

CALCIUM TARTRATE INSTABILITY - A new and increasingly widespread oenological challenge that can be managed by safe and easy-to-apply means.

The correct estimation of the risk of crystallization and the appropriate use of resolution tools allows effective control of this potential criticality.

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INTRODUCTION:

Tartaric stabilization of wines has historically been linked to the management of what is commonly known in oenology as cream of tartar, chemically represented by potassium bitartrate. In the last decade, and with increasing frequency, tartaric instability has also manifested itself as precipitation of another salt that forms under different conditions and with different timing from the cream of tartar: calcium tartrate. Today, the correct manner of tartaric stabilization cannot disregard the monitoring and management of both salts of tartaric acid, a practice that has not yet become part of the routine activity of many oenologists who hope not to have the need for it.

Case histories indicate that the spread of the problem occurs in parallel with the gradual rise in the pH of the wine, which in turn is related to the rise in temperature.

Many studies are underway to better understand the factors involved in the manifestation of calcium instability.

Here we will try to describe the subject in its main parts: the origin of calcium in grapes, its functions in the plant, its possible reactions in wine, monitoring and stabilization methods.

Calcium in grapes

The amount of calcium absorbed by the vine depends largely on the characteristics of the soil: the more alkaline the soil is, the greater the calcium accumulation will be (Figure 1).

In calcareous soils, therefore, high amounts of calcium are constantly available to the plant.

In general, nitrates promote calcium uptake, while some metals (e.g. K⁺, Mg²⁺) decrease it.

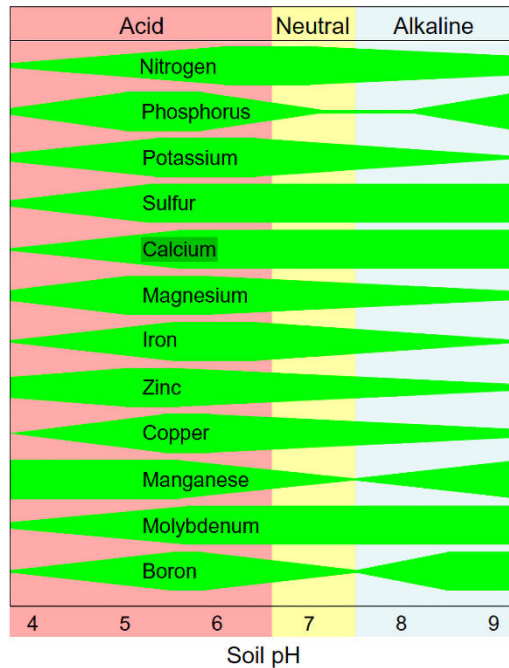


Figure 1. Nutrient availability depending on soil pH. ^[1]

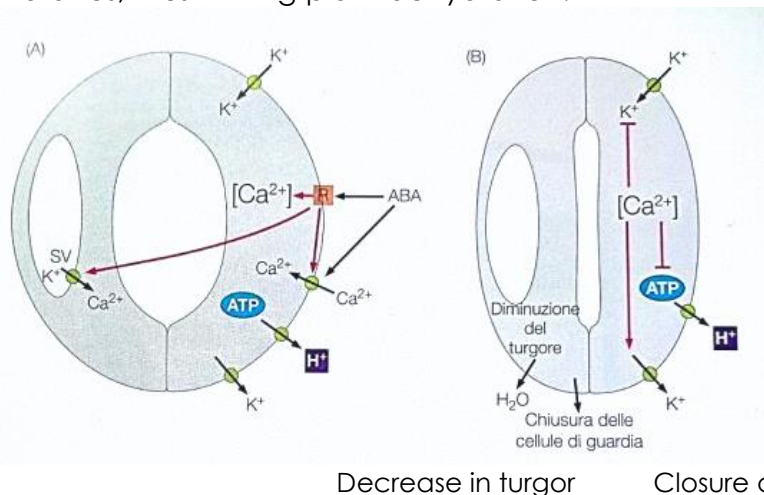
Role of calcium in the vine ^[5]

Calcium is an essential element for the growth and development of all plants. It has two main functions: a messenger in response to stress conditions and a component of cell walls and membranes. Most calcium is stored as calcium pectate in the cell wall while in the vacuole it is found in the form of calcium oxalate. It moves mainly through the xylem vessels depending on the transpiration activity of the plant. 75-90% of the calcium content is already present in the berry before veraison.

Calcium plays an essential role in thermal stress.

In leaves, it increases tolerance to high temperatures by activating a system to protect photosynthetic structures from oxidation. Heat-stressed cells accumulate calcium in the cell fluid to reduce cell membrane permeability and water loss. In buds, in the event of low temperatures and rapid variations in thermal conditions, part of the calcium is temporarily translocated from outside to inside the cell. This signal seems to activate the acclimatization process by which the plant acquires tolerance to cold. In the event of water stress, an increase in pH and calcium in the cell fluid indirectly causes potassium and anions to be released from the guard cells of the stomata which, by losing their turgidity, cause the stomatal openings to close (Figure 2). In addition, calcium accumulation

inhibits aquaporins, proteins that promote the passage of water through cell membranes, thus limiting plant dehydration. [2]



Decrease in turgor Closure of guard cells

Figure 2. Ca²⁺ and cellular regulatory mechanisms.

In conclusion, the increase in calcium content in the grape is due to a number of concomitant causes: soils with an alkaline pH, high availability of nitrates, high transpiration of the acid before veraison, mobilization of calcium in response to thermal and water stress.

Calcium tartrate in wine

Having understood the possible reasons for increased calcium content in grapes, it is now useful to summarize the main information about calcium tartrate and to define the oenological conditions in which the management of this salt can become problematic. Calcium tartrate forms crystals that are very different from potassium bitartrate and therefore easily recognizable under the microscope (Figure 3).

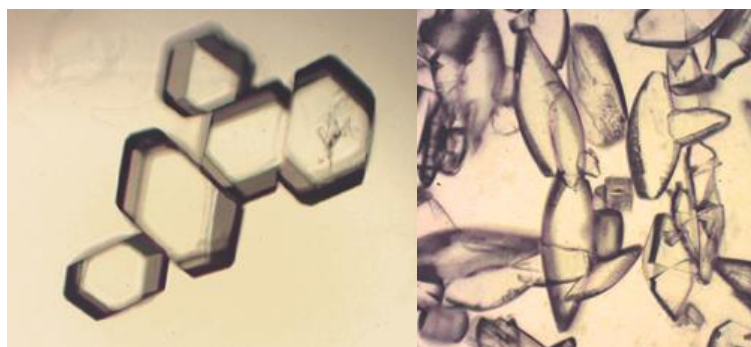
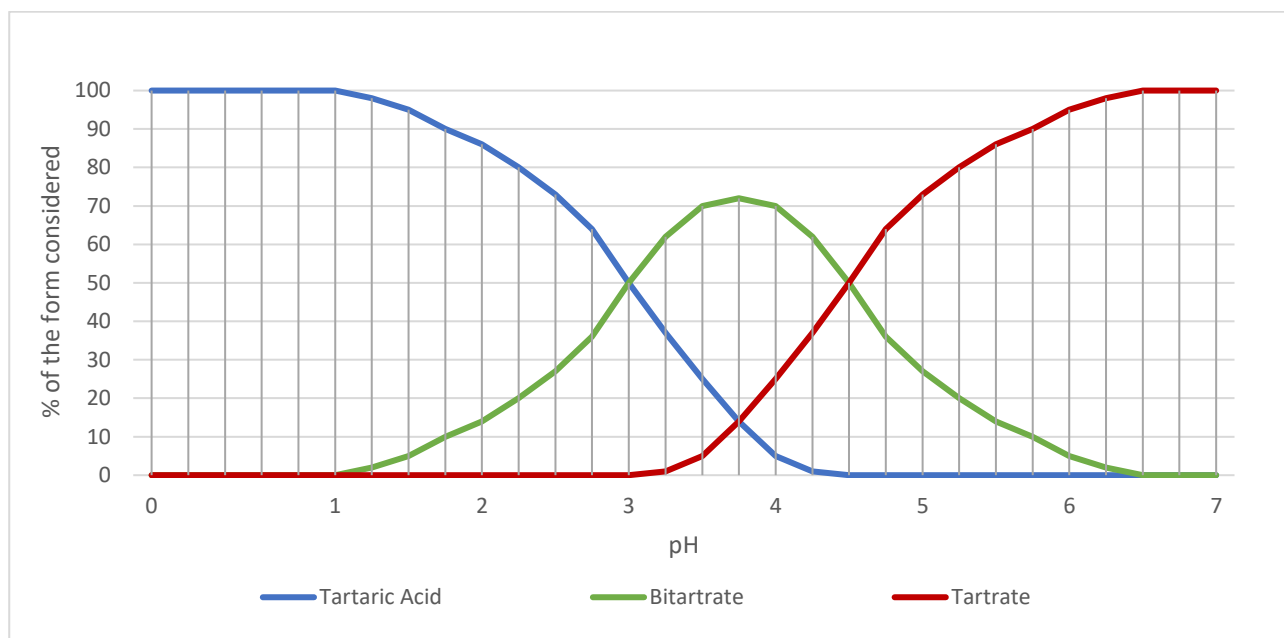


Figure 3. Typical crystal shapes of CaT (left) and KHT (right).

Its solubility in water at 20°C is 0.53 g/L, much lower than the 5.7 g/L of cream of tartar. The kinetics of crystallization are very slow. The limiting factor is the initial nucleation phase, which requires a lot of energy to form the crystallization germ. In addition, unlike potassium bitartrate, the precipitation of calcium salt is little affected by the temperature drop. The pH plays a key role in the formation of calcium tartrate because it regulates the dissociation equilibrium of the tartaric acid: the higher the pH, the higher the percentage of tartrate ion present and, consequently, the more likely it is that calcium tartrate will be formed (Graph 1).



Graph 1. Dissociation equilibrium of tartaric acid depending on pH. ^[4]

In wine, there are natural factors that hinder the formation of this salt, such as malic acid and magnesium.

Even today, the stability of calcium tartrate is often estimated on the basis of the calcium concentration found in wine. Many publications indicate 80 mg/L for white and rosé wines and 60 mg/L for red wines as threshold values above which the wine is considered unstable [3]. These values, which are the result of research carried out mainly between the 1950s and the beginning of the 1990s, need to be considered carefully today, given that the average pH values of wines at that time were very different from those of today. This makes these references not always appropriate to current conditions and a possible reason for underestimating criticality.

To better clarify the concept, let us give a numerical example. A red wine with a calcium content of 60 ppm at a pH of less than 3.5 produces no precipitate, whereas at a pH of 3.7 or higher, it is very likely to form an abundant crystalline sediment.

How can we tell if a wine is unstable?

In order to quickly identify wines at risk of instability, it was necessary to develop a method that takes into account the three parameters that most influence the crystallization process of calcium tartrate: pH, tartaric acid concentration and calcium concentration. Conductivity analysis tools, so useful in defining the stability condition of potassium bitartrate, are of no help in the case of calcium salt.

The test is based on the analysis of the calcium concentration of wine before and after the addition of 400 g/hL of micronized calcium tartrate and cooling at 0°C for 24 hours. The difference between initial and final concentration indicates the level of instability (Table 1).

Reference values ΔCa (ppm)	
< 15	stable
$15 \leq X \leq 25$	slightly unstable
> 25	unstable

Table 1. Reference values for defining the stability level of calcium tartrate in wine.

The application of this method to hundreds of wines monitored over a period of three years (as an example, the data for some samples are shown in Table 2), has made possible to build up a solid database from which a multifactorial statistical calculation method based on the Yates algorithm has been developed, enabling the level of instability of wine to be estimated in real time.

Samples	pH	Tartaric acid (g/L)	[Ca ²⁺] _i (ppm)	[Ca ²⁺] _f (ppm)	Δ[Ca ²⁺] (ppm)	Test result	Crystals in the sample
Wine 1	3,14	2,5	78	78	0	Stable	No
Wine 2	3,3	1	75	74	1	Stable	No
Wine 3	3,6	0,9	75	66	9	Stable	No
Wine 4	3,5	2	93	79	14	Stable	No
Wine 5	3,4	1	75	57	18	Slightly unstable	Yes after 35 days
Wine 6	3,3	1,8	85	62	23	Slightly unstable	Yes after 35 days
Wine 7	3,8	0,7	68	46	22	Slightly unstable	Yes after 35 days
Wine 8	3,35	3,2	87	39	48	Unstable	Yes after 20 days
Wine 9	3,35	3,2	117	48	69	Unstable	Yes after 20 days
Wine 10	3,26	4	111	22	89	Unstable	Yes after 20 days

Table 2. Example of analysis of samples in the database. Wines stored at 0°C. ¹¹¹

This new tool represents an important opportunity for winemakers because it allows them to decide in real time how to treat the wine based on the analytical values of pH, tartaric acid (g/L) and calcium (ppm). Examples of the response of the multifactorial statistical calculation method are shown in [Figure 4](#).

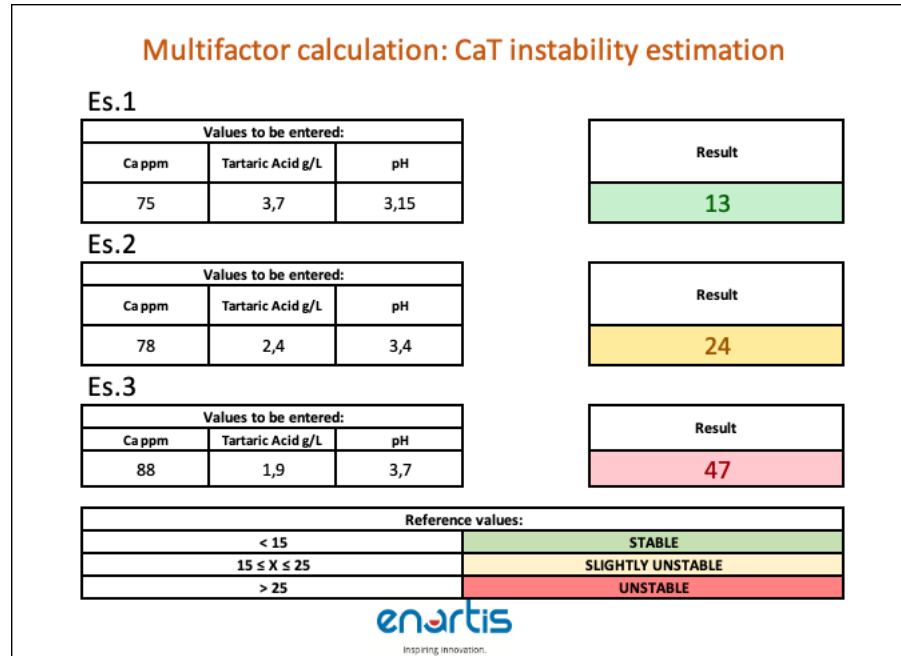


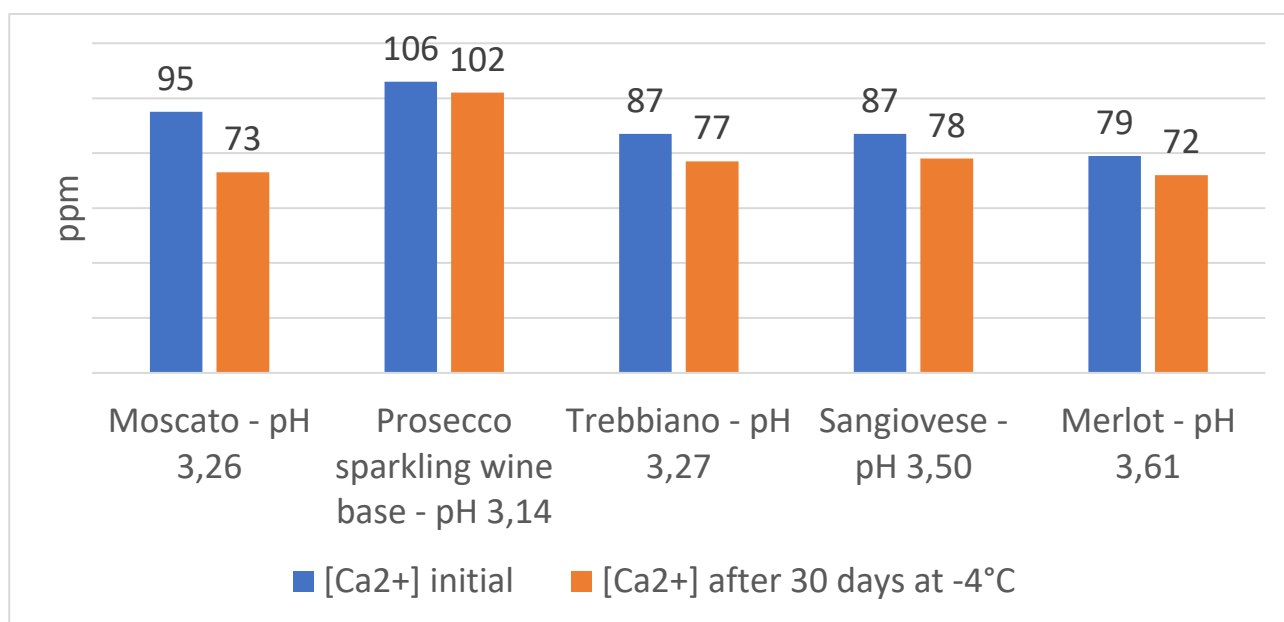
Figure 4. Example of results obtained through the multifactorial statistical calculation method. [11]

How to solve instability cases

If the tests described above indicate an unstable condition, it will be necessary to adopt appropriate solutions to avoid precipitation of calcium tartrate in the bottle.

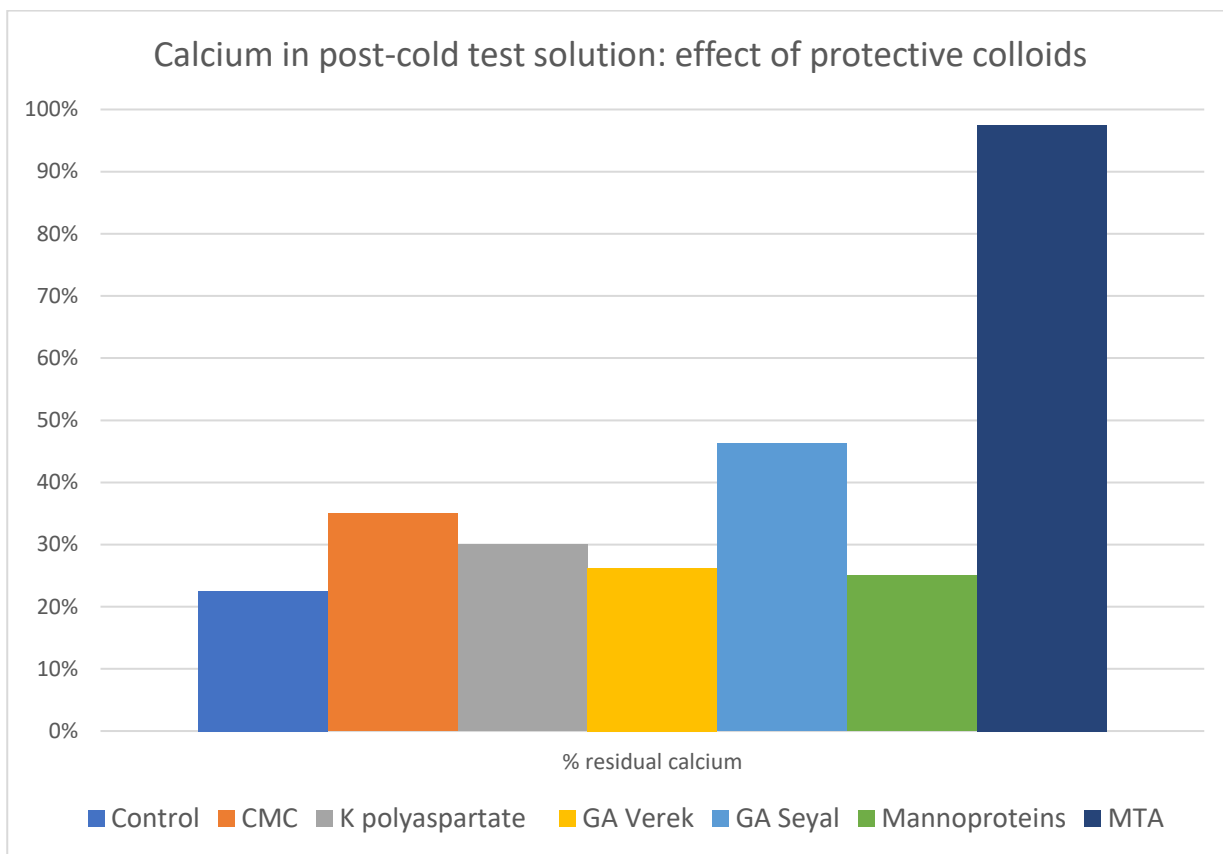
Among the available stabilisation techniques, which ones guarantee the stability of calcium tartrate?

The use of cold treatment or protective colloids is not a good solution. As mentioned above, the use of cold treatment, only slightly accelerates the sedimentation kinetics of calcium tartrate, so cooling the wine is not a solution, as the data in [Graph 2](#) show.



Graph 2. Calcium ion concentration (ppm) in samples of wine before and after prolonged cold treatment. ^[11]

Protective colloids generally do not have sufficient inhibitory action on CaT crystal formation, although they are able to partially modify its shape. Only metatartaric acid is able to prevent crystallization of the salt, but only for a limited time, due to its high susceptibility to hydrolysis, which causes it to lose its effectiveness rapidly.



Graph 3. Effect of oenological protective colloids on the CaT stability ^[11] of a wine-like solution containing 12% alcohol, 5 g/L tartaric acid, 80 ppm initial calcium and pH 3.4. Analysis of calcium in solution carried out after 6 days of storage at 0°C.

Greater effectiveness is found in the use of ion exchange resins and electrodialysis. The first, if specific for bivalent cations, improves the stability of CaT by removing calcium and, indirectly, by lowering the pH. The effectiveness of electrodialysis, on the other hand, is due to a reduction in the concentration of the two main instability factors: calcium and tartaric acid. Both techniques are not specific to CaT stabilization but can help reduce the risk of precipitation in the bottle. It should also be stressed that these practices are subject to local regulations and legislations and have a non-negligible sensory impact.

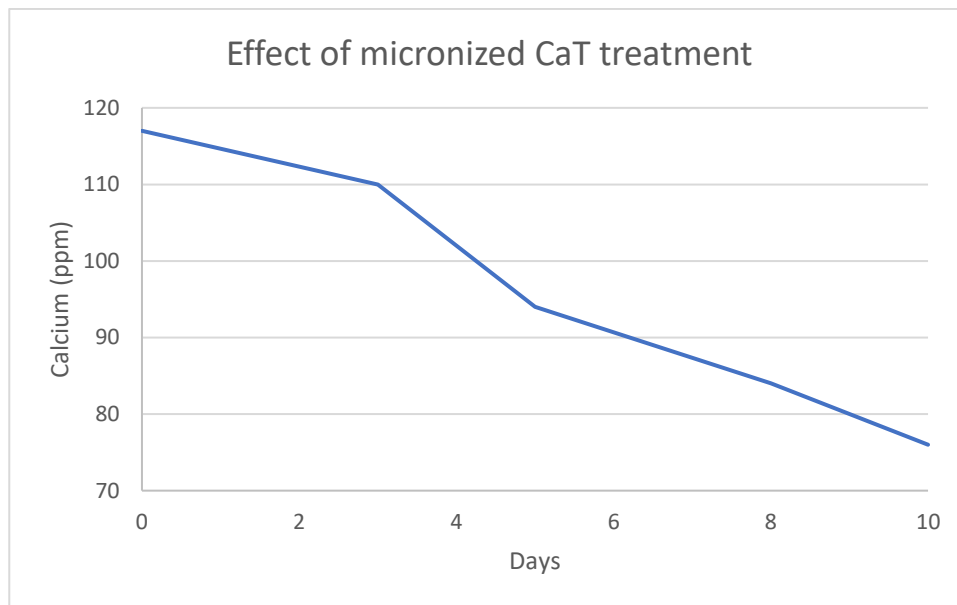
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Another technique is the use of crystallizers, i.e. salts of tartaric acid that accelerate the natural crystallization process of salts present in solution at concentrations above their solubility. Potassium bitartrate, used during cold stabilization, actually induces the precipitation of cream of tartar alone.

Racemic tartaric acid (DL) and its neutral salt of potassium, following salification with calcium, produce compounds with very low solubility: DL-Ca-tartrate has a solubility in water at 20°C of 35 mg/L, while the natural form L-Ca-tartrate is 300 mg/L. It is specifically the low solubility of racemic acid salts that represents the limitation of this strategy: the "crystallization tails" that can cause precipitate formation in the bottle are well known. Moreover, its effects on one's health are in question as it is suspected in causing kidney stones. The new revision of Regulation (EU) 934 still allows its use but following a commitment to provide new data on its effects on human health.

A particularly efficient crystallizer is L(+) calcium tartrate in micronized form. This calcium salt of the natural form of tartaric acid, as a result of the micronization process, when used at a dose of 50 g/hL is capable of providing around 2 million crystallizing germs per mL of treated wine, thus overcoming the limiting phase of the entire crystallization process: germ formation. The added germs can grow and form real crystals at cellar temperature, without the need to cool the wine and without being hindered by the presence of suspended particles. These characteristics greatly simplify its application, which can also be carried out at the same time as clarification. Contact times range from 7 to 15 days, depending on the needs of the winery, followed by racking and/or filtration. Treatment with L(+) micronized calcium tartrate has very little impact on the acidity of the wine and does not modify its sensory characteristics.



Graph 4. Reduction of Ca^{2+} ion concentration in a Merlot treated with 50 g/hL of micronized L(+) Ca tartrate. ^[11]

CONCLUSIONS

Current production conditions necessitate producers to make a detailed assessment of the instabilities of the salts of tartaric acid, taking into account both potassium bitartrate and calcium tartrate.

Reliable analytical methods now exist and must become more widely applied.

The estimation of calcium tartrate instability can nowadays even be carried out in "real time" and is of great help to oenologists who need rapid management.

Among the possible solutions, the addition of micronized calcium L(+) tartrate is the one that offers a guarantee of results combined with simplicity of implementation and maximum respect for the wine's sensorial qualities.

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