Effects of Reutilized Potassium Bitartrate Seeds on the Stabilization of Dry Sherry Wine

J. M. GARCÍA-RUÍZ[1]*, R. ALCÁNTARA[2], and J. MARTÍN[3]

The kinetics of potassium bitartrate precipitation were analyzed by the crystal seeding method. The influence of the seed size and the number of cycles of seed reutilization was studied. The results show that the stability achieved in dry sherry wines reusing the seeds was acceptable for long residence times (for instance, for classical methods of stabilization), but it should be carefully assessed for residence times of less than four hours.

KEY WORDS: wine stability, seeding, potassium bitartrate, potassium hydrogen tartrate

Potassium bitartrate (also called potassium hydrogen tartrate) is an ubiquitous component in wine, which does not affect its organoleptic properties and forms naturally, achieving concentration above equilibrium during wine production. Potassium bitartrate solutions usually present a broad metastability band, which means that they can remain stable even at relatively high values of supersaturation, with the consequent risk of undesired precipitation after bottling. Therefore, in order to avoid tartrate precipitation in the bottle, wine makers are particularly interested in reducing the concentration of this compound before bottling to such levels that the expected induction time for crystallization is much longer than the usual consumption period. This process of reducing potassium bitartrate precipitation is known as tartrate stabilization of wine.

Industrial stabilization of wine against tartrate precipitation follows two methods. The usual stabilization procedure (1,2) consists of cooling the wine to around -6°C (depending on its alcoholic degree) for not less than six to seven days, usually together with seeding of potassium bitartrate to enhance the kinetics of nucleation (1). Regarding the cost of this stabilization method, two parameters must be considered: *(a)* the residence time at temperatures below zero and *(b)* the consumption of potassium bitartrate in the seeding. Optimization of these parameters leads to a reduction of the additional cost to the end-product.

The second method, usually known as continuous treatment, is a new method studied by several authors as reported in several papers (4-12) and patents (13,14,15,16) being evaluated at present by some wineries in the area (3,4,5). It is based on successive cycles of seeding-recovery-seeding carried out at approximately -6°C with a residence time of few hours. Because of its low residence time, the continuous stabilization method requires a precise knowledge of the kinetic parameters, which are less important in the classical method.

In this paper, we present a study of the influence of seed size (solid potassium bitartrate) and the consecutive reutilization of seeds in the precipitation kinetics of potassium bitartrate in dry sherry wines.

Materials and Methods

Samples of dry sherry wines were supplied by Osborne S.A. (Puerto de Santa María, Spain), and they had undergone no previous treatment other than clarification and filtration. The saturation temperature of the wine was determined as a function of the potassium bitartrate concentration in each sample (3), obtaining a value close to 20°C. The samples were then cooled to -4°C; *i.e.*, they were located into the metastability region at conditions far from the equilibrium curve. Then, they were seeded with a concentration of 8 g of solid potassium bitartrate per liter. The two variables to be tested were the particle size distribution and the number of times the same seeds were reutilized. After a short time (typically two minutes), when the homogenization of the system had been assured, pairs of data on temperature and specific conductivity were recorded by a computer equipped with a 12-bit A/D data acquisition system. The total length of the experiment was approximately 11 hours ($\approx 4 \times 10^4$ sec). The software for data acquisition was home-designed. The equipment was programmed to file one data every eight seconds, each of these data resulting from the average of the values measured every tenth of a second. Under these conditions, the number of working data was 5000 out of a total of 4×10^5 measurements. Experiments designed to test the influence of the recycling of seeds were performed maintaining the seed size constant. After each experimental cycle the precipitate was recovered, dried, and milled to the initial seed size (35 ± 5 μm). To characterize the distribution of seed size, we used a Malvern 2600c particle sizer based on laser light scattering.

Results and Discussion

Two approaches can be used to characterize the efficacy of a precipitation method: *(a)* the study of the

[1,2]Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Avda. Fuentenueva s/n, Granada 18002, Spain; [3]Departamento de Química Física, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, Puerto Real, Cádiz. Spain.

*Corresponding author.

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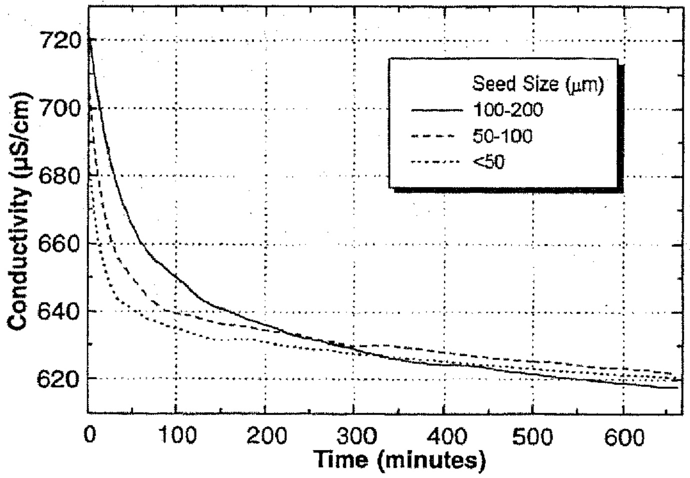

Fig. 1. Evolution of conductivity against time for three different sizes of pure potassium bitartrate seeds. Size range is specified in the figure.

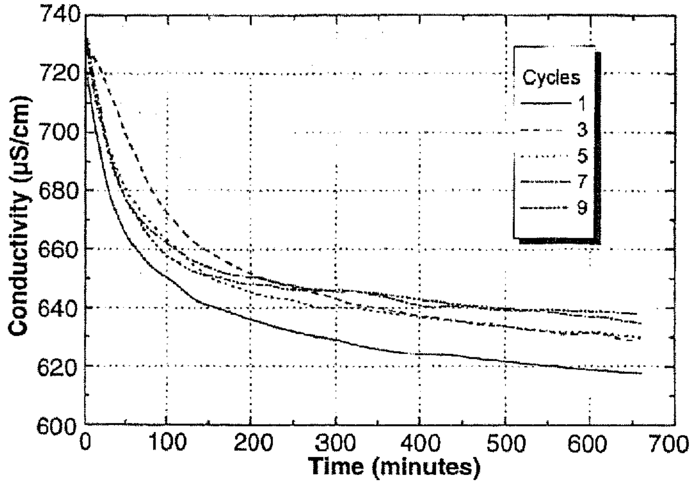

Fig. 3. Evolution of conductivity against time for nine consecutive cycles of reutilization of potassium bitartrate seeds. For the sake of clarity, only odd cycles are shown .

kinetics of the process, which provides information about the time required to reach a quasi-stationary situation; and *(b)* the measurement of the maximum attainable precipitation when t → ∞. For practical purposes, the efficacy of any stabilization procedure can be then quantified by the ratio of the precipitation obtained at a particular moment to the maximum attainable precipitation. Values can then be provided as percentages of the increase in efficiency of the process. Because of the direct relation of conductivity with potassium bitartrate concentration in the wine, the evolution of the precipitation process was monitored in our study by measuring the variation of conductivity with time. Figures 1 and 3 provide graphic representations of this variation for different seed sizes and reutilization cycles. Figures 2 and 4 show the kinetics of the process for each series of experiments, expressed as the first derivative of conductivity with time.

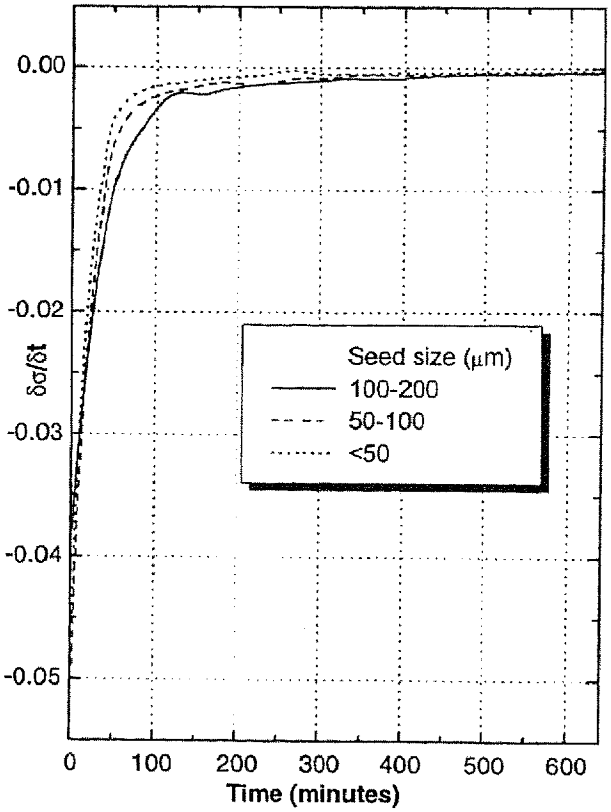

Fig. 2. Evolution of the first derivative of conductivity against time for three different sizes of pure potassium bitartrate seeds. Size range is specified in the figure.

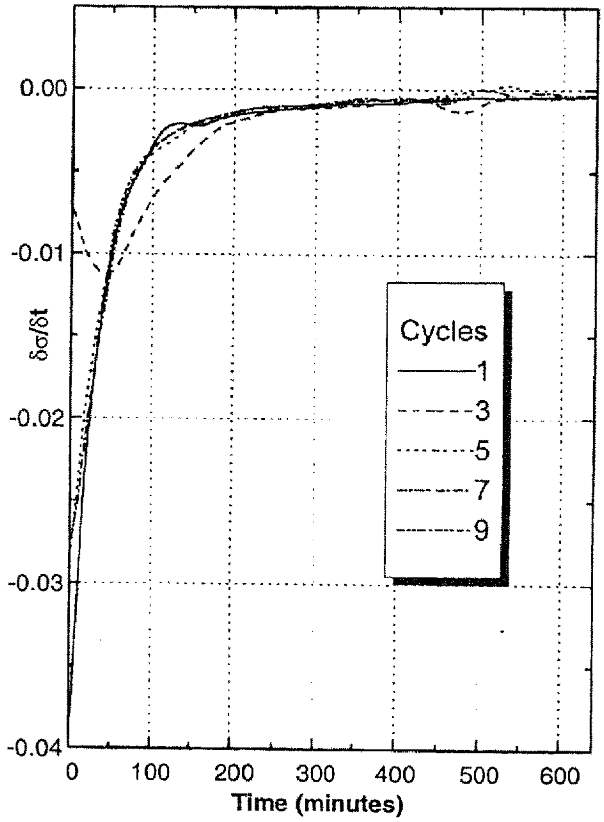

Fig. 4. Evolution of the first derivative of conductivity against time for nine consecutive cycles of reutilization of potassium bitartrate seeds. Only odd cycles are shown.

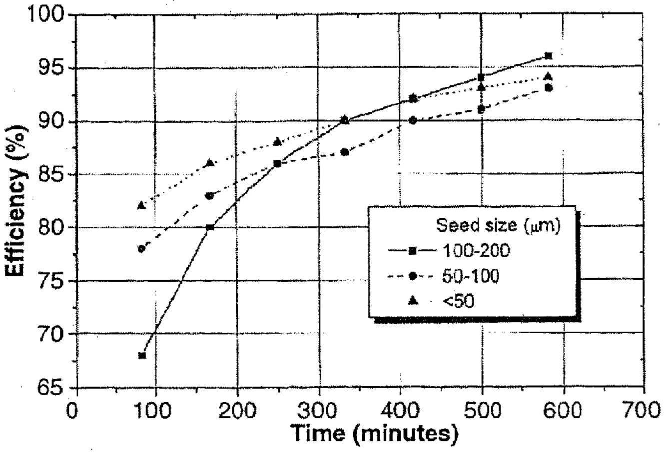

Fig. 5. Efficiency of the method (in percent) as a function of time and seed size. 100% efficiency was taken as the maximum obtainable conductivity difference, measured on Fig. 4, whose extreme values were: 735 μS cm^{-1} (start of measurement) and 615 μS cm^{-1} (end of experiment).

According to kinetic theory, precipitation is more effective the larger the contact surface between the crystal face and the mother solution. If the crystal particle is considered as a nonporous solid, its surface will bear relation to the size of the particles, varying with the second power of the particle radius. Smaller the lineal size of the seed the greater the surface and, therefore, the higher the efficiency of precipitation. This can be observed in Figures 1 and 2 for the following particle sizes: *(a)* less than 50 μm; *(b)* 50-100 μm; and *(c)* 100-200 μm. Figure 5 shows that the efficiency obtained for type "a" particles after 83 minutes (E_r = 82%) is similar to those obtained for "b" type particles after 167 minutes and "c" type particles after approximately 208 minutes. However, after a few hours (333 minutes), efficiency is practically constant no matter which type of particle is used.

In those processes involving reutilization of seed, poisoning of the growth faces occurs which leads to the cessation of growth in supersaturated solutions. This is due to the fact that, since wine is a multicomponent system, potassium bitartrate precipitation involves removal of other components of the wine. This co-precipitation provokes alterations of the growth surfaces of the crystal, making the effective surface area smaller than expected. It is, therefore, reasonable that further reutilization of the precipitate as seeds will never achieve the same efficiency as pure potassium bitartrate seed. This effect can be partially counterbalanced by milling prior to further reutilization, as the breakup of the seed produces non-contaminated crystal surfaces. Figure 3 shows that, at any given time, the degree of precipitation is always lower for reutilized seeds than for pure seeds. Figure 6 presents a quantification in terms of efficiency. In Figure 4, we can observe that after approximately six hours and 40 minutes the kinetics of precipitation is practically independent of the number of times the seeds were reutilized; *i.e.*, differences in efficiency remain constant throughout the process. Note that the curves in Figures 4 and 6 show the existence of several crossovers, which can be explained by the nature of the relations among crystal growth, face poisoning, the generation of non-contaminated surfaces by crystal breakup during milling, and cluster disintegration. The different values that can be obtained for each of these parameters for a given time mean that the process does not evolve with monotonous continuity, and since the curves are close together, intersections between them occur.

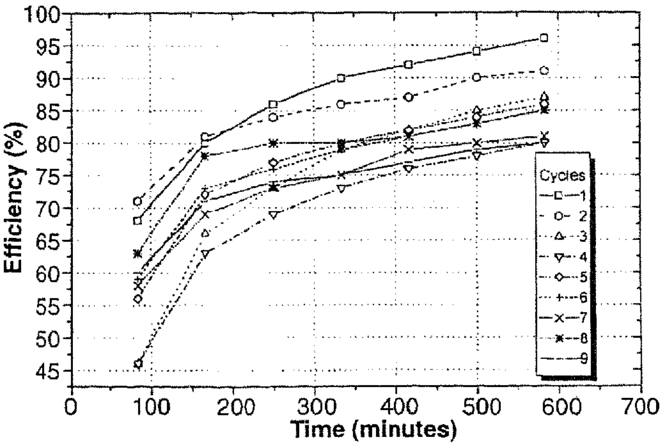

Fig. 6. Efficiency of the system (in percent) as a function of time and number of seed reutilization cycles. 100% efficiency was taken as the maximum obtainable conductivity difference, measured on Fig. 4, whose extreme values were: 735 μS cm^{-1} (start of measurement) and 615 μS cm^{-1} (end of experiment).

The difference in effectiveness under reutilization of seed can be quantified as the concentration of potassium bitartrate on the basis of the difference in conductivity between the curves at any one time. For cycles 1 and 9, we obtained a value of 20 μS cm^{-1} at -4°C, which corresponds to a difference in final concentration of approximately 0.13 g/L (at 20°C the potassium bitartrate concentration is approximately 2 g/L). This difference means that the final saturation temperature is around 1.5°C higher for seeds that have been reutilized nine times than for seed of pure potassium bitartrate. Although this difference is considerable, it may not be decisive for industrial applications if the residence time is so high that the final saturation temperature is always low enough for the induction time to be higher than the maximum consumption period. This is the case of the classic stabilization systems in which, as mentioned above, contact with the seed occurs for several days. On the other hand, in continuous stabilization methods, where residence time is very low (*ca* 2 hr), the size of the seed becomes a decisive variable.

Conclusions

We conclude that for the classic stabilization method, the most important parameter is loss of efficiency through reutilization of the seed. Considering the cost-reduction that it represents and the fact that a reasonably acceptable final saturation temperature is obtained, we recommend some degree of reutilization of the precipitate. However, regarding the continuous stabilization method for which conditions are much more demanding, the system should be optimized by using seeds milled to the smallest size possible, as the system is affected by all of the problems involved in reutilization of the seeds.

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