

Scientific paper

Monitoring of Potassium Hydrogen Tartrate Stabilization by Conductivity Measurement

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Abstract

In wine technology traditional procedure of uncontrolled potassium hydrogen tartrate (KHT) crystallization usually represents long term energy consumption process. Fast crystallization method, using the addition of potassium hydrogen tartrate, as crystallization initiator, joined with simultaneously cooling and followed by monitoring the crystallization process by using conductivity measurement, was tested in two sorts of white wine Sauvignon Blanc and Malvasia. Addition of various amounts of potassium hydrogen tartrate (1, 2, 4, 6 and 8 g/L) as initiator of crystallization and cooling temperatures 4 and 0 °C were applied. Addition of 6 g/L KHT and cooling temperature 0 °C were found to be the most suitable parameters for fast crystallization.

Keywords: Crystallization, potassium hydrogen tartrate, conductometry.

1. Introduction

Present potassium hydrogen tartrate (KHT) in wines can remain stable at relatively high levels of super-saturation, however, changing the outlet temperature could also influence in precipitation of KHT crystals as undesired sediment in the bottled wine what is unacceptable for many consumers.^{1,2} In some processes for KHT stabilisation also ion exchange resins techniques were used.^{3,4} Traditional procedure of uncontrolled potassium hydrogen tartrate (KHT) crystallization in the barrels and stainless steel tanks usually represents long term and energy consumption process. Therefore for newly formed wines methods for fast KHT crystallization are highly required.^{2,6,7}

The white wines differed considerably in KHT crystallization kinetics. Complete crystallization and stabilization of different white wines is usually achieved from 8 days to 6 weeks or even longer. Tartrate deposits consists of tartaric acid, polyphenols, polysaccharides (mannoproteins, rhamnogalacturonans), potassium ions, calcium ions and insoluble matter.^{5a,b,8,10}

Polysaccharides and phenolic acids comprised 0.2–0.8% of dry matter in tartrate deposits from white wi-

ne^{5a} and 2.5–2.6% from red ones.^{5b} Tannins are the main phenolic compounds in the tartrate crystal deposits of red wines.^{5b} KHT crystallization was indicated to be faster in the aqueous ethanol solution, and the slowest in red wines.^{1,10}

Crystallization of KHT in wine is also prevented by alcohol, proteins, polysaccharides and other high molecular weight compounds. Cold stability suggests that a wine has been sufficiently chilled to ensure that KHT will not precipitate under normal storage conditions.^{8,10} Higher degree of crystallization inhibition in reds is related to higher concentration of rhamnogalacturonans and polyphenols, that complicate cooling techniques in red wine stabilization. Mannoproteins extracted from yeast cell walls have also greater inhibition on KHT crystallization. However, their effect on crystallization inhibition decreases with decreasing temperature. In accordance with a theoretical model of crystallization, where the presence of rhamnogalacturonans inhibit crystallization by their binding to crystal growth sites.¹ Precipitation can be greatly accelerated by increasing the concentration or by addition of crystalline KHT. The rate of KHT precipitation, at a present temperature, is predominantly a function of the quan-

tity of KHT in solution above the saturation level.

For monitoring of KHT precipitation conductivity measurement was found to be very suitable. KHT crystals are formed in two concentration-related phases: an induction phase to develop nuclei and a crystallization phase. Adding crystalline KHT reduced the time factor in which nuclei should be generated.^{6,9} Still wines are usually tested for tartrate stability to eliminate the possibility of formation of crystalline sediment of KHT. Cold stabilization is widely practised, in which KHT is crystallized and precipitated by holding for about 1 week at -2 to -4 °C.^{6,7}

By the definition specific conductivity G (S, Siemens) of the material represents a reciprocal value of the resistance measurement R (Eq.1). It is specific characteristic of the material or liquid used. The same principle could be applied also for the solutions of the electrolytes.

$$G = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{L} \quad (1)$$

Where is: R – resistance (Ω), ρ – specific resistance (Ω m), L – distance between the measured Pt electrodes in conductivity cell (m), A – cross section (cm^2).

Conductivity κ (S m^{-1}) of the measured liquid is defined by Eq. 2:

$$\kappa = G \cdot k = G \cdot \frac{L}{A} \quad (2)$$

where k is the cell constant (m^{-1}), $k = 0.01$ m^{-1} for standard measuring cell.

For saturated potassium hydrogen tartrate (KHT) solutions the saturation product K_{sp} is a function of temperature, content of potassium c_{K^+} and hydrogen tartrate ions concentration c_{HT^-} in the solution. Saturation product is expressed by Eq.3.

$$K_{\text{sp}} = c_{\text{K}^+} \cdot c_{\text{HT}^-} \quad (3)$$

Conductivity is temperature dependent process that decreases by the decreasing the temperature. If the ion content exceeds the value of saturation product K_{sp} , then the applied solution becomes unstable and it initiates the crystallization of KHT.^{1,11} Related to the concentration of potassium $[\text{K}^+]$ and hydrogen tartrate $[\text{HT}^-]$ ions concentration, minimum temperature need for the system stability could be determined.^{8,10,11} Besides cold stabilisation in some processes also ion exchange techniques were applied.^{3,4}

2. Experimental

All of the experiments were carried out in 10 L laboratory bioreactor (Chemap AG, Switzerland). For conductivity *on-line* measurement Mettler-Toledo Pt InPro 7001/225 sensor with measuring range 0.02 to 2500 μS

with CR7350 detector in connection with analog/digital converter Advantech Adamin and standard PC computer was used. Visidq-Genie, Professional V3.11 software by Advantech was applied.

Total acidity was measured according to standard Mettler-Toledo procedure by using potentiometric titrator Mettler-Toledo DL58.^{13,14} For tartaric acid *off-line* determination a spectrometric method using wavelength 520 nm was used.^{9,15,16} Potassium ion concentration was measured by potentiometric titrator Mettler-Toledo DL58 including ion selective electrode.^{13,17}

Ethanol and the reducing sugars were analysed according to validated HPLC method, proposed by BIO-RAD.¹² The samples were analysed using 300 mm \times 7.8 mm Aminex HPX-87H organic acid cation exchange column (Bio-Rad Laboratories USA). Elution was performed at 65 °C. The mobile phase was 2 mM H_2SO_4 in bi-distilled water. The pump was operating at flow rate 0.6 mL min^{-1} . The injection volume was 20 μL ; the eluting compounds were monitored by a fixed wavelength ultraviolet (UV-VIS) detector at 210 nm. Detector was connected in series with a refractive index (RI) detector. Samples were filtered through 0.45 μm membrane. Ethanol and the reducing sugars were detected by the RI detector.

All of the experiments were performed in triplicate. The results were appreciated using standard deviation method.

On-line conductivity measurements were performed using Mettler-Toledo CR7350 conductometer with standard conductivity probe. Measuring range was from 0.02 to 2500 $\mu\text{S/cm}$.

For decreasing the rate of crystallization by induction of crystallization nucleus formation, pure KHT in concentrations of 1, 2, 4, 6 and 8 g/L were used. Process temperatures of 4, 0 and -4 °C were tested. The concentrations of potassium and hydrogen tartrate ion were controlled at the start and on the end of cooling process.

Cooling temperature of 0 °C was found to be the most suitable. All the experiments at this temperature were performed in triplicate and the most representative runs are presented as results.

2. 1. Sauvignon Blanc

30 hours after cooling down to 0 °C the requisite crystallization nucleus concentration was obtained and the induction of crystallization started. It ended after 70 hours of processing. This process was monitored by step change in conductivity of 55 $\mu\text{S/cm}$. The time of 25 hours of intensive crystallization process was considered as crystallization time (Fig.1).

In further experiments Sauvignon Blanc was cooled down to 0 °C followed with addition of various amounts of KHT crystals. In the first group of experiments 1 g/L of KHT was added, the drop of conductivity was 205 $\mu\text{S/cm}$ and crystallization time was 24 hours. In the second run at

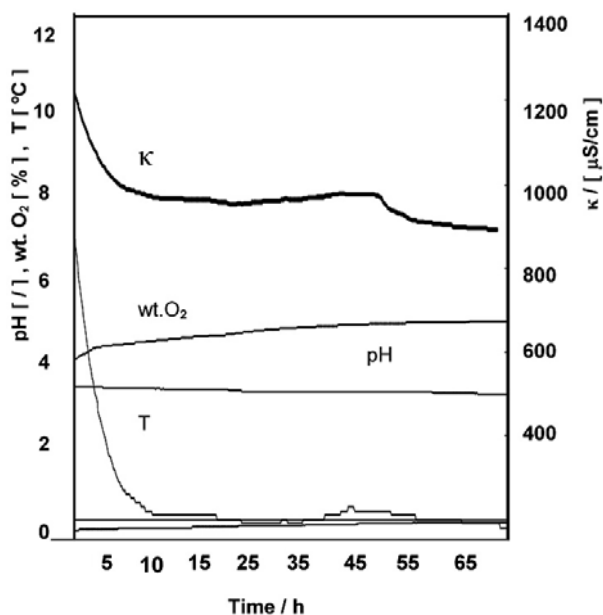


Fig. 1. Cooling of Sauvignon Blanc wine to 0 °C without KHT precipitation controlled by variation of pH, T temperature, wt. % of O₂ and κ electrical conductivity *on-line* measurement

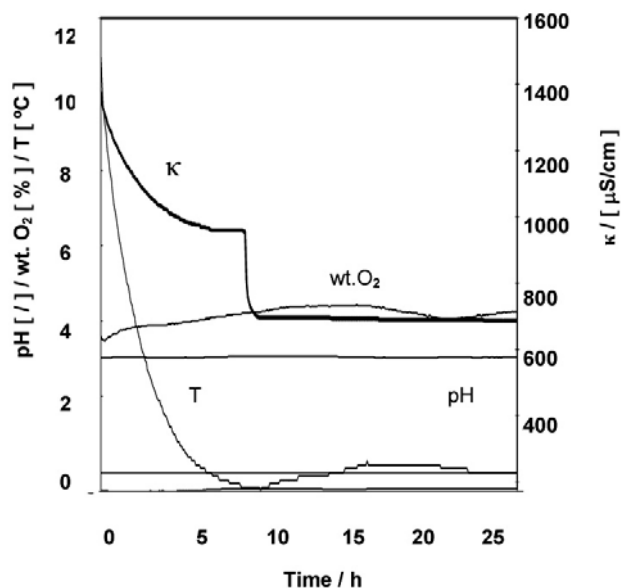


Fig. 2. Cooling of Sauvignon Blanc wine to 0 °C with KHT precipitation using 6 g/L variation of pH, T temperature, wt. % of O₂ and κ electrical conductivity *on-line* measurement

2 g/L of KHT added the drop of conductivity was 163 μS/cm and crystallization time was 6 hours. In the third run 4 g/L of KHT was added, the drop of conductivity was 245 μS/cm and crystallization time was 1 hour. In the fourth addition was 6 g/L of KHT was added, the drop of conductivity was 265 μS/cm and crystallization time was 55 minutes (Fig.2).

In the fifth run 8 g/L of KHT was added, the drop of conductivity was 245 μS/cm and crystallization time was 50 minutes. The influence of various amounts of precipitation agent on the time of crystallization and analytical

results of the samples at temperature of 0 °C in Sauvignon Blanc are presented in Tables I a,b,c and II a,b,c.

After the crystallization all of the samples were exposed at 0 °C. After six months of storage at 0 °C in all samples no crystal deposit was detected.

2. 2. Malvasia

Cooling down experiments was proceeded at 4 and 0 °C. In the experiments at 4 °C in 72 hours, no crystallization was detected, while at 0 °C after 25 hours cooling

Table I a,b,c. Influence of temperature variation in Sauvignon Blanc wine at 0 °C

a						
T (°C)	pH	Δ pH	Total acidity (g/L)	Δ Total acidity (g/L)	Tartaric acid (g/L)	Δ Tartaric acid (g/L)
10	3.13	–	7.573	–	2.439	–
4	3.14	+0.01	7.572	–0.001	2.439	0.000
0	3.10	–0.03	6.237	–1.336	1.389	–1.05
b						
T (°C)	Reducing sugars (g/L)	Δ Reducing sugars (g/L)	K (mg/L)	Δ K (mg/L)	Ethanol (vol. %)	Δ Ethanol (vol. %)
10	15.29	–	823	–	10.95	–
4	15.34	+0.05	824	+0.01	10.7	–0.25
0	15.18	–0.11	722	–101	10.8	–0.15
c						
T (°C)	κ (μS/cm)	Δκ (μS/cm)	Start of crystallization (hours)	Duration of crystallization (hours)		
10	1450	–	–	–		
4	1448	–2	–	–		
0	1395	–55	50	25		

Table II a,b,c. Influence of KHT addition on chemical analysis results and conductivity measurements in Sauvignon Blanc wine at 0 °C

a	Added KHT (g/L)	pH	Δ pH	Total acidity (g/L)	Δ Total acidity (g/L)	Tartaric acid (g/L)	Δ Tartaric acid (g/L)
	0	3.13	–	7.573	–	2.439	–
	1	3.15	+0.02	6.288	–1.285	1.639	–0.8
	2	3.14	+0.01	6.290	–1.283	1.645	–0.794
	4	3.11	–0.02	6.270	–1.303	1.625	–0.814
	6	3.14	+0.01	6.265	–1.308	1.635	–0.804
	8	3.11	–0.02	6.284	–1.289	1.630	–0.809

b	Added KHT (g/L)	Reducing sugars (g/L)	Δ Reducing sugars (g/L)	K (mg/L)	Δ K (mg/L)	Ethanol (vol. %)	Δ Ethanol (vol. %)
	0	15.29	–	823	–	10.95	–
	1	15.32	+0.03	750	–73	10.7	–0.25
	2	15.25	–0.04	752	–71	10.8	–0.15
	4	15.20	–0.09	748	–75	10.9	–0.05
	6	15.34	+0.05	745	–78	10.7	–0.25
	8	15.17	–0.12	740	–83	10.8	–0.15

c	Added KHT (g/L)	κ (μ S/cm)	$\Delta\kappa$ (μ S/cm)	Start of crystallization (h)	Duration of crystallization (hours/minutes)
	0	1450	–	–	–
	1	1245	–205	immediately	24 hours
	2	1287	–163	immediately	6 hours
	4	1205	–245	immediately	60 min
	6	1185	–265	immediately	55 min
	8	1205	–245	immediately	50 min

down to 0 °C the requisite crystallization nucleus concentration was obtained after 32 hours and the induction of crystallization started. Crystallization time was 17 hours. The drop in conductivity for 55 μ S/cm was observed

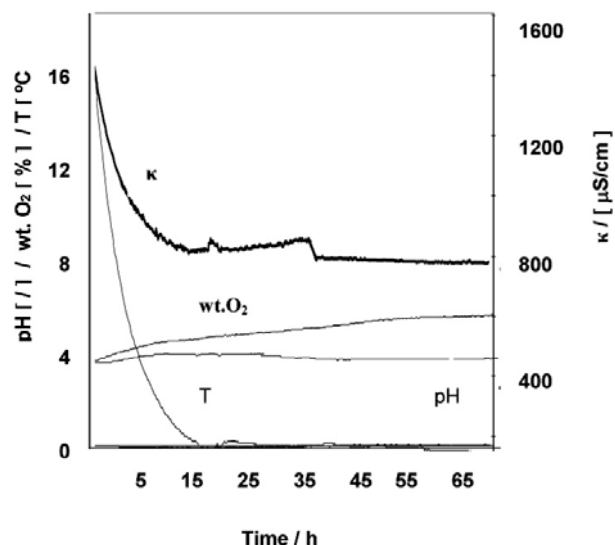


Fig. 3. Cooling of Malvasia wine to 0 °C without KHT precipitation controlled by variation of pH, T temperature, wt. % of O₂ and κ electrical conductivity *on-line* measurement

(Fig.3). This temperature was used in all further experiments.

In the first group of experiments when 1 g/L of KHT was added, the drop of conductivity was 132 μ S/cm and

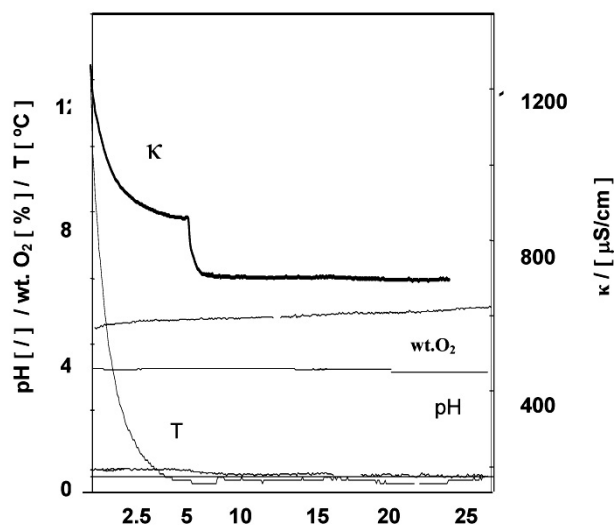


Fig. 4. Cooling of Malvasia wine to 0 °C with KHT precipitation using 6 g/L controlled variation of pH, T temperature, wt. % of O₂ and κ electrical conductivity *on-line* measurement

crystallization time was 16 hours. In the second one 2 g/L of KHT added it was 138 $\mu\text{S}/\text{cm}$ and 5 hours, at the third one 4 g/L of KHT added it was 132 $\mu\text{S}/\text{cm}$ and 95 minutes, at fourth one 6 g/L of KHT added it was 137 $\mu\text{S}/\text{cm}$ and 80 minutes and at the fifth one addition of 8 g/L of

KHT, the drop of conductivity was 150 $\mu\text{S}/\text{cm}$ and crystallization time was 75 minutes (Fig.4).

After the crystallization all the samples were exposed at temperature of 0 °C. In all samples after six months of storage at 0 °C no crystal sediment was detected.

Table III a,b,c. Influence of temperature variation in Malvasia wine at 0 °C

a						
T (°C)	pH	Δ pH	Total acidity (g/L)	Δ Total acidity (g/L)	Tartaric acid (g/L)	Δ Tartaric acid (g/L)
16	3.38	–	5.773	–	1.352	–
4	3.36	–0.02	5.772	–0.001	1.353	+0.001
0	3.37	–0.01	5.773	0.000	1.347	–0.005
b						
T (°C)	Reducing sugars (g/L)	Δ Reducing sugars (g/L)	K (mg/L)	Δ K (mg/L)	Ethanol (vol. %)	Δ Ethanol (vol. %)
16	3.34	–	795	–	11.6	–
4	3.32	–0.02	790	–5	11.6	0.0
0	3.40	+0.06	765	–30	11.7	+0.1
c						
T (°C)	κ ($\mu\text{S}/\text{cm}$)	$\Delta\kappa$ ($\mu\text{S}/\text{cm}$)	Start of crystallization (hours)	Duration of crystallization (hours)		
16	1130	–	–	–		
4	1129	–1	–	–		
0	1124	–6	–	32		

Table IV a,b,c. Influence of KHT addition on chemical analysis results and conductivity measurements in Malvasia wine at temperature of 0 °C

a						
Added KHT (g/L)	pH	Δ pH	Total acidity (g/L)	Δ Total acidity (g/L)	Tartaric acid (g/L)	Δ Tartaric acid (g/L)
0	3.38	–	5.773	–	1.352	–
1	3.37	–0.01	5.160	–0.613	0.903	–0.449
2	3.38	0.00	5.147	–0.626	0.875	–0.477
4	3.39	+0.01	5.120	–0.653	0.832	–0.520
6	3.40	+0.02	5.142	–0.631	0.860	–0.492
8	3.38	0.00	5.121	–0.652	0.830	–0.522
b						
Added KHT (g/L)	Reducing sugars (g/L)	Δ Reducing sugars (g/L)	K (mg/L)	Δ K (mg/L)	Ethanol (vol. %)	Δ Ethanol (vol. %)
0	3.34	–	795	–	11.6	+0.2
1	3.36	+0.02	784	–11	11.8	+0.3
2	3.37	+0.03	743	–52	11.9	+0.3
4	3.43	+0.09	722	–73	11.9	+0.1
6	3.34	0.00	732	–63	11.7	+0.2
8	3.40	+0.06	719	–76	11.8	+0.2
c						
Added KHT (g/L)	κ ($\mu\text{S}/\text{cm}$)	$\Delta\kappa$ ($\mu\text{S}/\text{cm}$)	Start of crystallization (h)	Duration of crystallization (hours/minutes)		
0	1130	–	–	–		
1	983	–147	1.50 hour	16 hours		
2	992	–138	1.10 hour	5 hours		
4	998	–132	immediately	95 min		
6	993	–137	immediately	80 min		
8	980	–150	immediately	75 min		

The influence of various amounts of precipitation agent on crystallization time and analytical results of the samples at 0 °C in Malvasia are presented in Tables III a,b,c and IV a,b,c.

3. Conclusions

In the classical crystallization method used in wine process technology long crystallization time is one of the main bottle necks. In 10 L stirred tank reactor by cooling to 0 °C without KHT precipitation in Sauvignon Blanc KHT crystallization process lasted for 25 hours (table I.c) and in Malvasia for 32 hours (table III.c). Shorter time needed for crystallization in Sauvignon Blanc wine was most likely due to lower natural mannoproteins content which is responsible for tartaric stabilizing effect in wine, while Malvasia contained higher alcohol concentration level and lower total acidity, tartaric acid and potassium ions influenced faster crystallization. Using simultaneously precipitation and cooling down to 0 °C at addition of 6 g/L KHT crystallization time was reduced to 55 minutes in Sauvignon Blanc and at the same conditions to 80 minutes at Malvasia.

The other parameters controlled in this process showed no significant changes. In Sauvignon Blanc reducing sugars content was reduced for 0.09 g/L, ethanol concentration for 0.25 vol. % and pH value decreased for 0.01. The difference in total acidity was 1.3 g/L and for tartaric acid 0.81 g/L. Reduction of potassium ion for 75 mg/L was detected.

Similar results were obtained in Malvasia where reducing sugars content at the KHT addition of 6 g/L did not change at all while ethanol concentration changed for 0.20 vol. % and pH value for 0.02. The reduction of total acidity was 0.63 g/L, difference in tartaric acid was 0.49 g/L and reduction of potassium ion for 63 mg/L was detected. Stabilization by contact process which included additions of finely-crystalline KHT had very little effect on the basic chemical composition and no detectable effect on the organoleptic properties of wines.

Simultaneously cooling with addition of crystallizing initiator significantly shortened potassium hydrogen

tartrate crystallization. Cooling to 0 °C and addition of 6 g KHT/L were found to be the most suitable in both wines. Cooling to –4 °C did not show significant differences; therefore these results were not shown.

Conductivity measurement was found very effective and it served as a window for very efficient monitoring of crystallization process. It indicates well the start and the end of crystallization process. Therefore it could be used in practice as a simple method and very practical indication for monitoring the crystallization of potassium hydrogen tartrate in wine technology.

4. References

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Povzetek

Tradicionalni postopki za kristalizacijo kalijevega hidrogentartarata (KHT) ali vinskega kamna v tehnologiji vina običajno predstavljajo dolg in energijsko potraten postopek. V našem raziskovalnem delu smo na osnovi sočasnega hlajenja in dodajanja iniciatorja kristalizacije razvili učinkovito metodo za hitro kristalizacijo KHT. Metodo smo preizkusili v dveh sortah primorskih belih vin v sauvignonu in malvaziji. Uporabili smo dodatek KHT (1, 2, 4, 6 in 8 g/L) ob temperaturah hlajenja 4 in 0 °C. Proces hitre kristalizacije smo zelo uspešno zasledovali z meritvami prevodnosti, kjer se je ta metoda izkazala kot izjemno primerna za zasledovanje procesa in poteka kristalizacije. Ugotovili smo, da je hitrost kristalizacije funkcija temperature in količine dodanega iniciatorja. Dodatek 6 g/L KHT in temperatura kristalizacije 0 °C sta se izkazala za najbolj učinkovito kombinacijo.