TARTARIC STABILIZATION

All production activities have always been subject and linked to their market. Today, however, the increasingly dynamic nature of the needs, preferences and even biases that inevitably determine the situation of the wine market require constant rethinking of the knowledge and production methods used. Some reputable experts stated that: "a quality wine is not made, it is earned, it is deserved". This gives an idea of both the economic and technical commitment that today's wine industry is making in order to produce a natural and healthy product that, although modifiable thanks to specific techniques or specialized processing, is able to stand the test of time.

There is no doubt that the first consideration a consumer makes about a food product is its appearance, and in the case of wine this first examination is very important. Color, especially its intensity and hue, limpidity and the absence of sediment are key parameters that buyers use to decide whether or not to buy a bottle.

Wine is an ever-changing product, but the modern market, rightly or wrongly, does not take into account the production problems, so it demands a product that is perfect in terms of physical, chemical and biological stability.

The grape, by nature, contains a large number of substances that are in balance with each other. Crushing puts them in forced contact, breaking this stability and thus creating the conditions for precipitation by supersaturation of some of them.

Under certain conditions, crystalline substances can precipitate in the wine and quickly settle to the bottom. The elements of these substances often aggregate into nuclei of a size that reveals their nature even to the naked eye. Basically, we are talking about two tartaric acid salts: potassium tartrate, also called potassium bitartrate or cream of tartar, and calcium tartrate, whose crystalline deposits can sometimes coexist. Their macroscopic diagnosis is readily apparent: potassium bitartrate is soluble in boiling water, whereas calcium bitartrate is not.

The concentrations of tartaric acid and potassium ions in ripe grapes are about 2-6gr/l and 1-2 gr/l, respectively. The concentration of bitartrate in the grape must is close to its saturation, and as fermentation progresses (increasing the amount of alcohol), the salt becomes supersaturated.
In that case, precipitation is inevitable and largely dependent on temperature. Another factor that affects tartar precipitation is pH. All these factors, i.e., pH, alcohol content, and temperature, affect the solubility and therefore the stability of the wine against tartaric acid precipitation.

But there are other factors in wine that affect the solubility of potassium bitartrate: for example, other organic acids and polyphenols present in red wine inhibit its precipitation. However, as the polyphenolic compounds polymerize and their content decreases during the aging process, their inhibitory power against potassium bitartrate crystallization decreases and small crystals begin to appear. This is why red wines aged in cellars, even at constant temperatures, always contain potassium bitartrate crystals.

Other substances that have an inhibiting effect on the massive formation of potassium bitartrate crystals are a number of colloidal substances. This is sometimes evident in the depleting effect that a fine-mesh filtration has on the protective colloid set, neutralizing the anti-aggregation effect on the microcrystals. The latter, although already

present in the wine, cannot transition from microcrystals, which are practically invisible, to macrocrystals, because of the specific action of these colloids, which consequently settle on the bottom of the vessel.
A slight precipitation of bitartrate has very modest, if any, consequences on the taste of the wine (a slight decrease in acidity, resulting in a barely perceptible loss of freshness and fruitiness), but commercially the consequences could be quite different. In fact, the consumer, either out of ignorance or to confirm a critical "connoisseur" attitude, does not accept the presence of a small translucent crystal; indeed, instead of considering the phenomenon natural, they are more inclined to think that the wine has been altered.

However, if the problem of calcium bitartrate precipitation is now very marginal, following the introduction of stainless steel tanks in the wine industry, with the consequent elimination of cement tanks, and the discontinuation of the use of calcium carbonate as a de-acidifying agent, the problem of potassium bitartrate is as relevant as ever.

To solve this problem, the market offers the expert several solutions.

***Chemical solution**:*
Metatartaric acid: has been used in oenology since the early 1950s. It is obtained from tartaric acid, which is melted by means of an appropriate technique at a temperature of approximately 170 °C (338 °F).
It inhibits the formation of potassium bitartrate and calcium bitartrate crystals. The inhibition is the result of this substance interacting with the crystal growth. The effectiveness of the inhibition and the duration of its activity over time depend on the storage temperature of the treated wine. By a fortunate coincidence, its efficacy is most stable at low temperatures, where the risk of tartaric precipitation is greatest; on the other hand, at higher temperatures, which the studies of C. Marota, Carafa and later Peynaud established to be between 20 and 23 °C (68-73.4 °F), its efficacy is limited to two or three months due to hydrolysis. It is therefore mainly used in products ready for consumption.

Gum Arabic: is a hydrophilic colloid, essentially a polysaccharide. It is extracted mainly from different species of tropical acacia. Ribéreau-Gayon is credited with having carefully and rationally studied the use of this product in 1933.
Studies on the properties of gum arabic obtain from Acacia Seyal trees have recently been published (M. Mannino G. Triulzi). Such work has highlighted the ability of this product to inhibit tartar precipitation in certain cases. It seems to have an effect on the surface of the crystals, coating them and preventing their enlargement.

Carboxymethylcellulose: is a colloidal compound derived from cellulose. As early as 1963, Cantarelli emphasized the inhibitory properties of this substance against tartaric precipitation. In wine, it acts like metatartaric acid and inhibits bitartrate precipitation, but it does not hydrolyze over time and its inhibiting effect is not altered by high temperatures.
Recently legalized, it is now widely used mainly in the preparation of white wines. This is because it is sensitive to the instability of the colorants in red wines.
***Biological solution**:*
Mannoproteins: relatively recent studies have explored the use of mannoproteins, which are long-chain protein colloids produced by yeast after cell wall lysis. Mannoproteins make up about 25-50% of the cell wall; they are macromolecules consisting of mannose chains that are linked to a protein in various ways. After a long struggle between researchers

and the chemical industry, the use of these products to prevent the precipitation of potassium bitartrate has been temporarily shelved because the dosages of the commercial preparations to be used are too high.

Physical solution:
Refrigeration: cold has a complex stabilizing effect on wine components and is widely used in oenological technology for this purpose. The main effects can be summarized as follows:
- t decreases the content of potassium bitartrate
- it facilitates the precipitation of calcium bitartrate
- it significantly decreases total acidity
- it renders the colorant insoluble in the colloidal state
- it decreases pectic and protein substances
- it has a precipitating effect on yeast and bacteria
- it facilitates oxygen intake resulting in the risk of oxidative phenomena.

With regard to the practical use of refrigeration in oenology, several observations made by a number of authors should be taken into account, which can be summarized as follows:
- by carrying out a slow and progressive cooling, the precipitation of the tartrates can take place with the formation of rather large and conspicuous crystals; however, it is an incomplete and very long process.
- with instantaneous cooling, crystallization is much more minute, with the formation of very small crystals, but with rather rapid and complete precipitation.
- agitation facilitates crystal formation.
- the presence of ice nucleating particles during rapid cooling effectively promotes macrocrystal formation.

The refrigeration temperature should never reach the freezing point of the wine, which is around -5 /-6 °C (41 / 42.8 °F); it should instead stabilize at approximately between 0 °C and -4 °C (32 and 39.2 °F) for a sufficient period of time to allow crystals to precipitate.
The time required to achieve tartaric stability depends on the kinetics of bitartrate crystallization, namely, as already mentioned, temperature, initial potassium ion concentration, tartaric acid, pH, alcohol content, and the presence of colloidal substances that may affect the rate at which solute ions migrate across the crystal surface to their final position.
Direct and indirect refrigeration systems are used for the purpose.
Direct refrigeration involves heat exchange between wine and refrigerant within the same evaporator. Due to the absence of any intermediate liquid, this system provides maximum refrigeration efficiency. The wine may be cooled down in one or more steps.
Indirect refrigeration consists in cooling an intermediate liquid (ethylene glycol solution) during the expansion phase inside the evaporator, which is then sent to special tanks, completely insulated and lined with an exchange cavity, containing the wine to be treated.
It is essential to maintain a constant temperature throughout the stabilization period.
The cycle is completed with a fine-mesh filtration to separate the crystals that have formed.
For several years now, continuous-cycle plants have also been used, in which potassium bitartrate crystals are continuously formed and then removed by membrane filtration.

Cation exchange resins: the importance of ion exchange was highlighted by Way more than a century ago for some applications in soil chemistry. Since then, many studies have been carried out on this subject, which led to the legalization of their use in oenology with Regulation (EC) 606/2009.

Resins are polymeric structures (cross-linked microspheres/beads) of high molecular weight; those commonly used in oenology are styrene-divinyl-benzene or acrylic or methacrylic polymers. Since these are selective materials, the ones that are most sensitive to potassium and calcium are used, although in practical terms the effect is mainly on potassium.

The treatment consists in letting part of the wine to be treated through one or more tanks containing cation resins, which exchange a hydrogen ion H^+ with cations present in the wine K^+, Ca^{++}, Fe^{++}, Cu^{++}. At the end of the cycle, the resins are washed and regenerated.

The treated wine, significantly depleted in potassium and rich in hydrogen ions, is reduced to a predetermined percentage of the total mass, thus achieving product stability with an increase in color intensity (in the case of red wines) and total acidity, and a decrease in the pH and cations present.

The limitations of this application are:

- the product to be treated must be practically limpid
- the pH value must be high, otherwise its reduction may have an effect on the taste of the final product.
- it is not recommended in young red wines with high polyphenol instability and high concentrations of tartaric acid
- there is a decrease in dry extract.

Electrodialysis: the first experiments on electrodialysis in oenology were conducted by Paronetto in 1940/41. However, the drawbacks encountered in terms of the organoleptic characteristics of the treated wines led him to abandon the research.

Later taken up by Oto and Kagami with different types of membranes, this technology began to show results, so much so that the EU approved its use in 2001.

It is a technique that uses an electric field applied to a series of selective cationic and anionic membranes, which are crossed by the flow of wine, resulting in the passage or retention of anions and cations.

The peculiarity of this technology, apart from the ultimate achievement of tartaric stability, is that it is not affected by the presence of colloidal substances, nor does it cause their reduction during the treatment. The colorant is also unaffected by the treatment, and total acidity generally decreases less than with cold treatment, resulting in a slight decrease in dry extract.

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