ANALYTICAL METHOD FOR OPTIMAL AND EFFICIENT USAGE OF MANNOPROTEINS FOR TARTRATE STABILIZATION OF RED, WHITE AND ROSE WINES

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Tartaric stability represents a key stage in winemaking and also for the quality as perceived by the consumer. There are several methods for obtaining wine stability in terms of potassium bitartrate precipitations: refrigeration, electrodialysis, ion-exchange resins or the addition of mannoproteins, carboxymethylcellulose or metatartaric acid. Whichever technique is used or tested, it is important that producers can evaluate the risks of tartaric precipitation in the laboratory. Several analytical methods exist for determining the level of wine instability and checking stability. At present the most commonly used methods for determining stability are the cold test (freezing or long term refrigeration), determining the degree of tartaric instability (DTI), the mini contact test and measuring the saturation temperature (Tsat).

TEST COMPARISON

Cold test: for white wines the most frequently used and most effective method is wine stabilization at -4°C for 6 days. Fairly precise qualitative indications can be deduced from this but the main drawback is the length of time required, despite the fact that it is possible to evaluate a wine's degree of instability after just 48 hours. Freezing the wine is however a very severe measure, as the entire colloidal structure is frozen and cannot interact in any way.

Measuring the DTI is a predictive analysis developed by INRA; it is based on the measurement of conductivity over time in crystallization conditions. This method allows highly unstable wines to be detected which obtain a DTI of over 20%.

Mini contact test is used to determine the wine's conductivity by using cold temperatures, with the addition of cream of tartar. It can be carried out in different ways, specifically in terms of duration: from a minimum of 4 minutes to a few hours. This test provides valid answers for white and rosé wines, this generally provides predictions for cold stabilization systems, but is rather limited for red wines, especially for short completion times as it tends to exclude the function of protective colloids.

Saturation temperature (Tsat) expresses the lowest temperature value at which the added potassium bitartrate dissolves in the wine. This parameter provides good indications concerning the instability of the wine, especially if associated with other methods and on observation of the graphs from -4°C to + 32°C as indicated by the device.

This article details the analytical method used for the addition of Claristar mannoproteins to white, rosé and red wines. The following tests carried out by Oenobrands demonstrate positive results obtained on white, rosé and red wines, which was essential to develop a standard reference method for determining the required dosages of Claristar mannoproteins. The method is the result of extensive laboratory tests carried out by Enolab (Capannoli, Italy), in collaboration with Oenobrands. This has allowed for fast interpretation of instability in a wine and the evaluation of obtained stability in wine In the case of Claristar mannoprotein addition for red wines, we require further studies in order to understand the impact of the protective colloids that remains in the wine.

It should be noted that Claristar mannoproteins make it possible to avoid the formation of potassium bitartrate crystal nuclei; this effect depends on the wine's degree of instability and on the way in which the wine in question has been prepared for bottling.

The use of Claristar mannoproteins allows the wine's organoleptic properties to be maintained and in many cases improved, especially when compared to the cold stabilization method. These properties have already been tested and the results will be published in an upcoming article.

METHOD

The method requires four successive stages.

Preliminary selection of the wine

Based on Enolab and Oenobrand's experience, it can be stated that the following preliminary conditions must be respected:

- white and rosé wines must firstly be stabilized in terms of proteins and undergo a clarifying filtration;
- red wines must be matured for at least 12 months, i.e. must have spent the winter in the cellar; young wines often present excessively high tartaric stability and/or considerable instability with regards to their color components.

Mini contact test

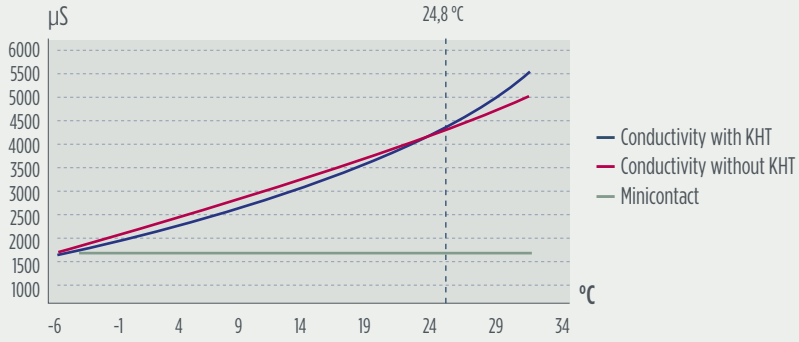
The mini contact test is used for evaluating a wine's level of instability and for deciding whether or not it can be treated with Claristar. It also provides information on the dosage of Claristar to be used on the wine in question.

For the mini contact test, the CheckStab® 2006 Rainbow appliance is used by Enolab.

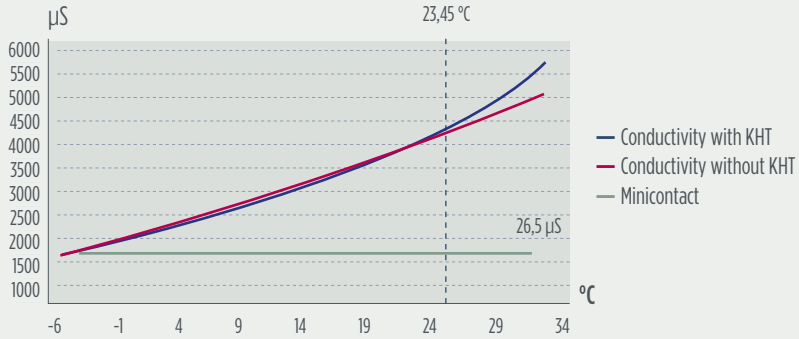
In the initial phase the test is useful for highlighting the degree of tartaric instability in boundary conditions; for red wines a sample of wine without Claristar is placed at -4°C for 3 hours following the addition of very fine particle cream of tartar (a very pure hydrogenotartrate) at a dosage of 2g/100ml. The mini contact test generally lasts 4 minutes and 30 seconds and has a tendency to overestimate tartaric instability in red wines. If the test result gives a declining conductivity value of between 60 and 140 µS it is considered that the wine could be stabilized with Claristar (see section "step-by-step"). A red wine can be considered stable if the drop in conductivity is below 60 µS, slightly unstable for values between 60 and 80 µS. The value for the drop in conductivity provides an indication as to the dosage of Claristar to be added to the wine; the lower the value, the smaller the dosage. The Claristar dosage to use is generally between 50 ml/hl and 110 ml/hl.

CONFIRMATION OF CLARISTAR DOSAGE

GRAPH 1 : analyse of saturation curve, on non-filtered control wine



GRAPH 2 : analyse of saturation curve, with 100 ml/hl Claristar



For trials on white and rosé wines, the duration of the test can be reduced to a minimum of 30 minutes. The recommended dosage for white and rosé wines is between 60 and 125 ml/hl. By using extrapolation the appliance can also provide values for the drop in conductivity after 4 hours and after 24 hours.

Turbidity measurement

This stage is only for red wines and white wines matured with wood.

Turbidity measurement in NTU using a nephelometer evaluates the reactivity of the colouring and polyphenolic matter in relation to Claristar mannoproteins.

Wine turbidity is first measured, and it is then measured following the addition of Claristar at the dosagrecommended for this wine at two time intervals namely; 1 hour and 16 hours following the first addition. The acceptable difference in turbidity between the untreated wine and the wine treated with Claristar must not exceed 10 NTU; the values are considered to be correct up to 8 NTU and acceptable between 8 and 10 NTU.

A subsequent evaluation can be made based on turbidity variation over time: a progressive increase reveals the wine's reactivity to the mannoproteins, with an unacceptable situation on the other hand, a drop in turbidity over time indicates that a fining effect has occurred. This situation is however acceptable, if it is maintained within the range of the expressed values.

Confirmation of Claristar dosage

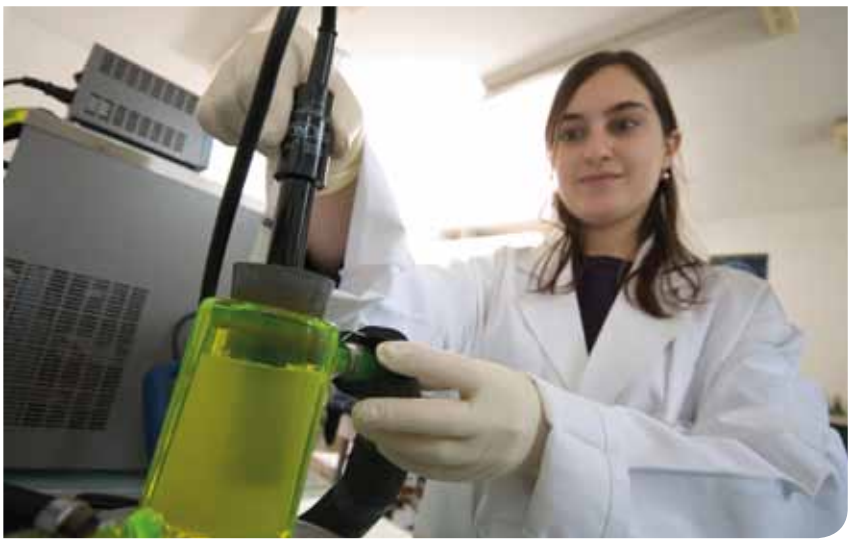
To confirm the validity of the dosage chosen based on the mini contact test, the behaviour of the wine treated with Claristar is assessed in relation to the saturation temperature according to two modalities (graphs 1 and 2):

- ➜ wine treated with Claristar (red curve);
- ➜ the same wine with the addition of cream of tartar at 2g/100ml (blue curve).

To determine the stability within the temperature range of -4°C and +32°C; two curves are obtained and by comparing them, wine instability can be studied in detail.

The Tsat value alone cannot confirm the positive effect of using mannoproteins in the wine, as the parameter does not evolve as a result of the addition of Claristar. The method described in this article is based on the comparison of the conductometric curves.

The first important parameter is represented by the intersection of the two curves, which corresponds to the wine's Tsat (saturation temperature). Claristar facilitates the crossover of the two curves; the second important parameter is the distance between the two curves preceding the intersection: the larger



Claristar®

the distance, the more unstable the wine.
When the correct dosage of Claristar is used in a wine the closer the curves become until they almost touch each other. In this way, the Tsat graph evaluates the increase in stable supersaturation in a wine treated with Claristar and consequently the critical temperature crystallization drop.
NB: for stages 2 to 4, the wine to be analysed will have been filtered at 1,2 µm in the laboratory.

LABORATORY EXPERIMENT

160 batches of wine were analysed using the described method, of which 70% were red wines. The wines were pre-judged based on their winemaking characteristics: on average, only 5% of the wines did not pass this first step; these were mostly wines that were too young, too sensitive in terms of tartaric reaction and in terms of colour components. The Claristar dosage for each wine obtained using the described method was compared using the cold test (standard reference method); in 95% of these cases the comparison of these 2 methods shows a perfect correlation.

TREATING YOUR WINE WITH PRECISION

The method for evaluating stability in wines treated with Claristar described in this article is a valid tool for understanding the degree of instability in wines and the effect of Claristar mannoproteins has on improving the tartaric stability index.
The current application method used on a large number of red wines ensures the correct interpretation of tartaric stability on these wines.
For the addition of Claristar mannoproteins, the following technical information must be respected:

- or red wines, given the complexity of their colloidal structure, Claristar must be added at least 4 to 5 days prior to bottling;
- as Claristar does not prevent the growth of crystal nuclei present in the wine, it is advisable to filter the wine before bottling. The finer the filtration, the more crystal nuclei will be eliminated; optimal filtration, under certain conditions, is a 1,2 µm porosity. It is essential to prevent clogging and excessively tight filtrations, in order to avoid retaining the Claristar mannoproteins. For white wines previously filtered on plates, filtrations of up to 0,45 µm or 0.2 µm have not created problems of efficiency loss;
- due to the fact that mannoproteins react physically with cellulose, filtrations using cellulose plate filters must be avoided once the Claristar has been added, as this would fix part of the Claristar and be detrimental to the wine stability;
- Claristar must be added after treating the wines with earth filters.

NB: the analysis method described here is based on the results of practical experiments. Adapting this method to your particular needs may require calibration.

STEP-BY-STEP METHOD

STAGE 1 : PRELIMINARY SELECTION OF THE WINE

The wine must be at least one year old (or have spent the winter in the cellar).

STAGE 2 : MINI CONTACT

-4°C for 45 minutes with the addition of 1g/100ml cream of tartar for white and rosé wines;
-4°C for 3 h with the addition of 2g/100ml cream of tartar for red wines

with the following results for Claristar dosage predetermination:

EVALUATION WHITE/ROSÉ WINE	MINI CONTACT VALUES	CLARISTAR DOSAGES
Stable	Δ µS < 50 µS	0
Slightly unstable	50 µS < Δ µS < 90 µS	60-80 ml/hl
Moderately unstable	90 µS < Δ µS < 130 µS	80-100 ml/hl
Very unstable	130 µS < Δ µS < 160 µS	100-125 ml/hl
Too unstable	Δ µS > 160 µS	NO – wine not to be treated

RED WINE EVALUATION	MINI CONTACT VALUES	CLARISTAR DOSAGES
Stable	Δ µS < 60 µS	50-60 ml/hl
Moderately unstable	60 µS < Δ µS < 90 µS	60-80 ml/hl
Very unstable	90 µS < Δ µS < 140 µS	80-110 ml/hl
Too unstable	Δ µS > 140 µS	NO – wine not to be treated

STAGE 3 : TURBIDITY MEASUREMENT (for red wines and whites matured in barrels)

AFTER 1H	
Δ NTU > 10	NO – wine not to be treated
No increase in NTU	Wait until 16 h
AFTER 16 H	
Δ NTU < 10	Continue studying curves
Δ NTU > 10	NO – wine not to be treated

STAGE 4 : TSAT CURVE STUDY

If the two conductivity curves of the wine with Claristar according to the temperature, with or without KHT, overlap or are very close together, the Claristar dosage is correct.
If there is no overlap or there is obvious distance between the curves, it is recommended to use Claristar at a higher dosage (and to be retested – go back to stage 1).

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