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ENARTIS NEWS
WINE TARTRATE STABILITY

The presence of tartrate crystals in a bottle is commonly perceived as a fault by consumers. Crystals are mostly composed of potassium bitartrate but precipitation of calcium tartrate is becoming more and more frequent. While the formation of potassium salts can be prevented with the use of protective colloids, calcium stabilization requires specific interventions.

POTASSIUM BITARTRATE

Testing wine potassium tartrate stability

The Minicontact test (measurement of wine conductivity variation before and after refrigeration for 30 minutes with potassium bitartrate seeding) and the cold test (6 days storage at -4°C) are quite reliable tests for evaluating wine stability.

Wineries that do not have access to the Minicontact test and that want to save time, often prefer to use the freeze/thaw test (wine is frozen for a few hours and then thawed before being inspected for any sign of crystalline tartrate precipitation). This method overestimates wine instability. As ice formation occurs, all solutes, including potassium, tartaric acid and alcohol, are concentrated and the precipitation that happens is not related to wine concentration condition. Furthermore, ice formation damages protective colloids structure that consequently lose their stabilizing effect. For this reason, its use is not recommended.

Potassium bitartrate stabilization

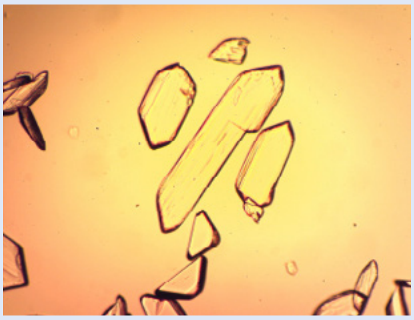
There are various methods that can be used during the winemaking process to reduce potassium bitartrate (KHT) precipitation in bottled wines. Some techniques are considered "subtractive" and involve reducing the concentration of tartaric acid and/or potassium in wine (tank cooling, electrodialysis, cation exchange resins). Other "additive" techniques make use of protective colloids or crystallization inhibitors which can be added to wine. Additive techniques are more respectful to sensory qualities, environmentally friendly and economically sustainable. However, not all permitted protective colloids are effective in the same way and some of them have specific limits under certain circumstances (table 1).

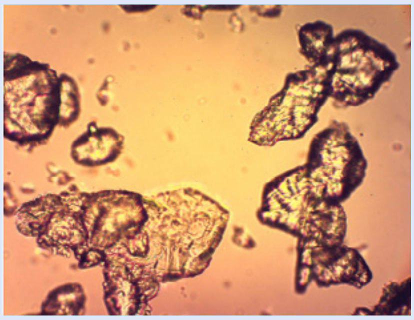
Despite the differences among protective colloids, the stabilizing effect depends on their capability of opposing the growth of the nuclei around which crystals are formed. If the dose is too low, inhibition is only partial and anomalies and unevenness are observed in the shape of the crystals (picture 1).

Table 1: Protective Colloid Characteristics

	METATARTARIC ACID	MANNOPROTEINS	CMC	POTASSIUM POLYASPARTATE
Stabilizing Effectiveness	Very good	Medium	Very good	Very good
Lasting Stabilizing Effect	Scarce	Very good	Very good	Very good
Filterability	Very good	Medium-good*	Medium-good*	Very good
Reactivity with Color Compounds	None	None	Yes	None
Reactivity with Wine Proteins	Yes	None	Yes	Yes

*Dependent on CMC degree of polymerization and mannoprotein average molecular weight.





Picture 1: Inhibitor colloids interfere with KHT crystal growth. Left: KHT crystals. Right: KHT crystals formed in presence of CMC.

Wine suitability for stabilization with colloids

When protective colloids are used for KHT stabilization, wine must meet some requirements:

1) ***Protein stability***
   Metatartaric acid, CMC and potassium polyaspartate (KPA), unlike mannoproteins, are quite reactive with wine proteins due to their high negative charge. For this reason, it is imperative to check wine protein stability and be sure wine is well below the maximum stability limit, whatever the analytical method used. Wines close to the stability limit can form haziness or sediment when metatartaric acid, CMC and/or KPA are added. Preliminary lab addition trials can easily be performed and are very useful for preventing problems and extra labor in the cellar. If haziness appears, bentonite fining is necessary.
2) ***Color stability***
   Color stability is a necessary requirement for all red and rosé wines, regardless of whether they are tartrate stabilized through the use of colloids.
   With the only exception of CMC, tartrate stabilizing colloids do not stabilize nor destabilize wine color. CMC, on the other hand, can react with color compounds causing their precipitation also in color stable wines. This is the reason why CMC is not permitted for red wine stabilization neither by the EU regulation nor by the OIV. In case of application in rosé wine, it can be safer to use it in combination with gum Arabic.
3) ***Filterability***
   Wine filterability must be adequate for final filtration.
   Metatartaric acid and KPA do not change wine filterability. Once they are homogenously distributed, wine can immediately be bottled.
   On the contrary, mannoproteins and CMC can decrease wine filterability.
   CMC effect depends in its degree of polymerization (DP): the higher the DP, the greater the clogging effect. With high DP CMC, waiting 3-4 days between the addition and final microfiltration helps to bring the filterability index back to acceptable values. Mannoproteins can have very different average molecular weights depending on the method used for their production. Consequently, they can have a different impact on wine filterability. Information provided by suppliers are helpful to understand how to manage filtration.

CALCIUM TARTRATE

Testing wine calcium tartrate stability

The main problem with calcium tartrate (CaT) is understanding if wine can form precipitate.
Stability tests used to verify KHT stability (cold test and minicontact test) do not confirm if wine is calcium unstable. The reason is that cold temperatures have little effect on the rate of CaT precipitation and the tests are not long enough. In fact, wine low calcium content together with the high energy required by the formation of nuclei of crystallization make CaT precipitation very slow, it can take years, and unpredictable.

Wine calcium content is the most used parameter to classify a wine stable or unstable. For red wines, 60 mg/L is considered the safe maximum limit, for white wine the limit is 80 mg/L. These indications, which are the result of research carried out mainly in the 1950s and early 1990s, must be considered carefully today, given that the wines of those days are very different from those of today. This makes these references not always appropriate to current conditions and a possible reason for underestimating the problem. To clarify the concept, let's make an example. A red wine with 60 ppm of calcium, at pH 3.4 does not produce precipitate, whereas at pH of 3.7 or higher, it is very likely to form an abundant calcium tartrate sediment.

A more reliable test consists of seeding a sample of wine with micronized calcium tartrate and measuring the quantity of calcium precipitated after 24 hours storage at a cold temperature. The difference between initial and final concentration indicates the level of instability:

$\Delta Ca < 15$ ppm	Stable
15 ppm $< \Delta Ca < 25$ ppm	Lightly unstable
$\Delta Ca > 25$ ppm	Very unstable

Calcium tartrate stabilization

The only colloid that has a significant effect for CaT stabilization is metatartaric acid. Unfortunately, since it hydrolyzes quickly, its effectiveness is short and can only be used for wine with a very rapid rotation.

Alternatively, techniques based on calcium or CaT removal provide a more reliable and long-lasting stability (table 2). This can be achieved by using physical treatments or chemicals.

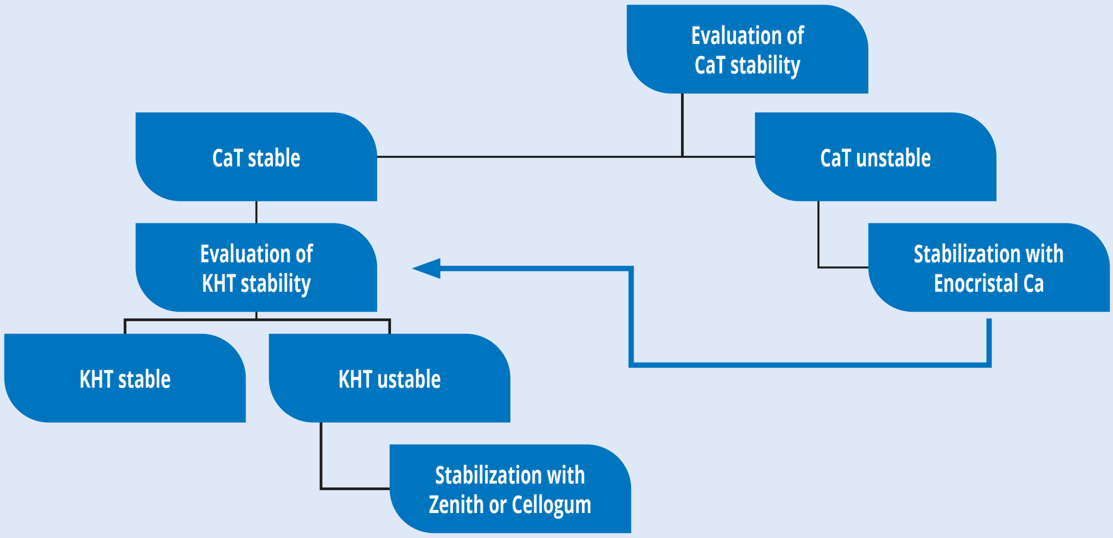
Electrodialysis is very effective but this technology is not broadly available to everyone and, by removing tartaric acid and potassium, it has an impact on wine sensory qualities and ageing potential.

Cation exchange resins help reduce calcium content, but their effectiveness on CaT stability is mainly due to their action of lowering wine pH. Unfortunately, the lowering of pH is not always organoleptically pleasing.

Table 2: treatments that impact wine calcium tartrate stability

	Cold Stability	Electrodialysis	Cation Exchange Resins	Metatartaric Acid	D,L-Tartaric Acid	Micronized Ca-Tartrate
Stabilizing Mechanism	Precipitation of CaT	Removal of Ca	Removal of Ca; Reduction of pH	Interference on CaT crystal growth	Ca removal by formation of Ca D,L-tartrate	CaT removal by seeding nuclei of crystallization
Effectiveness	Scarce	Good	Medium	Good short-term; None long-term	Very good	Very good
Limits	Cold temperature has little effect on CaT precipitation	Removal of tartaric acid; lower wine ageing potential	Uncontrolled Ca removal, strong sensory impact due to pH reduction	Short-term stabilizing effect	Risk of abundant crystal precipitation over time	Treatment takes 7-10 days
Advantages		Fast and controlled process		Easy and repectful of wine quality		Easy-to-use and respectful of wine quality

Cold stability is not a reliable technique. Low temperatures do not significantly increase or accelerate CaT precipitation and the usual 7-14 days cooling treatment can be too short.
Calcium tartrate and D, L-tartaric acid are the only chemicals permitted by the OIV for CaT stabilization.
D, L-tartaric acid effectiveness is supposed to depend on its capability to form a calcium salt that is much more insoluble than the one formed by the L-tartaric acid naturally present in wine. This characteristic is not enough to make D, L-tartaric acid a reliable stabilizer. The formation of nuclei starting the crystallization process takes a long time and, because of the high insolubility of calcium D, L-tartrate, its application can easily cause abundant precipitation over time. Furthermore, D-tartaric acid is NOT generally recognized as safe, and neither is the racemic D,L mixture, because it can form kidney stones.
Calcium tartrate, and specifically micronized calcium tartrate, is used for seeding nuclei of crystallization. In this way, it is unnecessary to wait for the spontaneous and unpredictable formation of nuclei, while at the same time promoting a rapid formation and precipitation of crystals. Because of the insolubility of calcium tartrate, treatment can be done at cellar temperature, (10-15°C), avoiding cooling. Crystal precipitation takes approximately 7-10 days and guarantees wine stability without impacting wine sensory.
Since CaT precipitation induces KHT precipitation and not the other way around, it is more convenient to start stabilizing calcium first then potassium (picture 2).



Picture 2: Wine tartrate stabilization procedure flow-chart.

ENARTIS SOLUTIONS FOR COMPLETE TARTRATE STABILITY

SOLUTIONS		Application				
		KHT Removal	KHT Removal	KHT Removal	CaT Stabilization	Color Stabilization
AMT PLUS QUALITY	Metatartaric acid		✓		✓	
ENOCRISTAL Ca	Micronized calcium tartrate			✓		
ENOCRISTAL SUPERATTIVO	Rapid crystallizer for cold stabilization of tartrates, containing neutral and acidic potassium tartrates.	✓				
CELLOGUM L	5% CMC solution		✓			
CELLOGUM LV20	20% solution of highly filterable CMC		✓			
CELLOGUM MIX	Solution of highly filterable CMC and gum Arabic seyal		✓			
ZENITH UNO	10% solution of A-5D K/SD potassium polyaspartate		✓			
ZENITH COLOR	5% solution of A-5D K/SD potassium polyaspartate (KPA) and gum Arabic Verek		✓			✓
ZENITH PERLAGE	Solution of A-5D K/SD potassium polyasparate and mannoproteins specifically designed for sparkling wine stabilization		✓			
ZENITH WHITE	Solution of A-5D K/SD potassium polyasparate, highly filterable CMC and gum Arabic seyal		✓			
ENARTISSTAB CLK +	Formulation of mannoproteins and A-5D K/SD potassium polyaspartate		✓			

Via San Cassiano 99, - 28069 San Martino Trecate NO, Italia - www.enartis.com