to KPA. The material is a colloid that entraps tartaric ion species, keeping them far enough apart to prevent precipitation.

The only special requirement for the use of this product is that the wine must be protein stable before it is added. The vast majority of all wines are routinely treated for protein stability. This requirement is especially important when treating red wines. If the wine is not protein stable, the color may drop out; and even after treatment, the wine may not be completely cold stable.

Initially, there was concern that this compound would have a longevity problem similar to that associated with CMC since it operated in basically the same mode of action. However, a paper in 2019 by R. Eder, et al., reported on an extensive study that looked at trials where wines were subjected to treatments comparing two wines against CMC and KPA.[2] One treatment held wines at 2° C and one at 20°C. The wines were incubated over 20, 70 and 175 days at these temperatures. In all cases, only the KPA-treated wines passed with no precipitates. To emulate long-term aging and the potential for the colloid to break down, the researchers added extra potassium and tartrate to overload the potential for precipitation. Again, only the KPA passed without incident.

Based on the above results and tests that I have conducted at Tamanend Wine's lab, it is my understanding that this treatment provides one of the more consistent sets of information that wines in both short- and long-term storage will have one of the best chances of remaining a "safe" wine.

APPROXIMATE COSTS FOR THREE COLD STABILIZATION PROCEDURES

	Cold Hold / 10 Hl		Electrodialysis / 10 Hl		Inhibitors / 10Hl	
Power	98 KWh@ .15/H	$14.70		$3.26		
Supplies	KHT	$0.05	Membrane Use Fee	$18.20	Zenith Uno	$1.80
Labor $17/hour		$21.60		$7.25		$2.50
Total		**$36.35**		**$28.71**		**$4.30**

TABLE 1

THE ECONOMICS OF THE TREATMENT OPTIONS

There are many elements to consider when looking into the various treatment possibilities to achieve cold stability. Among the considerations are winery size, desired quality level, length of time absolutely required, degree of risk and consumer tolerance to that risk. TABLE 1 gives the approximate costs for three cold stabilization procedures of 10 Hl (260 gal) lots. That information can be scaled up for the size of a given winery.

For the refrigeration method of cold stabilization treatment, the cost is about $36.35 per 10 Hl. Of that cost it is about 50:50 labor and power. For electrodialysis to treat a similar amount of wine, the costs are spread differently. There is a membrane cost of depletion of about $18 per 10 Hl, plus labor and remediation of wastewater for a total of 28.71 per 10 Hl. Finally, the only cost for KPA is $1.80 for materials and the time it takes to add 100ml to a tank and mix it into the wine, or about $5.

Conclusions

With all of the uncertainty about cold stabilization, the evidence so far indicates a high degree of confidence that KPA can and will be adopted by wineries of all sizes. It is easy to see why as the cost to treat the wine is low, the risks are at best the same as other methods, with what appears to be a better upside for long-term stability and no organoleptic changes to the wine. WBM

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