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

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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).

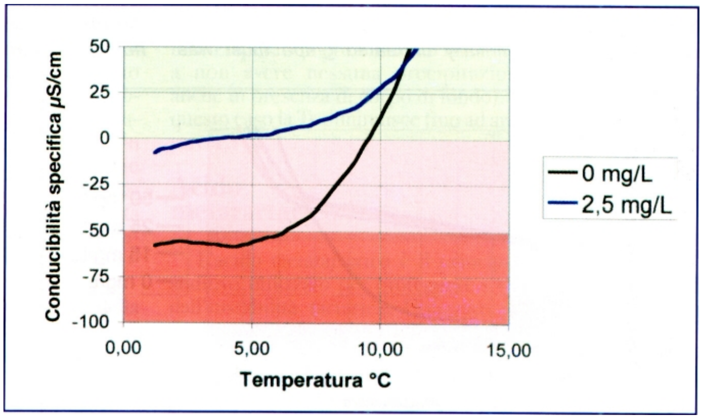

Figure 1 – The behaviour of a technolagically stable must where 2,5 mg/L of metatartaric acid has been added which indicates the essential points in this discussion.

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.

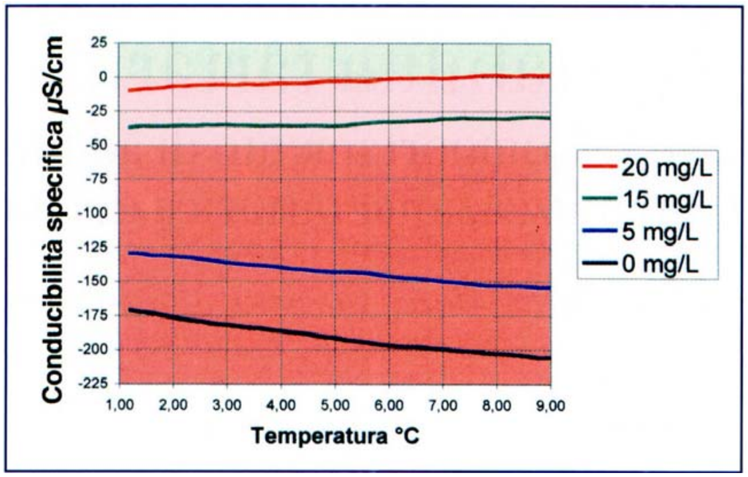

Figure 2 – Drop in conductrivity at a low temperature for an instable must with increasing doses of meta tartaric.

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.

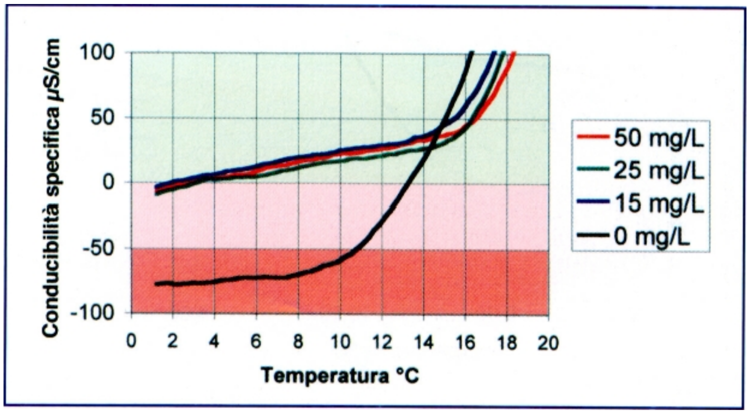

Figure 3 – Once reaching perfect stability, increasing doses of metatartaric does not modify the dropping of conductivity of the must

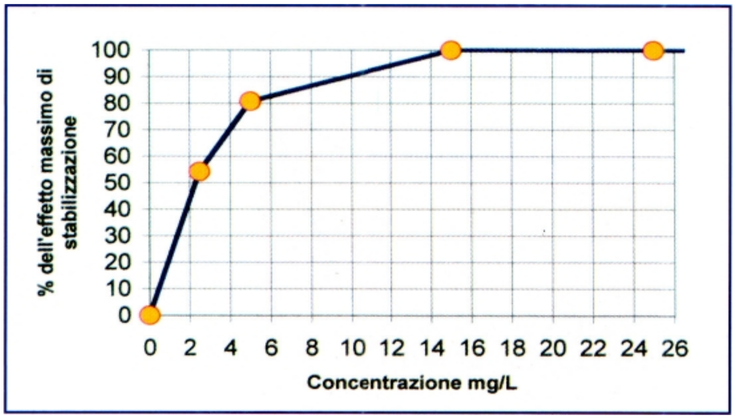

Figure 4 – The stabilizing effect of metatartaric acid does not follow a linear path.

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.

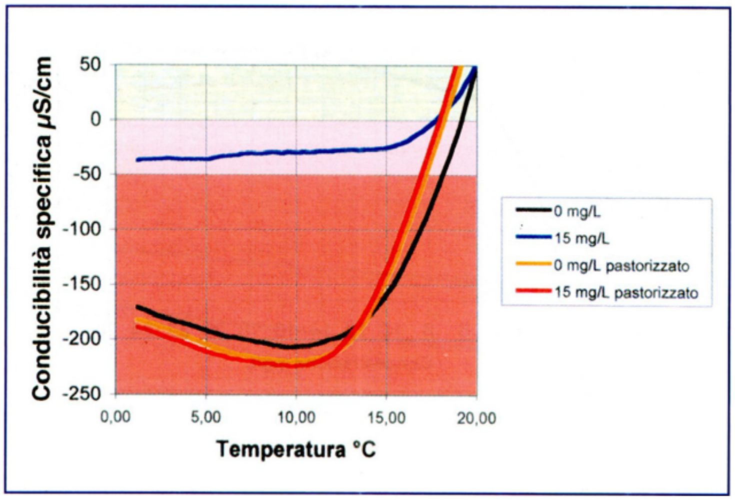

Figure 5 – The analytical method of the analysis allows to determine the presence of small quantitiies of metatartaric acid, thanks to the evedent loss of the protective effect after hydrolysis.

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).

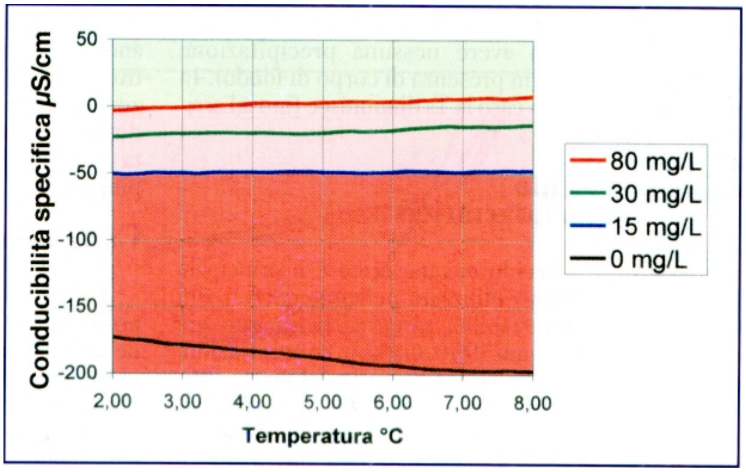

Figure 6 – Drop in conductivity at low temperature for an instable must instabile at increasing doses of Carboxymethylcellulose.

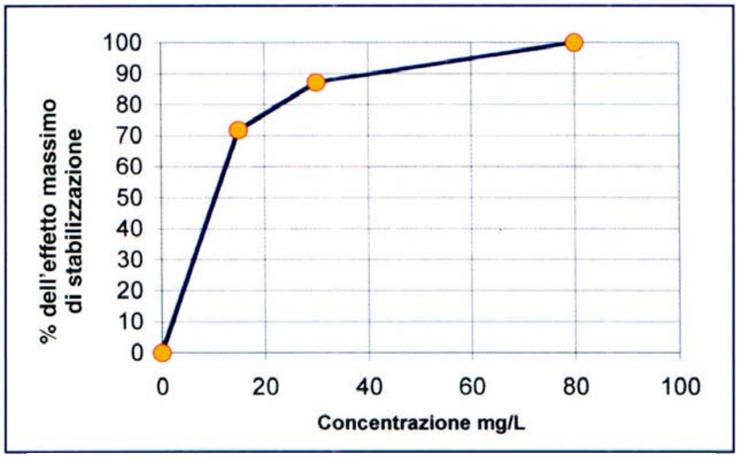

Figure 7 –The effect in percentage stabilization of Carbossimetilcellulosa does not follow a linear path.

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.

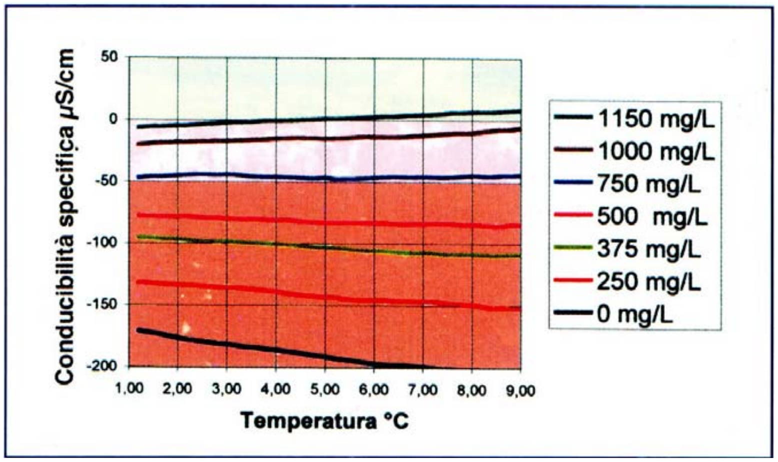

Figure 8 – Drop in conductivity at low temperature for an instable must at increasing doses of mannoprotein.

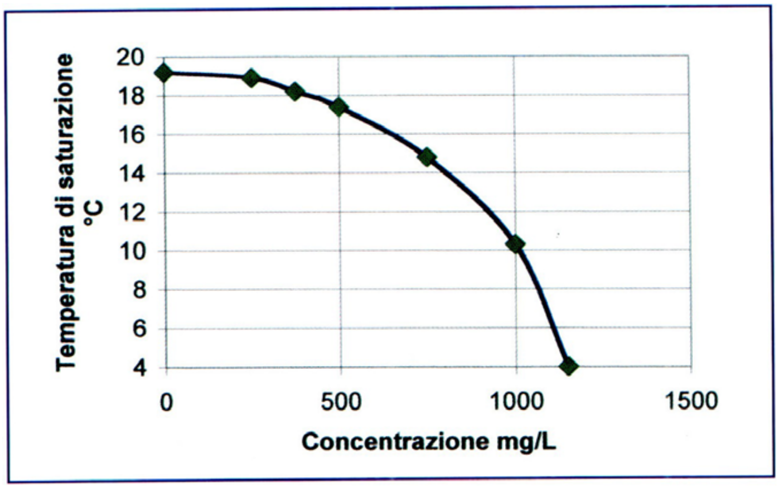

Figure 9 – Variation of Ts with increasing doses of mannoprotein.

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.

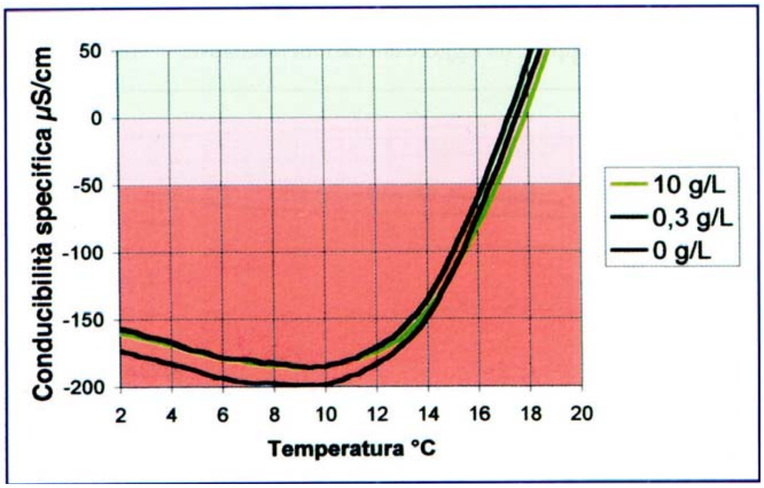

Figure 10 – Sabilization Test on a must utilizing gomma arabica. The preparation utilized has no influence on tartaric stability of musts.

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.