CLARIFICATION AND STABILIZATION IN WINE INDUSTRY
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Abstract

Grapes contain several organic acids including tartaric acid, and they contain potassium.
Tartaric acid (H2T) and its salt, potassium bitartrate (KHT), are considered normal constitutents of wine.
Potassium bitartrate is a clear, crystalline material, and grapes always contain some of this material. Sometimes potassium bitartrate is called "cream of tarter," but winemakers often call this material "tartrate."
Most producers stabilize their base wines to prevent bitartrate precipitation which can influence taste (KHT is both salty and bitter) and gas release from sparkling wines.
***Keywords**: tartaric acid, potassium bitartrate, cold stabilization, wine.*

Introduction

Our first impression of any wine is a visual one. Wine is seen before it is tasted, and wine is expected to be brilliantly clear and have an appropriate color. The consumer is always disappointed when a wine does not meet these visual expectations. Even zealous wine advocates shy away from turbid, dirty-looking wines. Judges at home wine competitions occasionally face this problem, and sometimes real courage is needed to taste a particularly ugly wine

The prevention of tartrate crystals in bottled wine is an important task for the winemaker. Although the crystals are harmless, the average consumer isn't likely to see it that way. With all the talk of contamination of foodstuffs, it is deemed necessary to ensure that wine is cold stable, i.e. that no tartrate crystals are present in the finished product.

Cold stabilization of wines takes a considerable amount of refrigeration power, and can cost a considerable amount of money. Winemakers should always strive to use the minimum amount of refrigeration to make the wine cold stable. Not enough refrigeration and the wine won't be stable, although too much refrigeration will certainly make the wine stable but will waste refrigeration resources unnecessarily.

Several techniques are in use to check the cold stability (also known as tartrate stability) of a wine. The most commonly used techniques will be discussed in this article.

Potassium Bitartrate

Potassium bitartrate (KHTa) is formed in wine, through the reaction between the bitartrate ion (HTa-), from tartaric acid (H2Ta), and the potassium ion (K+) found in grapes, especially grape skins.

K+ + HTa- <==> KHTa

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Potassium bitartrate (KHT) (Figure 1) is believed to be produced after veraison with the movement of potassium from the soil into the fruit. During ripening, the amount of undissociated tartaric acid decreases as the mono and dibasic potassium salts are formed. Simultaneously, tartaric acid is diluted at a rate depending on the variety and climatic conditions. Additionally, the tartrate content is also influenced by location, cultural practices, and the state of maturity.

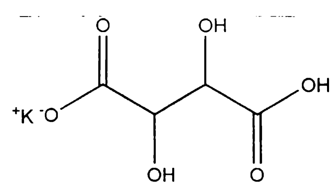

Fig. 1: Potassium bitartrate formula

The potassium uptake of the vine is dependent on factors such as rootstock, soil type and depth, irrigation treatment, etc. Thus, both tartrate and potassium contents differ widely with variety, region, climate, a viticultural practices. As a consequence, the enologist handles juices and wines that have large variations in KHT concentrations.

All wines differ in their "holding" or retention, capacity for tartrate salts in solution. If the holding capacity is exceeded, these salts will precipitate, resulting in the formation of "tartrate casse". Solubility of potassium bitartrate is dependent primarily upon the alcohol content, pH, the temperature of the wine, and the interactive effects of various cations and anions.

Although KHT is soluble in grape juice, the production of alcohol during fermentation lowers the solubility and gives rise to a supersaturate solution of KHT. In wine, the following equilibrium exists:

$$H_2T \rightleftarrows H^+ + HT^-$$
$$HT \rightleftarrows H^+ + T^-$$

Vines manufacture tartaric acid through the photosynthesis process, and the vines obtain potassium from the soil. Potassium reacts with tartaric acid and forms a material called potassium bitartrate.

Potassium bitartrate is a clear, crystalline material, and grapes always contain some of this material. Sometimes potassium bitartrate is called "cream of tarter," but winemakers often call this material "tartrate." Potassium bitartrate has several interesting physical properties:

- ✓ Only small quantities of this material can be dissolved in grape juice.
- ✓ After grape juice ferments, even less potassium bitartrate is soluble in the water-alcohol mixture.
- ✓ The quantity of potassium bitartrate dissolved in wine is strongly dependent upon the temperature. Cold wine cannot hold as much potassium bitartrate as warm wine.

In combination, these three properties produce an interesting winemaking problem. Generally, grape juice contains all the potassium bitartrate it can hold when the grapes are picked. Alcohol begins to accumulate when the grapes are fermented. As the alcohol concentration increases, the new wine becomes saturated, and potassium bitartrate precipitates out of the wine. As fermentation continues, more alcohol is produced, and more tartrate is forced to precipitate out of wine. By the end of fermentation, the new wine is over saturated with potassium bitartrate. The tartrate continues to drop out of the solution, but at normal cellar temperatures, tartrate precipitation is very slow. Often the tartrate crystals continue to precipitate for a year or more, so potassium bitartrate causes serious long term stability problems for the wine industry.

The following example illustrates a common tartrate stability problem. A new white wine is clarified and aged for several months. The wine is then filtered with a 0.45 micron membrane and bottled. The newly bottled wine is clear and bright, but the wine is still nearly saturated with potassium bitartrate. Ultimately, a consumer puts a bottle of this wine into a refrigerator for a few hours before it is served. The wine cools rapidly in the refrigerator, and potassium bitartrate precipitates out of the cold wine.

As tartrate drops out of solution, suspicious looking crystals are formed in the bottle, or dense hazes form. Tartrate hazes are very unsightly, and sometimes the consumer mistakes the tartrate crystals in the bottle for glass particles. In any case, the consumer is unhappy, and the winemaker is embarrassed.

All commercial white and blush wines are cold stabilized sometime during the winemaking process to remove the excess tartrate material before the wine is bottled.

Potassium Bitartrate Stability

Most producers stabilize their base wines to prevent bitartrate precipitation which can influence taste (KHT is both salty and bitter) and gas release from sparkling wines. There is wide variation in the exact procedure used by producers to determine KHT stability. A freeze test relies on the formation of crystals as the result of holding wine samples at reduced temperatures for a specified time period. Often a sample is frozen and then thawed to determine the development of bitartrate crystals and whether or not those crystals return to solution. Zoecklein et al. (1995) discussed some of the problems associated with using a freeze test to predict bitartrate stability. Several winemakers use a slight variation of the freeze test. Realizing that the prise de mousse will create anywhere from 1.1 - 1.5% additional alcohol (in mouseux production), they will fortify a small quantity of their cuvée and perform a freeze test on the fortified sample. Alcohol, among other factors, affects KHT precipitation. Fortification may be a desirable change to the freeze test procedure, but the inherent problems of the freeze test still exist even when the sample is fortified. An electrical conductivity test is a much more accurate method of determining bitartrate stability (Zoecklein et al., 1995).

Tartaric acid species in solution are available in three forms, as undissociated tartaric acid (H2T) as bitartrate ions (HT-) and as tartrate ions (T=). The percentage of tartrate present as HT- is maximum at pH 3.7, generally as a precipitate. Therefore, winemakers are concerned with the potential for bitartrate precipitation and preventing "tartrate casse" formation in the bottle. Crystallization depends on (1) the concentration of the salt and other components that may be involved in the crystallization equilibrium; (2) the presence of nuclei upon which crystalline growth may occur; and (3) the presence of complex factors that may impede crystal growth. In general, a certain level of supersaturation is necessary for adequate nucleation. Once nucleation has occurred, further crystal growth results in precipitation. During alcoholic fermentation, KHT becomes increasingly insoluble, resulting in supersaturation. Thus, bitartrate stability is frequently achieved naturally. Potassium bitartrate stability is also achieved by chilling (with or without seeding), ion exchange, or combinations of both. In conventional cold stabilization (chill proofing), wines are chilled to a selected low temperature in order to decrease KHT solubility. The optimum temperature needed for bitartrate stabilization is:

Temperature (EC) = % ethanol (vol/vol), divided by 2, minus 1

KHT precipitation occurs in two stages. During the initial induction stage, the concentration of KHT nuclei increases due to chilling. This is followed by the crystallization stage, where crystal growth and development occur. During conventional chill-proofing, precipitation is most rapid during the first 12 days. After the initial period, KHT precipitation decreases due to decreased levels of KHT saturation. Temperature fluctuations during cold stabilization may have a significant effect on reducing precipitation rates, because of the effect on the speed of nucleation. Without crystal nuclei formation, crystal growth and subsequent precipitation cannot occur. Therefore, simply opening the cellar doors in the winter, although cost effective, may not be ideal for KHT precipitation. Because of the potential for increased absorption of oxygen in wines held at low temperatures, alternatives have been sought.

Today, cold stabilization is the most widely used process to reduce the amount of tartrates in wine. Not only is it believed to help make wines more stable once bottled, but rounder and finer to the taste. Clark Smith co-founder of winemaking consulting firm Vinovation, Inc, disagrees. He believes the cold stabilization process actually tears the wine apart, leaving it a lesser wine than before being chilled to near freezing. "Cold stabilization is inconvenient, unreliable and expensive, robbing the wine of colloidal structure," he said. Smith believes colloids are imperative to a wine's structure, and that a new system of stabilizing wine, called electrodyalisis, removes unwanted tartrates without disrupting the colloidal structure.

Smith claims that the substantial amount of attention to detail in the winemaking process is all for naught because the wine is irreversibly damaged by cold stabilization. In some cases its heated back up after being frozen, further affecting the wine. "After cold stabilization, the wine falls apart, and many winemakers feel that those problems are a result of bottling, but in fact the problems began the day before, when they started chilling the wine."

In conventional cold stabilization procedures (chill-proofing), wines are chilled to a temperature designed to decrease potassium bitartrate(KHT) solubility, which optimally results in precipitation. The most important

Variables affecting the precipitation of potassium bitartrate during chilling are:

1) the concentration of the reactants, specifically tartaric acid,
2) the availability of nuclei for crystal growth, and
3) the solubility of the potassium bitartrate (KHT) formed. Perin (1977) determined the following relationship for determination of the temperature needed for KHT precipitation: KHT precipitation occurs in two phases. The induction phase is when the level of KHT in solution increases due to chilling. This is followed by the crystallization phase where crystal growth and development occurs. The rate of precipitation of potassium bitartrate at low temperatures is more rapid in table than in dessert wines and more rapid in white than red wines (Marsh and Guymon 1959). During conventional chill-proofing, precipitation is usually rapid during the first 12 days, then the rate of KHT precipitation diminishes considerably.

This reduction is due to a decreased level of KHT saturation in solution.

Temperature fluctuations during cold stabilization can have a significant effect in reducing the rate of KHT precipitation due to the large effect this has on the speed of nuclei formation. Without crystal nuclei formation, crystal growth and subsequent precipitation cannot occur. Simply opening the cellar doors in the winter, although cost effective, may not provide optimal temperatures for KHT precipitation or product palatability of certain wines. The increased absorption of oxygen into the wine at low temperatures over longer periods, and the subsequent oxidation of wine components, makes alternatives to conventional cold stabilization desirable.

Wine stabilization

Wine is often exposed to considerable heat when shipped long distances in the summer time. Most white and blush wines are chilled to about 50 degrees for several hours before they are served. Practically all commercial wines are specifically treated to make them stable, and after stabilization, wine appearance or quality will not be altered by reasonable temperature extremes. Most commercial winemakers consider wine stable if the wine does not show significant changes when exposed to storage temperatures ranging from 40 to 100 degrees.

Stabilizing a light, fruity white table wine is not trivial. Light, fruity wines can be damaged easily by over processing, excessive handling or oxidation, and producing good long term bottle stability without reducing the quality of a delicate wine requires considerable wine making skill.

Occasionally, a winemaking bottles a wine without doing stability tests. The wine has been brilliantly clear for several months, so the winemaker assumes the wine is stable. A few weeks after bottling, the wine develops a bad haze or drops ugly sediment in the bottles. Now the winemaker has little recourse because un-bottling, treating and re-bottling would destroy wine quality. Bottling unstable wine can be a discouraging event for any winemaker, and winemaker, and it can be an economic disaster for a commercial producer.

Cold stabilization

Practically all new wine contains excessive quantities of potassium bitartrate, and the tartrate precipitates out of cold wine as crystals or hazes. All wine and bluish wines require cold stabilization before bottling, and most commercial producers cold stabilize their red wine as well. Wine can be effectively cold stabilized in several ways. A few large wineries use ion exchange columns to remove potassium from the wine. Ion exchange columns are filled with resin and work on the same principle as domestic water softeners. This type of wine cold stabilization requires large, expensive equipment, and a trained chemist is needed to establish the proper operation of the exchange column. However, once the equipment is operating, the ion exchange method is a fast and economical cold stabilization process. Unfortunately, wine quality can be reduced when the ion exchange method is used inappropriately.

Smaller wineries use a much simpler method to stabilize their wines. The wine is cooled to about 27 degrees and held at this low temperature for a week or two until the excess potassium bitartrate precipitates. This method of cold stabilizing wine also has advantages and disadvantages. Low temperatures are beneficial to new wine in several ways. Besides causing the potassium bitartrate to precipitate, the cold temperature helps other unwanted materials settle out of the wine. Sometimes suspended pectin and gums can be removed by chilling the wine. In addition, several days of low temperature storage can be helpful in developing long term wine stability.

Unless the wine is carefully handled, considerable oxygen can be absorbed while the wine is cold. The oxidation problem can be managed by purging wine containers with an inert gas, keeping the containers completely full and by maintaining adequate levels of sulfur dioxide in the wine. The high cost of energy needed to operate the large capacity refrigeration system raises production costs, and many wineries use specially insulated tanks to stabilize their wines.

Tartrate crystals also form in red wines, but the dark color obscures small deposits of tartrate crystals. Red wines are not chilled before serving , so a haze seldom forms. Often the tartrate crystals in red wines are found adhering to the cork, and the crystals are removed when the cork is pulled. Tartrate crystals are not so noticeable in red wine, so a few smaller wineries and many home winemakers do not bother to cold stabilize their red wines.

However, most commercially produced red wines are cold stabilized before being bottled.

Hot Stabilization

Commercial wine is shipped long distance;; in warm weather, and under these conditions, protein stability causes hazes lo form in while or blush wine. Protein hazes are very unsightly, and the wine industry considers excess protein removal an indispensable treatment for all white and blush wines. Excess protein is not difficult to remove from most wines, but sometimes Sauvignon Blanc wines can be difficult to stabilize completely without damaging aromas and flavors. The standard treatment for all new white and blush wines is to fine with bentonite. The bentonite fining can be done anytime during me winemaking process, but the procedure is more efficient when the bentonite fining is done after the new wine has been rough filtered Nevertheless, many winemakers find it more convenient to stabilize their wines by removing the protein earlier in the winemaking process.

Bentonite additions rang from one to ten pounds per thousand gallons of wine. However, high dose rates can strip desirable flavors, so bench testing should always be done lo measure the minimum quantity of bentonite needed The treated wine is allowed to settle for a week or so before it is racked.

Tannin in red wine reacts with protein and causes the protein to precipitate out of the wine during fermentation. Little protein remains at bottling tome, so protein hazes are seldom a problem in red wine.

Combined Hot and Cold Stabilization

All white and blush wines require both hoi and cold stabilization treatments, and some winemakers combine both stabilization procedures into a single operation to reduce handling. First the wine is fined with bentonite and then the wine is immediately chilled to about 27 degrees. The wine is held at the cold temperature Tor a week or so while the tartrate precipitates when the excess tartrate is gone. The cold wine is racked or filtered off the bentonite and tartrate lees This combined procedure has some advantages The tartrate crystals settle on lop of the soft benionite lees forming a crusty layer, and the wine is much easier to rack off the compacted lees Both procedures are accomplished m a single winemaking operation, so labor is reduced Wine manipulation is reduced, and the risk of wine oxidation is reduced.

Conclusions

Wine enjoyment is strongly influenced by firt impressions, and our first impression with any wine is visual. Consequently , clarity and stability are extremely important to both homemade and commercial wines.

Practically all wines can be clarified, stabilized and prepared for bottling using standard winemaking practices These procedures include cooling the wine to cold temperatures, fining the wine with suitable materials and using appropriate filtration methods.

All white and blush wines require both hot and cold stabilization. and most commercial red wines are cold stabilized. Although they are perfectly clear, red wines can throw a noticeable deposit after bottling unless they have been stabilized fining, filtering or bulk aged for an unusually long time

Many factors are involved in producing high quality wine, and time, effort and good judgment are required.

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