NUCLEATION AND GROWTH OF POTASSIUM BITARTRATE IN WINE

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Among the organic compounds and ions in fermented wines, potassium bitartrate (KHT) often crystallizes out during storage at low temperature. Wines obtained by fermentation are usually stored for a long period at moderately low temperature to decrease KHT concentration from 2000–3000 ppm to a few hundred ppm by the precipitation of KHT. Such a method of KHT removal is uneconomical because of the long time storage, and control of KHT concentration to the prescribed value is considerably difficult.

To make clear the crystallization behavior of KHT in wines, studies have been made, mainly for estimation of the limiting stability of wines by measurement of the maximum degree of supersaturation[1,2,3,4]. It was also reported that the control of KHT concentration was possible by the proper combination of cooling temperature and holding period[5,6,7,8]. However, the crystallization behavior of wine has been little investigated.

In this study, the control of KHT concentration using seed crystals was investigated. The secondary nucleation and growth rates in a model aqueous solution and four kinds of wines were measured. The surfaces of KHT crystals from the model aqueous solution and wines were observed with SEM and compared with those of crystals obtained in the model aqueous solution. Additionally, the rate retardation was studied on the basis of crystallization behavior.

1. Experimental

Three white wines denoted by W1, W2, W3 and a red wine R1 were used in the experiments. The compounds present in the wines are listed in **Table 1.** Organic acids were quantitatively analyzed using high-performance liquid chromatography (HPLC). A model aqueous solution (M.S.) composed of KHT, ethanol and water was used for the purpose of comparison with the wines. From the result of preliminary experiment, it was confirmed that only KHT was removed as crystals on cooling the wines.

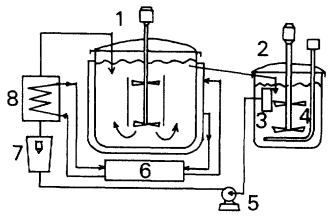
As shown in **Fig. 1**, a MSMPR crystallizer ① ($1.3 \times 10^{-3} m^3$) fitted with a draft tube and equipped externally with a cold-water jacket was used. Two

Table 1. Composition of model aqueous solution and wines

Sample	Organic acids [ppm]				Cations [ppm]		TP* [ppm]	Ethanol [v/v%]	pH
	Tartaric	Malic	Lactic	Acetic	K	Ca			
Model solution	2140	0	0	0	560	0	0	12.0	3.76
W1	2890	2800	650	650	664	50	246	11.5	3.20
W2	2510	2200	2290	930	697	42	337	11.7	3.19
W3	2870	3270	850	740	1015	69	436	12.7	3.30
R1	1890	140	1800	520	1131	71	1958	11.9	3.24

* Total phenolic compound concentration as gallic acid

* Received November 5, 1991. Correspondence concerning this article should be addressed to H. Tanahashi.



1 Crystallizer 2 Dissolver 3 Filter
4 Heater 5 Pump 6 Refrigerator
7 Flow meter 8 Cooler

Fig. 1. Schematic diagram of experimental apparatus

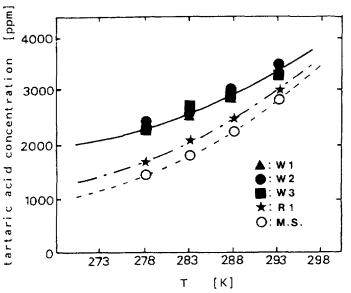


Fig. 2. Solubilities of KHT in model aqueous solution and wines

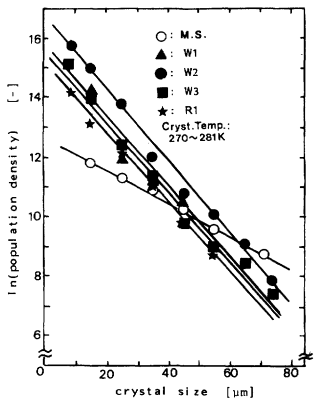


Fig. 3. Population densities of crystals from model aqueous solution and wines

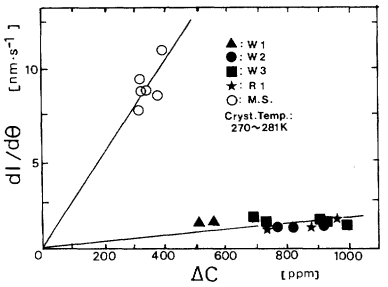


Fig. 4. Relation between crystal growth rate and supersaturation

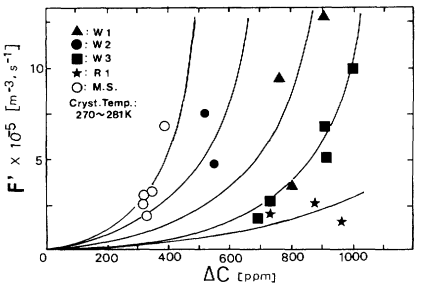


Fig. 5. Relation between nucleation rate and supersaturation

2. Results and Discussion

The population densities of KHT crystals are plotted against crystal size in **Fig. 3.** Although the plots for the wines are slightly convex downward, the nucleation and growth rates were determined by the ordinary method under the approximation as a straight line. The growth rates are plotted against ΔC in **Fig. 4.** The growth rates were expressed by the two lines. The ΔC dependency of the growth rates in all the wines is the same, and the growth rates in wines are about one fifteenth of that in M.S. The rate retardation is supposed to be caused by compounds present in wines. The nucleation rates are plotted against ΔC in **Fig. 5.** The nucleation rates in wines are smaller than that in M. S. and are different from one wine to another. Although the data include values measured at different temperatures, the temperature effect on both rates can be neglected because of the narrow temperature range such as 270–281 K.

To make clear the influence on both rates of organic compounds and ions, SEM photographs were taken. **Figure 6** shows KHT crystals obtained in M. S. at low ΔC in the crystallizer. The shapes of crystals of various sizes are almost polyhedric with plane surfaces, and all surfaces are bounded by straight edges. **Figure 7** shows KHT crystals obtained in a stagnant solution of W1 at low ΔC. Although the crystals smaller than several tens of micron have a crystal habit similar to

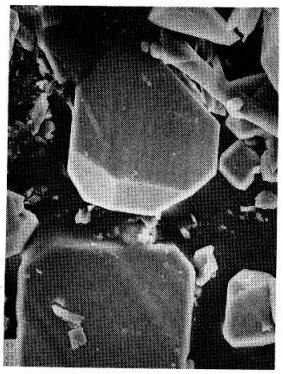


Fig. 6. KHT crystals from MSMPR crystallizer for model aqueous solution (× 750, $\Delta c = 320$ ppm)

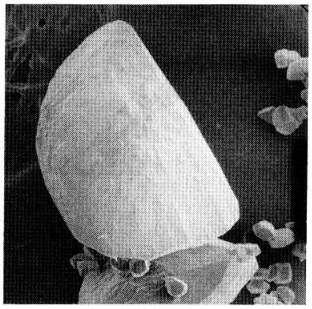


Fig. 7. KHT crystals from stagnant solution of W1 (× 1000, $\Delta C = 370$ ppm)

that in M. S., the large crystals, grown up to several hundred microns, change their crystal habit. Such a transformation of crystal habit during growth is considered to be caused by the effect of organic compounds and ions present in W1. **Figure 8** shows KHT crystals obtained in R1 at low ΔC in the crystallizer. The crystal habit of KHT crystals from R1 is considerably different from those obtained in M. S. and W1. The KHT crystals grown in R1 have a peculiar shape, resembling a pile of plate-like crystals. This phenomenon is thought to be caused by the presence of the large amount of phenolic compounds present in R1, as shown in Table 1. From these results, it can be considered that the crystal habit of KHT changes notably due to some organic compounds and ions present in wines, and the retardation of nucleation and growth rates is also caused by the same components.

Fig. 8. KHT crystals from MSMPR crystallizer for R1 (× 500, $\Delta C = 735$ ppm)

In conclusion, it was found that the crystal growth rates of KHT in different wines had the same values at same ΔC, although they were smaller than those in M. S. The nucleation rate in the M. S. became the highest, white wines followed and the red wine was the lowest at the same ΔC. The difference in the two rates was thought to be caused by the effect of some organic compounds and ions present in the wines.

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Nomenclature

ΔC	=	degree of supersaturation in ppm	[—]
F'	=	nucleation rate	[$m^{-3}s^{-1}$]
l	=	crystal diameter	[nm]
T	=	temperature	[K]
θ	=	time	[s]

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