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Tartaric Stability
Part I: Behavior of additives in tartaric stabilization of musts

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TARTARIC STABILITY

Part I: Behaviour of additives in the tartaric stabilisation of musts

For the first time, a device capable of measuring the degree of stability of a Ovine was used to carry out an in-depth analysis of the behaviour of additives providing tartaric stability.
This paper presents the results obtained on musts, using metatartaric acid, gum arabic, mannoproteins and carboxymethylcellulose.

Tartaric stability of wines is a problem that all wineries must face and plays a key role in the presentation and marketing of wines. The slightest error at this stage of the technological chain, could lead to undesirable commercial consequences. Groundwork research carried out between 1990 and 1993 (Berta, 1993), was used as the basis to develop a laboratory device and a series of software programmes, capable of providing a quick, reliable and precise reading of the degree of stability of any given wine. Later research led to the development of the latest generation of the Check Stab a 2001 Millennium device (Delta Acque - Florence), that has been used by the authors of this paper to shed further light on the tartaric stability of musts and wines.

The present article is the first of a series presenting the results of the comparative study, to be published over the next issues of this magazine. In this paper we shall deal with the effectiveness of certain additives in ensuring the tartaric stability of musts (products that do not contain alcohol). Fresh and desulphurised musts of the 2000 harvest were used. The additives tested were: Metatartaric acid (Polytartryl 40 - J. Laffort & Cie); Gum Arabic (Stabivin - J. Laffort & Cie); Mannoproteins (Mannostab - J. Laffort & Cie); and Sodium-Carboxymethylcellulose (Akucell AF2205 - Akzo Nobel).

The results obtained using the same additives on products containing alcohol (partially fermented musts and wines) will be presented in a later issue.

Methodology - Analysis and interpretation of the results

The theoretical foundations of the work have been explained in previous articles (Berta, 1993): one must however bear in mind that graphics used to present the results, are differential.

This type of graphical presentation highlights the difference in specific conductivity between an untreated control must sample, and a sample of the same must with potassium bitartrate crystals. If the specific conductivity value is negative at a certain temperature, this means that the must was initially supersatured, and therefore the addition of potassium bitartrate crystals led to crystallisation that in turn provoked a decrease in specific conductivity. Inversely, if at a certain temperature, the value is positive, this means that the must was initially unsatured and therefore dissolved more potassium bitartrate, leading to an increase in specific conductivity. The theoretical and practical details of the analytical method are outlined at the website www. oicce. it.

Initially untreated grape must was enriched with increasing doses of various additives that, by inhibiting potassium bitartrate precipitation in proportion to the dose added, led to a corresponding drop in specific conductivity. At a certain level of additive concentration, the must becomes fully stable and no loss of specific conductivity is observed when potassium bitartrate crystals are added to the must. This concentration is defined in the graphics as the point at which a stabilising effect of 100% is reached. As a general rule, this concentration is higher than the dose required to reach "technological stability", that is to say, a degree of stability sufficient for practical winemaking purposes, usually marked by a drop in specific conductivity to a level below -50 PS/Cm.

It is remarkable the fact that for the first time, a laboratory instrument capable of providing a quantitative reading of the stabilising effect of an additive, is available. The data presented in scientific literature so far, have been qualitative or semi-quantitative, and did not allow for a real comparison between results obtained using various research methods. Furthermore, since most efficiency tests were based on visual checks for potassium bitartrate precipitation in samples maintained under refrigeration for varying periods of time, the results had more to do with "technological stability" rather than the actual degree of saturation. The data so far presented in scientific literature are therefore susceptible to a margin of error, generally falling short of the concept of total kinetic stability (perfect assurance that no precipitation will take place, even if crystal seeds are added).

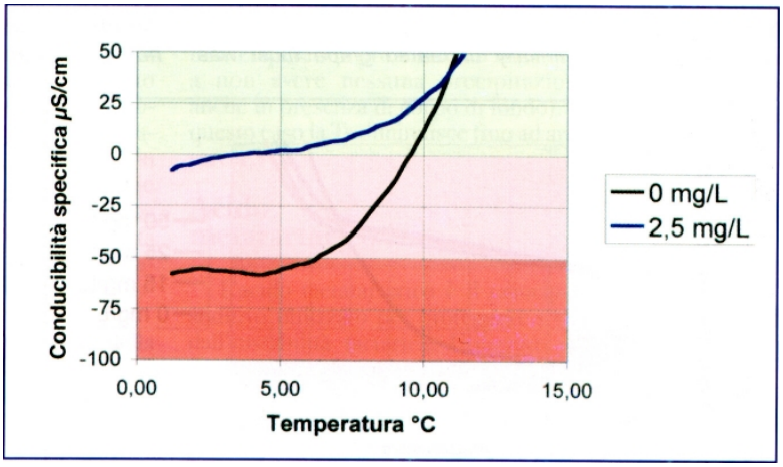

Figure 1 – The behaviour of a technolagically stable must where 2,5 mg/L of metatartaric acid has been added which indicates the essential points in this discussion.

A useful indicator of tartaric stability is the saturation temperature (Ts). The graphs generated by the instrument provide a very precise reading of the Ts, that can then be compared to the theoretical figures obtained using thermodynamic principles. The addition of a stabiliser entails a drop in the saturation temperature. As the graphs show, quantitative readings also provide a precise and coherent indication of the effects of additives on the saturation temperature.

Figure 1 presents an example of how the results have been interpreted. The must in question was maintained at a low temperature for several months and had therefore reached technological stability. In all the graphs, therange of technological instability is indicated in red, while pink is used to indicate the range at which the must is technologically stable (although crystal growth is still possible from a kinetic viewpoint) and green indicates the range of totally stability. As the figure shows, at temperatures close to 0°C specific conductivity does not fall far below -50µS/cm (the generally accepted stability threshold). The curve meets the ordinate axis at the temperature of 9,5°C, which is the saturation temperature. The addition of a small quantity of metatartaric acid significantly changes the outcome. In this case, 2.5 mg/L of additive are sufficient to bring the must to totally stability (that is to say, without precipitation even in the presence of added crystals) at the temperature close to zero, while the TS falls to 3°C.

Metatartaric acid

Already in use in the 1950s, metatartaric acid is the main additive used to protect wines from tartaric instability. Even at very low concentrations the additive can protect wines against tartaric instability for several months. As a result of surface interaction, metatartaric acid acts as a nucleation and crystal growth inhibitor.

The dosage recommended in scientific literature for the stabilisation of wines is variable, especially because of the instability of the product in an acid environment. Metatartaric acid is easily hydrolysed, losing its effectiveness. Hydrolysis is accelerated in proportion to acidity and temperature. A dosage of 50-100 mg/L of metatartaric acid is generally sufficient to ensure the technological stability of wines stored at room temperature, for several months.

Our research showed that effective protection to must featuring slight instability could be obtained by adding just 2.5 mg/L of metatartaric acid.

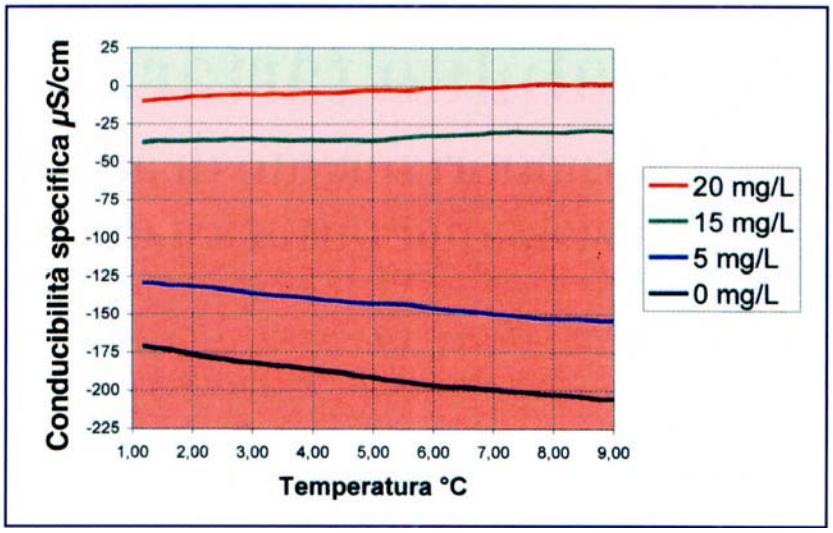

Figure 2 – Drop in conductrivity at a low temperature for an instable must with increasing doses of meta tartaric.

Figure 2 presents the results obtained using a highly unstable must: the effect of the additive is already obvious at a dose of 5 mg/L, although in this case, 15 mg/L were required to reach technological stability, while full stability was attained at 20 mg/L.

Once full stability is reached, the addition of further quantities of metatartaric acid do not significantly change the general outcome. The figure 3 shows, after full stability is reached at a dose of 15 mg/L , additional amounts of metatartaric acid, up to 50 mg/L, provide almost identical results. This effect is further highlighted in figure 4 that illustrates the fact that, expressed in percentages, the stabilising action of the additive is not linear in nature.

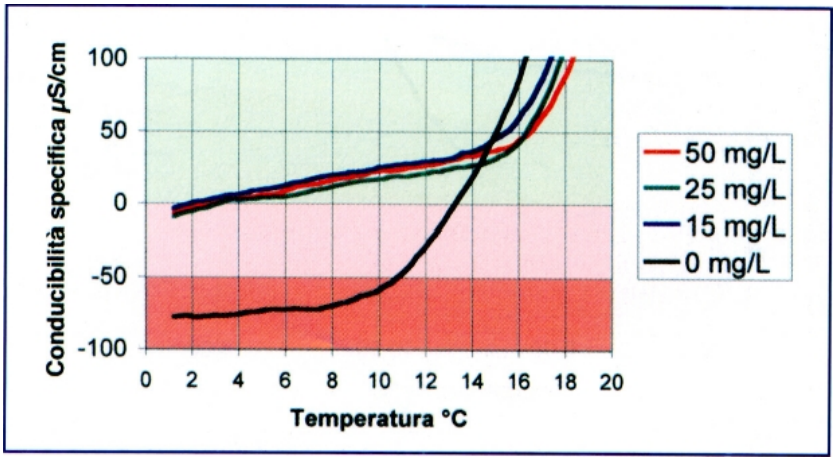

Figure 3 – Once reaching perfect stability, increasing doses of metatartaric does not modify the dropping of conductivity of the must

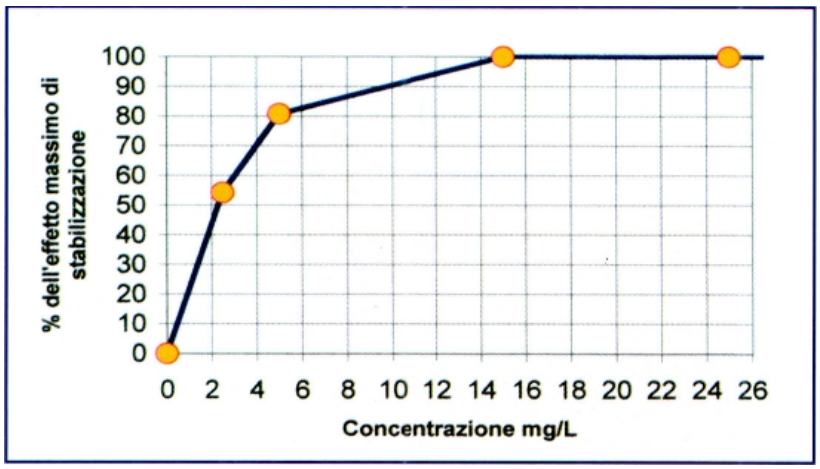

Figure 4 – The stabilizing effect of metatartaric acid does not follow a linear path.

The analytical methods used highlight the loss of protection arising from the hydrolysis of metatartaric acid. By graphically recording changes before and after hydrolysis, even low concentrations of additive (1 mg/L) can be detected. Figure 5 provides a reading for a must before and after hydrolysis at 90°C for 60 minutes.

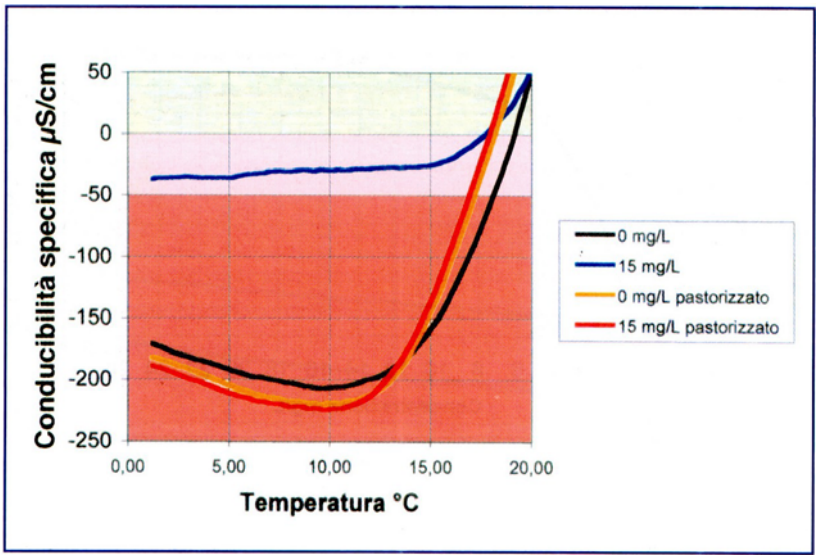

Figure 5 – The analytical method of the analysis allows to determine the presence of small quantitiies of metatartaric acid, thanks to the evedent loss of the protective effect after hydrolysis.

Carboxymethylcellulose (CMC)

CMC is produced by reacting cellulose with carboxymethyl compounds.

It is widely used in the food industry (icecream, sauces, soups, fats...) as well as in alcoholic and alcoholfree beverages, and has never been known to have caused any sort of contamination in the foods in which it is used.

Although CMC has not yet been approved for use in the enological sector, its industrial applications are currently being experimented on large quantities of wine. The semi-quantitative data available in scientific literature generally recommend a dose of 100 mg/L of CMC to attain stability (Paronetto, 1986). Recent research by Crachereau et al. (2001) has shown that technological stability against tartaric precipitation can be obtained at doses of around 40 mg/L. Once again, in this case, our research benefited greatly from the availability of an quantitative analytical tool that provided precise readings of the additive's stabilising effect. As shown in figure 6, by adding increasing concentrations of CMC to a highly unstable must, technological stability is reached at a concentration of about 15 mg/L. At 80 mg/L, the product is totally stable. CMC is similar to metatartaric acid insofar as their stabilising action is not linear (see Figure 7).

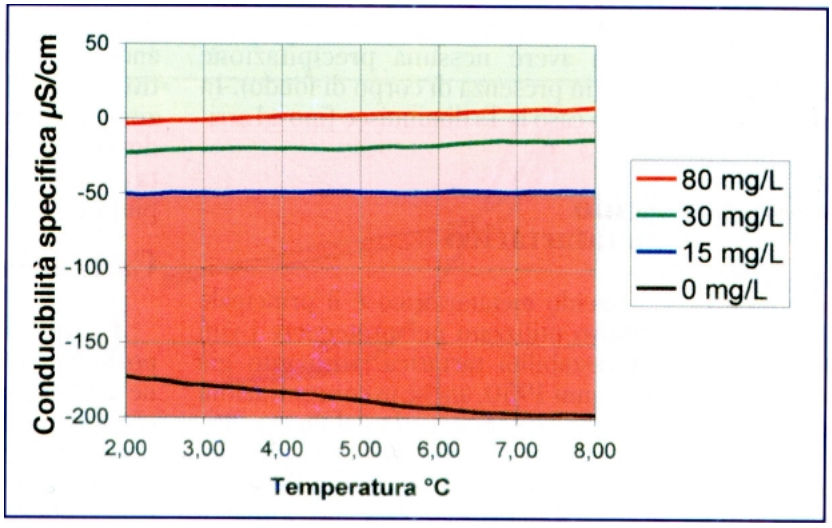

Figure 6 – Drop in conductivity at low temperature for an instable must instabile at increasing doses of Carboxymethylcellulose.

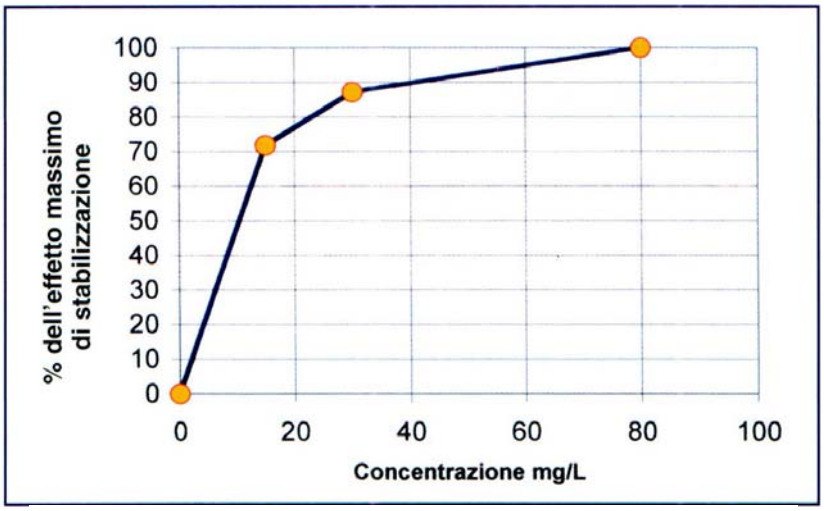

Figure 7 –The effect in percentage stabilization of Carbossimetilcellulosa does not follow a linear path.

Mannoproteins

Relatively recent studies have highlighted the effects of mannoproteins on wine, especially their ability to inhibit tartaric precipitation. Mannoproteins produced using state-of-the-art enzymatic and thermal thermal techniques, have been tested on standard solutions and wines. Like CMC, mannoproteins have not yet been approved for use in the wine industry.

Feuillat's semiquantitative findings published in 1999 indicate that the stabilising effect of various mannoprotein preparations becomes enologically significant at concentrations of between 250 and 1,000 mg/L, while the industrial stability of wines can be attained at doses of between 100 and 300 mg/L.

As in the case of the other additives, our research on the enological application of mannoproteins uses a precision instrument to measure to the stabilising effect of each preparation. As indicated in figure 8, by adding increasing doses of mannoproteins to a highly unstable must, the effect of the additive becomes apparent at a concentration of 250 mg/L, and technological stability is reached at about 750 mg/L. At 1150 mg/L, the product is fully stable.

Mannoproteins drop the saturation temperature of the must, more or less to the same extent as other additives. As indicated in figure 9, the stabilising action once again does not follow a linear trend.

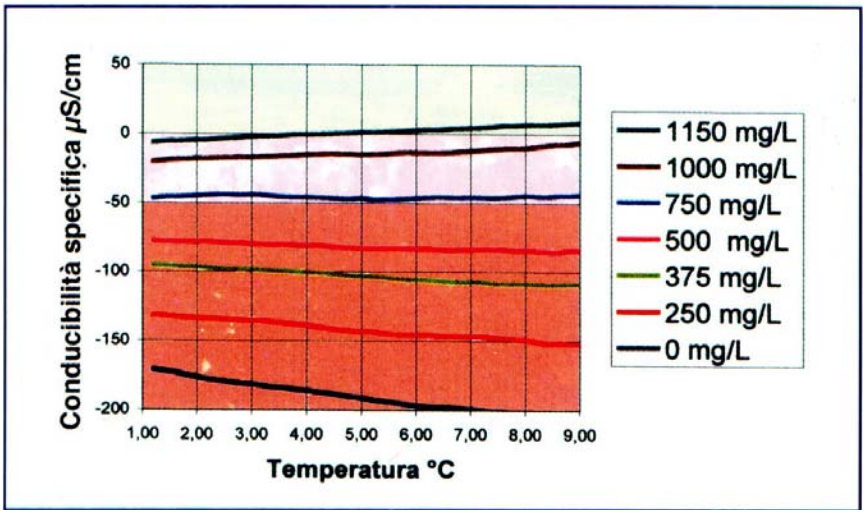

Figure 8 – Drop in conductivity at low temperature for an instable must at increasing doses of mannoprotein.

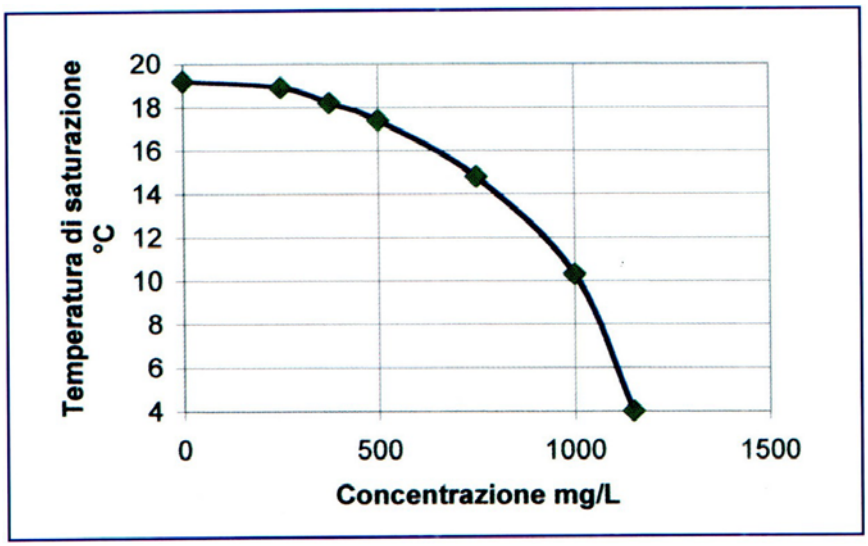

Figure 9 – Variation of Ts with increasing doses of mannoprotein.

Gum arabic

While the earliest scientific mention of gum Arabic dates to the late 19th century, its stabilising properties were first studies by Ribéreau-Gayon in 1933. Gum Arabic is used in white or rosè wines to prevent the cloudiness caused by copper and in red wines, to combat the formation of deposits left by colouring additives or slight alterations due to oxidation.

Previous scientific research (Dal Cin, 1982) seemed to indicate that gum Arabic had little or no effect on the tartaric stability of musts and wines. These findings were confirmed by our research. As figure 10 shoes, even by gradually increasing the concentration of gum Arabic to very high levels (10,000 mg/L), no significant changes are observed when compared to the untreated control sample. Similarly, the Saturation temperature does not vary significantly, regardless of the quantity of gum Arabic added.

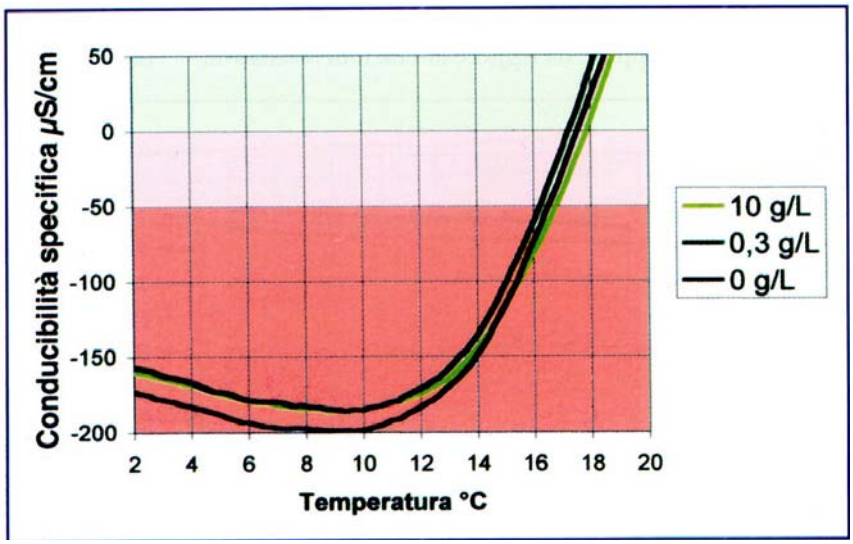

Figure 10 – Sabilization Test on a must utilizing gomma arabica. The preparation utilized has no influence on tartaric stability of musts.

Conclusions

The analytical method adopted is precise and sensitive, allowing for an indepth study of the effects of the tested additives, even at very low concentrations (less than 1 mg/L in the case of metatartaric acid). In particular, the presence of metatartaric acid can be confirmed by subjecting the must to hydrolysis that eliminates the additive's inhibitory action. Even at very high concentrations, gum Arabic failed to provide any protective effect, confirming previous findings. The effect of carboxymethylcellulose (CMC) was found to be similar to that of metatartaric acid, although at higher doses. In the case, however, the stabilising action continues even after heating. The results obtained are in keeping with previous scientific findings. The stabilising effect of mannoproteins becomes manifest at concentrations much higher than those required in the case of metatartaric acid. Like CMC, mannoproteins do not lose their ability to inhibit potassium bitartrate precipitation, after heating.

Tartaric stability
Part II: the measurement of the precipitation of potassium bitartrate

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TARTARIC STABILITY

Part II: The measurement of the precipitation of potassium bitartrate

There are two fundamental kinds of analysis which test stability of wine, both of them are based on comparison measurements: the testing of specific conductibility variations - when a known quantity of Potassium Bitartrate crystals is added to wine - and the experimental measurement of saturation temperature. With the use of both methods, together with thermodynamic data, it is possible to know, precisely, the level of saturation of potassium bitartrate of a wine.

A wine put in contact with potassium bitartrate crystals (KHT) at a certain temperature can demonstrate various behaviours, on the basis of its state of saturation at the temperature of the experiment. After a certain period of contact, equilibrium is established. After reaching equilibrium between the wine and added crystals, it can be observed that a part of Potassium Bitartrate present in the wine has precipitated, or that a part of the added KHT remains dissolved in the wine. When Potassium Bitartrate precipitates one obtains a decrease of the total concentration of electrolytes in solution. This provokes a decrease of the specific conductivity of the wine. On the contrary, the dissolution of added crystals increases the electrolyte concentration, and consequently the specific conductivity of the solution.

The measurement of the variation of the specific conductivity at a certain temperature is therefore one indirect measure of the state of saturation of the wine at that determined temperature. In order to measure the conductivity variation it is possible to choose one at any temperature. Generally, if the temperature of the experiment is indicated with Tx, with χbefore, the specific conductivity of the wine before KHT is added, with χafter, the specific conductivity of the wine after adding KHT and with $\delta\chi$ the difference between the measurement of conductivity before and after adding, that is $\delta\chi = (\chi\text{after} - \chi\text{before})$

It can be verified that:

- if Tx < Ts then it will have $\delta\chi < 0$ (that is a decrease of χ)
- if Tx = Ts then it will have $\delta\chi = 0$ (that is a constant of χ)
- if Tx > Ts then it will have $\delta\chi > 0$ (that is an increase of χ)

One can observe the presence of a value of the temperature threshold (Ts) for which there has not been any variation in the measurement of specific conductivity. This threshold value is defined “Temperature of Saturation”. When measure the specific conductivity in function of the temperature of a wine, a must, or a Potassium Bitartrate solution, in presence and absence of precipitated KHT crystals, determines two complex curves, as shown graphically in Figure 1.

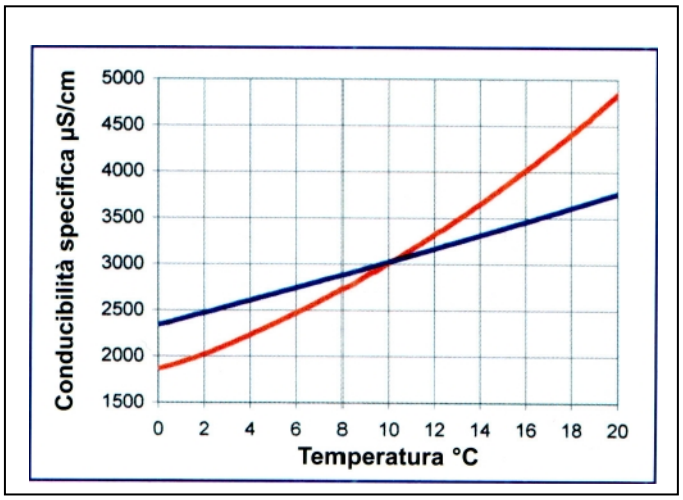

Figure 1 – Measure of the χ in function of the temperature for one solution in water of 2,90g/L of bitartrate of potassium and 0,65g/L of KCL in absence of precipitated crystals (blue curve) and in presence of crystals (red curve)

The figure introduces the measurements of χ in function of the temperature for a solution in water of 2,90 g/L of Potassium Bitartrate and of 0,65 g/L of KCI in absence precipitated crystals (blue curve) and in presence of precipitated crystals (red curve).
Between the various hypothetical equations, it has shown that those that correspond better to the experimental decreasing or increasing trend of the curve are the equations of the type:

$\chi_{t\text{-reduction}} - K + K't + K''t^2$

$\chi_{t\text{-climb}} - K + K't + K''t^2 + K'''t^3$

Basically corresponding to the average equations obtained by M. Domeizel e coll. (1992).

One can see that at a determined temperature the presence of Potassium Bitartrate crystals does not provoke variations of specific conductivity. At this temperature one does not have either dissolution or precipitation of KHT. We are found therefore at the temperature of thermodynamic equilibrium of the Potassium Bitartrate solution with precipitated crystals.

This measurable experimental temperature, at which equilibrium is found, is the one that is defined Temperature of saturation (Ts). The two curves intersect at the temperature of 10,1 °C: this value of temperature corresponds to the Ts for this particular solution.

The differential graphics

To make the analysis of the tartaric stability of a must or a wine the differential graph is normally used.
The differential graphics are obtained subtracting the values of specific conductivity measured in presence of precipitated crystals from the values measured in absence of KHT crystal. An example is shown in figure 2. This is the differential graph obtained from the curves shown in Figure 1. The temperature at which $\delta\chi = 0$ is Ts. For more elevated temperatures the curve moves into the dissolution zone: at these temperatures the solution is un-saturated, therefore it dissolves the KHT, and it increases its specific conductivity. For lower Ts temperatures the graph is in the precipitation area. The solution is over-saturated, therefore the KHT crystallizes, and therefore the specific conductivity of the solution diminishes.

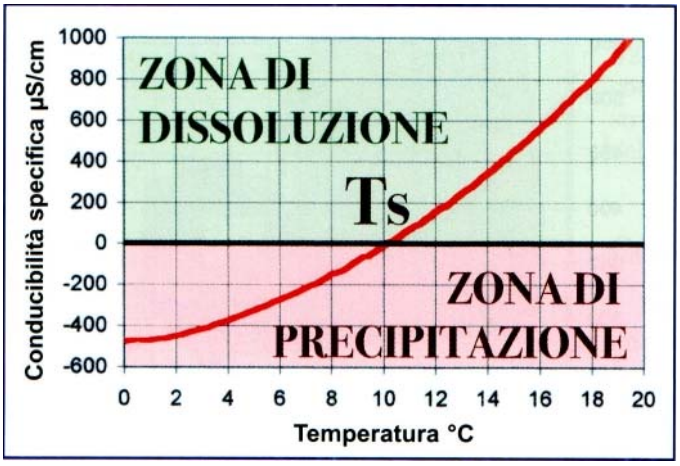

Figure 2 – Differential graphic of the values of the curves shown in figure 1

Examples of measure on the wine

In Figure 3 we see variations of specific conductivity in real wine cellars. This is a white wine in three successive periods of treatment. Graph 3a has been obtained by measuring the variation of conductivity of the wine to the end of the fermentation, before any clarification operation begins. Graphic 3b has been obtained on the same wine after being clarified, while Graph 3c was created after the phase of tartaric stabilization (stabilization to -5 °C for 15 days).
For the analyses made on the wine before the stabilization phase, one observes a similar trend of the curve. In both cases, for lower temperatures than the Ts a decreasing trend of the specific conductivity is observed, while for higher temperatures an increase of the specific conductivity is observed. If the general trend of the curve is the same as the wine before and after being clarified, the difference being is the variation of the amplitude of the phenomenon. The value of the Ts varies slightly in the two cases being examinated. For the stabilized wine a Ts of approximately 16°C is obtained, while for the un stabilized wine the Ts is approximately 15,5°C. Between the two wines we see very different values of specific conductivity ($\delta\chi$) at cold temperatures. For example, at 0°C we see that for the clarified wine the variation of specific conductivity is -127 µS/cm, while for the unclarified wine it is -67 µS/cm.
The stable wine measurements show a curve of specific conductivity that lies above 0. For example, at 0°C it has +8 µS/cm, therefore a slight solulability of KHT.
Usually we choose the temperature of 0°C for the analysis. For the practical necessities of wine cellar, we can use from 2 and 6°C, on condition that once a specific temperature is established you continued to operate without modifying this temperature.
The method that normally is used for the measurements is the following: put the sample at the temperature of the test (in our case 0°C) and to measure the specific conductivity at this temperature, add bitartrate crystals of Potassium, and wait until we get the stabilized measurement of the conductivity. The difference between these two measurements gives us an index of the amount of KHT precipitated at 0°C.

MEASURENTS OF TARTARIC STABILITY CONDUCT AT VARIOUS PHASES OF WORKING OF A WHITE WINE

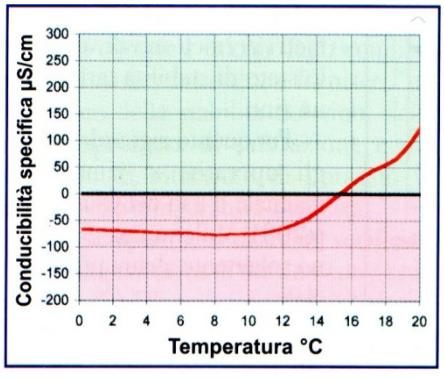

Figura 3a – White wine unrefined

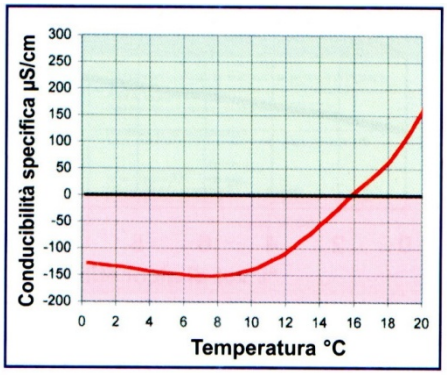

Figura 3b – Afte clarifying

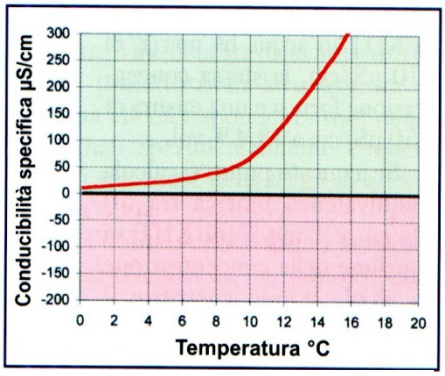

Figura 3c – After tartaric stablization

The meaning of the dropping of the specific conductivity

Generally speaking, the following observations can be made on the basis of the experience and the historical data indicated in the bibliography at end of this article: for the dropping of conductivity at 0°C of more than 50 µS/cm the wine can be judged to be technologically unstable; for the dropping of conductivity at 0°C of less than 25 µS/cm the wine can be judged stable. It must emphasized that this argument is difficult to generalize. It is possible to try to deepen the topic confronting the dropping of specific conductivity with the KHT amounts that precipitate.

In the first place it must be pointed out that the specific conductivity of a KHT solution is very different if working in damp atmosphere or with a mixture of water/alcohol.

In Figure 4 we see the specific conductivity in µS/cm for a solution of 1 g/L of KHT at the temperature of 0°C. We see that by increasing the concentration of ethanol, the specific conductivity of the same concentration of KHT diminishes a lot. Meanwhile a solution of 1 g/L of KHT in water has a χ of 510 µS/cm, the same concentration gives us a measurement of 250 µS/cm at 13,4 % vol.

If at this point it is estimated the theoretical equivalence between the 50 µS/cm and mg/L of KHT in function of the alcohol concentration, we can build graph 5. We see therefore that 50 µS/cm is equivalent to 100 mg/L for a water solution, while they are equivalent to 210 mg/L for a solution of 14 % vol. This means, for example, that the maximum risk of precipitation for a wine of 14 degrees that has a $\delta\chi$ of 50 pS/cm is approximately 150 mg of KHT per bottle. Is this an acceptable risk? A generalized answer does not exist. Every wine cellar must establish the level of risk that it wants reach for its bottled products.

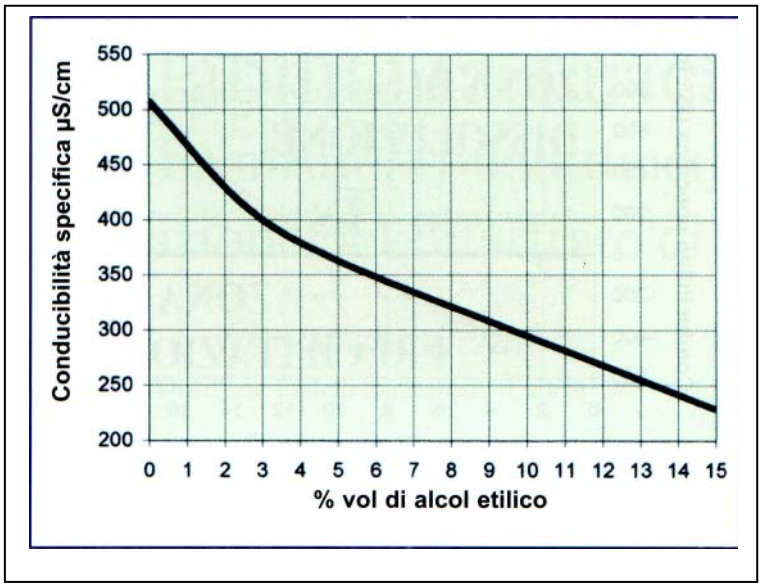

Figure 4 – Specific conductivity in µS/cm of a solution of 1g/L of KHT at the temperature of 0°C, with increasing concentrations of etanolo.

Conductivity measurement of saturation temperature

The precipitation of Potassium Bitartrate can be influenced by many natural and technological factors, and therefore, in certain cases, cannot represent very well the state of saturation of the wine. For this reason, it has been proposed by various Authors the use of the Temperature of saturation as a parameter to identify the state of technological stability of a wine. (L. Angele, 1992; M. Domcizel and others, 1992; L. Usseglio-Toma.SSCt and others, 1992). J. M. Garcìa-Ruiz (1991), for example, pointed out that varying the speed of the descent a lot, and the increasing of the temperature, the maximum cooling temperature of the sample, the amount and the granulometry of the added KHT crystals or the force applied during the mixing of the solution during the measurement phase, all influence the maximum error of the measurement of the saturation temperature of saturation appears of about ± 0,6°C.

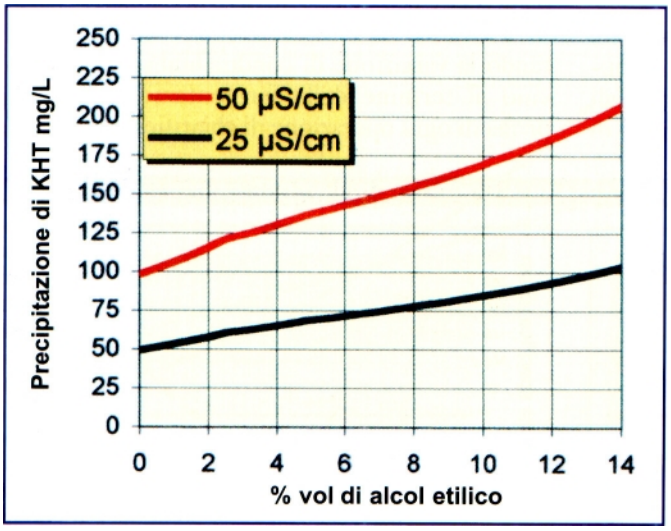

Figure 5 – Graphic that indicates theoretical equivalence between the specific conductivity of 25 and of the 50 µS/cm and mg/L of KHT in function of the alcohol

The measurement instrument

The laboratory measuring instrument Check Stab α2001 Millennium (Delta Acque - Florence) has been used for the analysis, with a conductivity cell of 2 electrodes in platinum platinato at constant 1,00 (mod. SENTEK, plates of 10 dimensions millimetre x 10 millimetre approximately, distanced 10 millimetre approximately); double scale of measure 3,000.0 µS and 30,000 µS; automatic calibration of the conductivity; automatic compensation of the temperature to 0,0°C. With this equipment it is possible to determine the curves in presence and absence of KHT, therefore can determine the value of the Temperature of saturation, Ts, and the measurement of conductivity variation when the wine is put in contact with a pre determined amount of KHT crystals at 0°C. These parameters allow verifying the state of tartaric stability of a wine. As far as operational details it comes with the handbook user guide of the Check Stab α2001 Millennium. Some crucial points are pointed out.

The calibration of the probe is done with a standard solution of KCI of equal conductivity to 1278 µS/cm at 0°C, waiting for the temperature is become stabile at 0,0 °C. In case in which the wine is clear and without dissolved gas, it does not require particular treatment for preparation. In the case of sparkling wines, or carbon dioxide present during fermentation, the wine is degassed by mixing vigorously the solution. In the case of obvious turbidity of the wine, it undergoes centrifugation. In order to measure the conductivity variation, at a stable 0°C, we add (approximately 2,0 ±0,1 grams of Bitartrate of Potassium Merck, equal to adding of approximately 16 g/L. For correct measurements carried out by the instrument, we add a solution of KHT and KCI in water. The results must be those shown in Figure 1: Ts = 10,1 ±1°C e δχ a 0°C=-480 ±50 µS/cm.

Figure 6 – Check Stab α2001 Millennium (Delta Acque - Firenze)

The thermodynamic calculation of Ts

It is possible to compare the value of experimental Ts with the value obtained through thermodynamic calculations experiments, using the method described from UsseglioTomasset ET al. in a series of works publishes between 1978 and 1992, slightly modified and adapted to a calculation on line. On the Internet web site www.oicce.it, there has been inserted a calculation program online that allows, with only a few analytical parameters, the degree of, pH, the concentration of tartaric acid and the concentration of the ionic potassium, to determine the degree of stability of musts and wines at any desired temperature.
The using the system is easy: write in the analytical data in the requested spaces (paying attention to put a point (.) to separate decimal numbers), then press the key "calculate". Automatically the program completes the calculations of the relative thermodynamic equilibriums, and supplies an indication of the stability of the wine, its saturation temperature and the mg/litre of bitartrate of potassium in excess at the requested temperature.
For example, if it is desired to verify the tartaric stability of a wine with alcohol 10,5% vol. with pH 3,20 with 2.5 tartaric acid concentration of grams/litre and concentration of potassium of 800 milligrams/litre, inserting the data in the online program, and inserting the temperature of analysis of 0° C, the results will be obtained that the wine is UNSTABLE, than its temperature of saturation is of 18.77 °C, and the Bitartrate excess of potassium (at the temperature selected of 0°C) is 1180 milligrams/litre.
We remind you that the results correspond to the thermodynamic data, that they are equivalent to the laboratory measurement only in case the sample has a complete absence of crystallization inhibitors. The presence of crystallization inhibitors like for example metatartaric acid prevents practically the formation of precipitation also in an unstable wine, therefore the theoretical data is unreliable. This phenomenon is the basis of the method of verification of inhibitor presence in crystallization.
If this method of calculation for the standard solutions is used as previously cited (2,90 g/L of Bitartrate of potassium and 0,65 g/L of KG in water) we obtain the following theoretical data as shown: a Ts equal to 10°C and an excess Potassium Bitartrate of 834 mg/L, equal to theoretical drop of specific conductivity of -425 µS /cm.

Figure 7 – Program screen for the calculation of the tartarica stability inserted in the www.oicce.it

The theoretical data has an excellent correlation with the data measured by the instrument, demonstrating therefore the validity of the method.

Conclusions

In order to verify the level of stability of a wine two fundamental types of analysis can be completed, both based on comparison measures. The first type of analysis is based on the measurement of the variation of specific conductivity, when to the wine is added a known Bitartrate crystal amount of Potassium. We are talking about a quick measurement and easy execution, that can be completed by using various protocol experiences. At the moment we have not been able to demonstrate a particular superiority of one protocol experience with respect to others, being careful to use particular care in doing the calibration of the Check Stab instrument and the precise control of the temperature. The method is subject to certain experimental errors, none the less it can give a complete guarantee if the experiment is repeated three times, with the aim of avoiding anomalies.
For the dropping of conductivity at 0°C of more than 50 µS /cm the wine can be judged technologically unstable; for the dropping of conductivity at 0°C of less than 25 µS /cm the wine can be judged stable. In the area between 25 and 50 µS/cm the situation is of increasing risk. It must be remembered we are dealing with measurements influenced by all variables that influence the kinetic precipitation of KHT.
The second kind of measurement is the saturation temperature. It has a longer testing time, and needs a program that allows for obtaining curves of conductivity variation in relation to temperature. This measurement is influenced by the presence of protecting colloids. In their absence, we finds a good correlation between experimental values and those calculated on the base of the laws of mass action. With the use of both methods and with the data from a thermal dynamic point of view, it is possible to have perfect knowledge of the state of saturation of KHT in a wine.

Tartaric stability

Part III: Behavior of the additives in tartaric stabilization of white wines

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Distillerie Fratelli Ramazzotti - Canelli (Italia)

The effectiveness of certain additives (tartaric acid, carboxymetilcellulose, mannoproteins) has been compared for the tartaric stabilisation of white wines.
All three additives allow the wine to be satisfactorily stabilised.
The only additive that loses its effectiveness with temperature is tartaric acid. This means that its presence in wines and musts can be analysed even at low levels of concentration.
The three additives behave very differently from the dissolution of potassium bitartrate. The mannoproteins increa se the solubility of salt, both in wine and in water solution, and behave like complexants of species in solution.
The mechanism with which mannoproteins operate in the stabilisation of wine thus appears to be different from that of tartaric acid and carboxymetilcellulose.

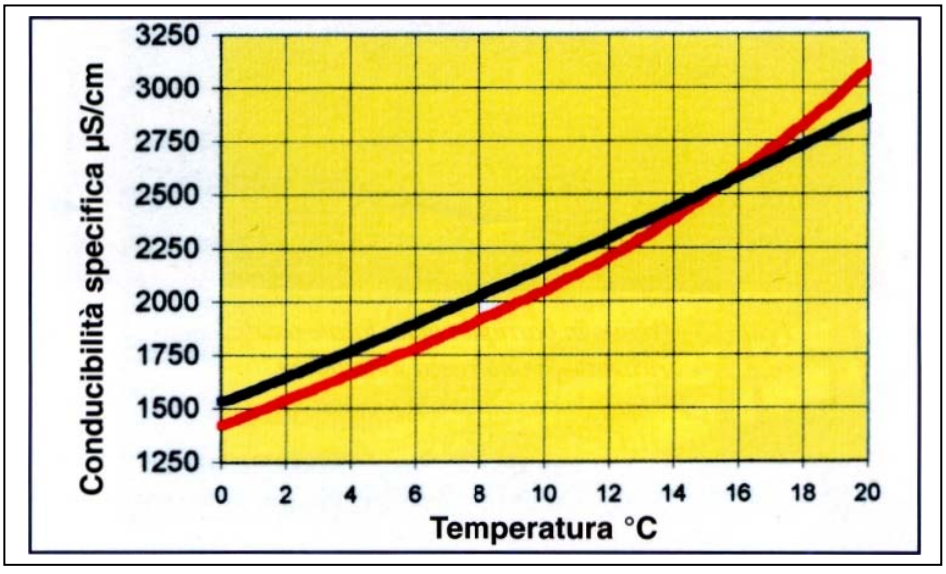

Figure 1- Measurement conductivity in relation to temperature for a white wine, in absense of precipated crystals (blue curve) and with precipated crystals (red curve)

What is a stable wine?

From the moment of the tampering of the grape, potassium and tartaric acid are present in the solution at the same time, creating a state of over-saturation in the must. Their concentration is not modified substantially from successive activity of leavening, and therefore during fermentation and conservation they produce the evident phenomena of potassium bitartrate (KHT) precipitation.

If the precipitation does not happen completely in the wine cellar, it will happen a second time, in the bottle. In less serious cases, the appearance of little, small crystals can take place, especially in red wines and can pass unnoticed. However it is also possible to have abundant bitartrate crystals of potassium being more evident, especially if they are found in white wines. The presence in the bottle of small amounts crystal does not alter the characteristics of the product, and it is not sign of a "defect" of the wine. It is, however, increasely less and less accepted by the consumer. The aspect of the sediment, that can be crystalline and transparent, sometimes creates doubt in the minds of the consumers about the genuineness of the wine. Moreover it must be remembered that for the sparkling wines the crystal presence can modify the development speed of carbon dioxide.

It is therefore always important, for a company, to determine attentively the degree of stability to maintain regarding the precipitation of potassium bitartrate. Besides the concept of thermodynamic stability, in oenology, more and more importantly is the concept of "technological stability".

The degree of stability of a wine must be estimated on the base of the requirements of each single wine cellar, and its interest of how this product is to be presented to its consumers. Once established the degree of technological stability desired, estimated in terms of milligrams/liter of potassium bitartrate that at maximum can precipitate in a bottle stored at a certain temperature, then one can select the opportune method to use for tartaric stabilization.

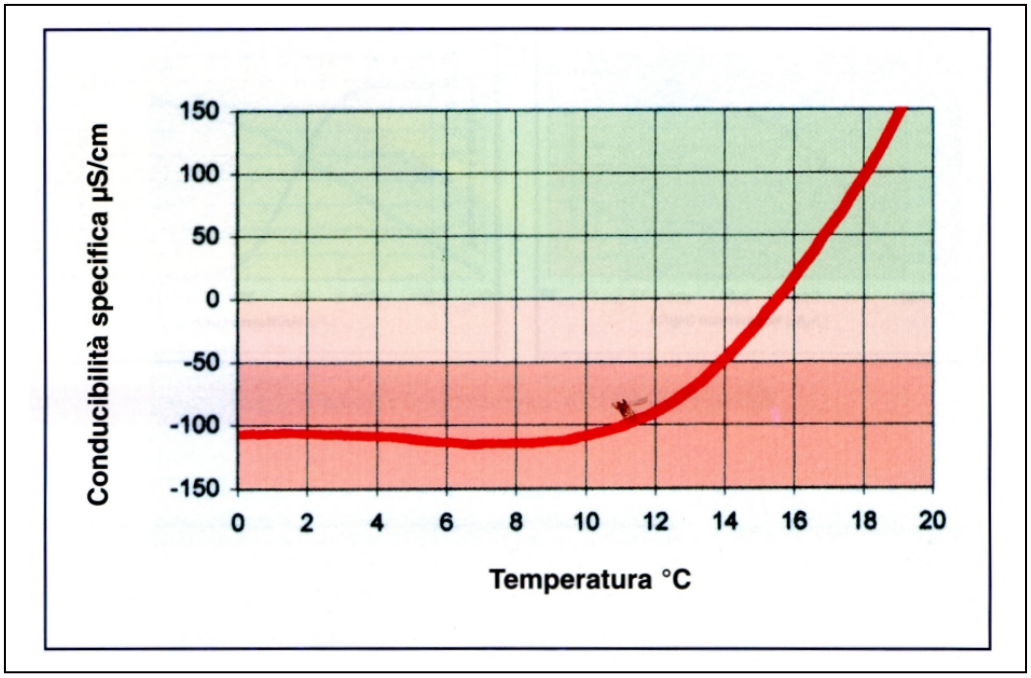

Figure 2 - Differential graphic of the values of the curves shown in Figure 1

Tartaric stabilization

The wine cellar has a goal with respect to Tartaric stabilization to avoid any future crystal formation in bottle. These goals are precautionary, using methods to slowing down precipitation or to prevent totally further precipitate formations. From a theoretical point of view, there are two methods to obtain the same technological result: one can use thermodynamic point of view, eliminating the state of over-saturation, or one can use kinetic of precipitation, stabilizing further the wine so that the state of over-saturation stays for a long period of time, also in the bottle, without leaving sediment.

Practical techniques can be of a chemical type or a Physical type. The methods of chemical prevention can be subdivided in an adding type method or subtraction type method. The “Additional type” are those that imply adding an external material that serves to inhibit the precipitation of bitartrate potassium crystals. Various authors have proposed many products that have all the characteristic to inhibit the precipitation. At the moment the only widely used substance is metatartaric acid, but it has the disadvantage of hydrolyzing itself in the wine after a certain period of time, losing therefore its protecting action. The first tests using colloids obtained from cellular walls of leaven have been promising, but at the moment they have not had widespred practical application in wine cellars. Carboximethylcellulose, that has all the positive characteristics of met tartaric acid without introducing defects, at the moment, is

forbidden in the European community.
Basically, the hypothesis of “additional type”of crystallization inhibitors, and the fact that they also able to describe the degree of stability or instability of a wine, is that of "protecting colloids". It has been demonstrated that colloidal type substances are present in the wine, that they slow down or prevent the formation and the growth of crystals. The generally accepted hypothesis is that the colloids have mainly kinetic type action. The formation of bitartrate potassium crystals is slowed down until being stopped or blocked. In this way these compounds protect the wine from precipitation. This is the reason colloids having such an effect have been defined "protecting colloids".

The tartaric stabilization

Wine	
Variety	Carganeca
Grape harvest	2001
Alcool	10,2%
pH	3,0
Tartaric acid (gli,)	3,37
Potassium (mg/]_.)	600
Conductivity data	
Experimental saturation temperature	15,7 °C
Conductivity Dejection to 0° C	- 108 µS/cm
Conductivity Dejection to 0° C after permanence in autoclaves for 1 hour to 80 °C,	- 107 µS/cm
Thermodynamic calculations	
Theoretical saturation temperature	19,2 °C
Theoretical excess of KHT to 0° C	1088 mg/L

Table 1 – Analytical data of the white wine used for the tests

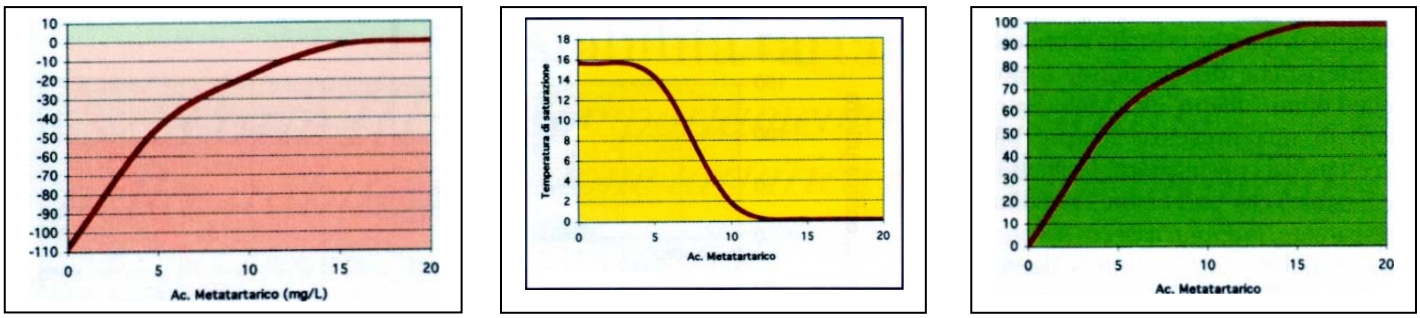

Figure 3 – The effect of increasing metatartaric acid concentrations on the various analyzed parameters.

Many substances have been found that have these qualities. Some are naturally present in the wine, like rubbers, pectine or polifenoli. Others can be added from externally, like metatartaric acid or carboximethilcellulose.
The methods of chemical stabilization called "subtraction type" are those that remove in a specific way an ion, so as to to create a Concentration Product of salt at an inferior level to that of its Solubility Product (PS) at the desired temperature. Even if they can be eliminated theoretically from a wine, either ion potassium or bitartrate ion, at the moment only potassium has been subject to subtractive techniques, that occur by the substitution with an other ion. The "subtraction type" methods experimented with in wines are those of the elettrodialisis and the use of ionic exchange resins. Both systems show good technological results, but they can be used only within specific normative (legal) contexts.
This laboratory will conduct the analysis of chemical methods of stabilization, on the basis of the indications and of the methods introduced to you in previous editions of this review magazine. The metatartaric acid, the carboximethilcellulose and the mannoproteins will be analyzed in particular. This article presents of obtained results: we refer in particular the verification of the effectiveness of some additives in tartaric stabilization of white wine of the grape harvest of 2001. The tested additives were metatartaric acid (Polytartryl - J.Laffort & Cie), mannoproteins (40 Mannostab - J.Laffort & Cie) and Nacarboximethilcellulose (Akucell AF2205 - Akzo Nobel). For the analyses we used the instrument Check Stab alfa2001 Millennium (Delta Acque - Florence), with the same practical methods indicated in previous article (1).

Metatartaric acid concentration mg/L	Conductivity decrease at 0°C µS/cm	Saturation temperature °C	Percentage of stability %
0	-108	15,7	0
5	-45	14,3	58
10	-18	1,8	83
15	-2	0,1	98

Table 2 – Behavior of matatartaric acid.

Carboximethilcellulose concentration Mg/L	Conductivity decrease at 0°C µS/cm	Saturation temperature °C	Percentage of stability %
0	-108	15,7	0
10	-55	14,3	49
30	-20	3,7	81
60	-5	0,4	95
80	0	0	100

Table 3 – Behavior of carboximethilcellulose.

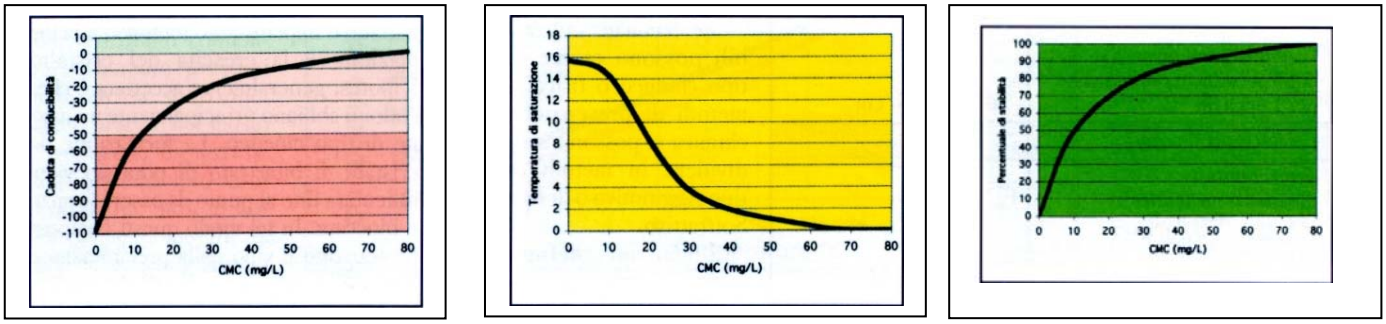

Figure 4 – The effect of increasing concentrations of carboximethilcellulose on the various parameters analyzes to you.

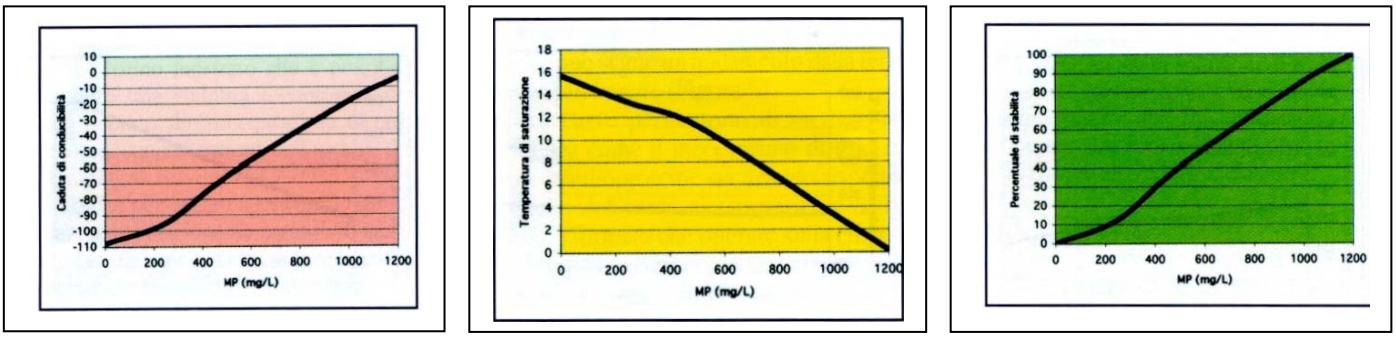

Figure 5 – The effect of increasing concentrations of mannoproteins on the various analyzed pararameters

mannoproteins concentration mg/L	Conductivity decrease at 0°C µS/cm	Saturation temperature °C	Percentage of stability %
0	108	15,7	0
250	-95	13,1	12
500	-66	11,3	40
1000	-19	3,3	86
1200	-4	0,2	100

Table 4 – Behavior of mannoproteins.

Method of analysis and interpretation of results

As has been demonstarated in previous articles, it must be pointed out, that all graphs illustrating the results are differential graphs (1, 2). The graphs show the difference of conductivity between the wine sample and the same sample at equilibrium with precipitated potassium bitartrate. If at a certain temperature the value is negative, this means that the wine was originally over-saturated, therefore by adding potassium bitartrate crystals causes crystallization and therefore a decrease in conductivity. On the contrary, if at a certain temperature the value is positive, it means that the wine is unsaturated, therefore is in a position to dissolve more potassium bitartrate, leading to a conductivity increase. The theoretical aspects and pratical methodology of analysis has been inserted also in the web sit www.oicce.it.

Wines where there has been increasing quantities of the various additives added, thereby inhibiting proportionally the precipitation, reducing the value of the drop of conductivity, depending on the concentration of additives used.

At a certain additive concentration, complete stabilization is obtained, therefore there is no drop of conductivity when more bitartrate crystals are added. This concentration is that one defined in the graph as the concentration where stabilization is 100% effective. Generally speaking, this quantity is more than

the quantity necessary to reach "technological stability", which is to say, sufficiently stable for the practical needs of the wine cellar, normally considered equivalent to a drop of less than 50 µS/cm.

For every addition of an additive and for every treatment to improve the tartaric stability of a wine, there are three types of measurements possible that give an index of the degree of stability of the product. The three data that give a rating of the relative stability are obviously inter related, but they do not follow a linear relationship. The three data are: the fall of conductivity at a specific temperature (in our case to 0°C), the temperature of saturation and the percentage of stability. The three additive analysis present three parameters, so as to point out their respective correlation. It is therefore opportune to give some explanations about their meanings.

The drop in conductivity

This is the measurement of how much the conductivity diminishes when the wine is put in contact with with KHT crystals, at a determined temperature (normally at 0°C). This is due to the ionic drop of the species in solution, an experimental measurement directly proportional to the amount of KHT that can precipitate from a determined wine.

The saturation temperature

This is the temperature at which a determined wine is in equilibrium with the precipitated crystals. At higher temperatures a dissolution of KHT will occur, while at lower temperatures, you will have precipitation. It must be emphasized that the temperature of saturation is not directly proportionl to the drop of conductivity at a given temperature.

The percentage of stability

This is a practical parameter that can help identify how much additive to add in order to reach stability, for a determined wine. The percentage of stability is calculated in function of the drop of conductivity at a determined temperature and can serve to empirically correlate the stabilizing activity of the various additives. The percentage of stability of the such wine is placed at zero which, without adding addititives. Meanwhile we get 100% stability when there no dropping of conductivity. Also this is a parameter that varies in a non linear way, in function to the quantities of added additives.

The tests in question have tested substances in various white wines. All graphs in this article have be created by adding various additives to the same instable white wine. The wine used as an example for comparisons between products is a white wine of Veneto (Garganega) region of the grape harvest 2001, with obvious tartaric instability. The essential analytical data of the wine are those shown in Table 1. The measured temperature saturation is 15,7 °C, while the drop of conductivity at 0°C is 108 µS/cm. The wine is therefore technologically unstable. Calculating with the method on-line OICCE (found on web-site www.oicce.it) the thermodynamic data on the basis of equations that regulate the equilibriums present, we found a saturation temperature higher than the data is found in experiements at 3,5 °C, at sign of a probable protecting colloid presence in the wine. The wine has been heated to 80 °C for an hour to verify that no change occurs. After heating the analytical data are identical to the previous data. The differential graphs of the wine is shown in Figure 2. It is calculated using the differences of the data measured in Figure 1. Increasing amounts of metatartaric acid (from 5 to 15 mg/L) has been added to the wine, of carboximethilcellulose (from 10 to 80 mg/L) and of mannoproteins (from 200 to 1200 mg/L) so that it can be compared to results obtained with the three additives.

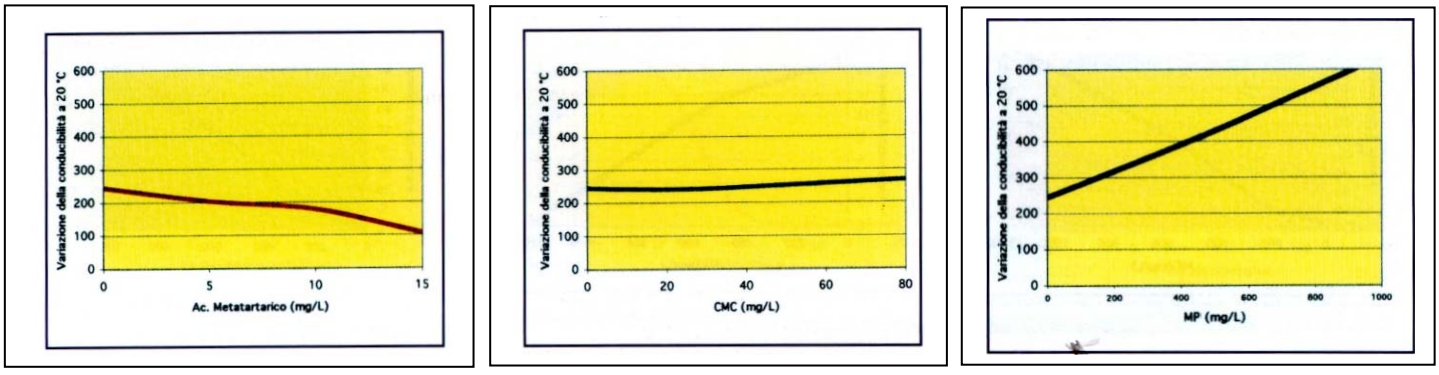

Figure 6 – Measurements of the variation of the specific conductivity at 20°C in function of the concentration of the three additives.

The behaviour of Metatartaric acid

The metatartaric acid is principal main adjuvant additive used to protect wines from the tartaric instability 13). It has already been used since 1950, also in very low concentrations which guarantee tartaric stability for several months. Its effect is connected to phenomena of superficial interaction, that prevent the formation and increase in formation of crystals. The quantities suggested in the bibliography for the stabilization of wines are variable, also due to the instability of the product in an acid environment. The metatartaric acid hydrolizes, thereby losing its effectiveness. The hydrolizing speed depends on the pH and the temperature. It is generally considered that doses of 50-100 mg/L of metatartaric acid guarantee the technological stability of wines for several months if stored at room temperature.

In the cases where the wines are only slightly instable (dropping of approximately -50 pS/cm) one obtains an effective protecting action with 2,5 mg/L. In Table 2 we see results obtained from unstable wine. We see evidence on the effect already at amounts of 5 mg/L, in order to obtain a technologically stable product. Beginning at 15 mg/L the product is completely stable.

Once complete stability has been reached, additional amounts of metatartaric acid does not modify the general picture. In the graph Figure 3 we see well the effect: the complete stability is reached with the concentration of 15 mg/L of metatartaric acid, and successive additions, do not change the situation. We see also that the effect on the temperature of saturation does not follow a linear course.

The method of analysis allows us to put in evidence the effect of loss of the protection due to the hydrolizing of metatartaric acid. In this way, the method renders possible the estimatation of the presence of small metatartaric acid concentrations thanks to the variation of the graphs that represent before and after hydrolizing.

It has been pointed out by some researchers that metatartaric acid introduces an effect also on the dissolution of potassium bitartrate. With the measurement instrument it is possible to determine with precision this phenomenon. Measuring the variations of conductivities that happen at a temperature of 20°C it is possible to have a determination of the solubility of the KHT. We see that the presence of metatartaric acid inhibits the dissolution of KHT, in proportion to the concentration of the additive (Figure 6).

The behavior of the carboximethilcellulose

The carboximethilcellulose is a chemical compound made for esterificazion of the carboxmethil cellulose. They are used in many alimentary products (ice cream,sauces,soups,fats...) and in alcoholic or non alcoholic drinks. Used a great amounts in the food industry, CMC has never had hygienic problems on the products where they have been used. Not yet admitted in the oenological field, they are object of industrial experimentation on large volumes of wine. Partial data quoted in the literature give us generic indication of the dose of 100 mg/L of CMC to obtain stability in wines.

Additive	Technological stability	Total stability
Metatartaric acid	5 mg/L	15mg/L
Carboximethilcellulose	13 mg/L	75mg/L
Mannoproteins	650 mg/L	1200mg/L

Table 5 – Comparison between additives. Concentrations necessary in order to get technological stability and stability total.

Recent works of Crachereau ET to. (5) have shown that it is possible to obtain technological stability of wine with respect to tartaric precipitations with concentrations in the order of the 40 mg/L . Also for this additive, having an instrument to measure quantitativly an analysis gives us precise determination of its stabilizing effect. Adding to the wine increasing quantities of CMC we get data as seen in Table 3. We get a technologically stable product with the concentration of approximately 13 mg/L. Beginning at 75 mg/L the product is completely stable. As already pointed out with metatartaric acid, we see also that CMC that the stabilization effect does not follow a linear course (Figure 4).

The behavior of the mannoproteins

Relatively recent studies have demonstrated various actions that mannoproteins can exercise on a wine, and in particular its role as a stabilizing agent in relationship to tartaric precipitation. Preparation of Mannoproteins techniques have recently been proposed both via enzymatic modes and thermal mode. The effect of these preparations have been studied on both wines and standard solutions. The mannoproteins preparations still are not allowed for use in the oenological field, but are wided experimented in various countries.

The semi quantitative studies introduced by Feuillat (7, 8) show that the stabilizing effectiveness of the various preparations of mannoproteins which use doses from 250 to 1000 mg/L. The industrial stability can be obtained on wines with doses from 100 to 300 mg/L.

Having an effective and precise method of analysis of tartaric stability of a must or a wine, allows us to measure with precision the stabilizing effect of various preparations.

We see as in table 4 when adding to the wine being examined increasing doses of mannoproteins. The effect of the additive can be noticed beginning at the dose of 250 mg/L, reaching a technologically stable product with the concentration of approximately 650 mg/L. Beginning from the 1200 mg/L product is completely stable. The saturation temperature is modified with the addition of mannoproteins, behaving differently than other substances, the variation tends to follows a more linear course(Figure 5).

The curves demonstrates differences in the mechanism of how the behavior of mannoproteins varies compared to metatartaric acid and CMC. Rather than working on the kinetic properties of crystallization, the mannoproteins influence the thermodynamic equilibrium, working to seize one or more of the properties in solution. This mechanism is demonstrated by the effect that the additive has on the solubility of KHT. In fact in both wines and in standard solutions the presense of mannoproteins increases the solubility of KHT. The increase moves in direct proportion to the concentration of mannoproteins, which demonstrate a complex activity(Figure 6).

The comparison between additives

The three additives used allow you to stabilize the wine in a satisfactory way. Table 5 shows the esamined case and the equivalent doses to reach technological stability and total stability. Arabic rubber, also at elevated concentrations, has not shown to have a sensible protecting effect, confirming therefore the bibliographical data.

The only additive that loses its action with temperature is metatartaric acid. Heating to 80°C for 90 min., or 60°C for various days, treatment that hydrolizes completely metatartaric acid, does not provoke any decrease of the effectiveness of the mannoproteins and the carboximethilcellulose. This phenomenon allows us to analyze its presence in musts and wines. The described methods of analysis is precise and sensitive, and is able to demonstate the presense of metatartaric acid, also in very low concentrations.

Moreover we see a very different behavior of the three additives with respect to the dissolution of potassium bitartrate at a higher temperature than the satuation temperature. In particular, the carboximethilcellulose is absolutely neutral respect to the dissolution equilibriums, while the mannoproteins increase the solubility of the KHT at a given to temperature showing its typical behavior as complex. This effect is proportional to the mannoproteins concentration and also occurs in solutions of KHT in water. The mechanism with which the mannoproteins operate in the stabilization of wines appears therefore different from the other additives we analyzed.

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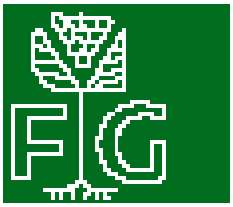


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